



Review

Ultrasound-assisted biomass valorization to industrial interesting products: state-of-the-art, perspectives and challenges

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ABSTRACT

Nowadays, the application of ultrasound (US) energy for assisting the lignocellulosic biomass and waste materials conversion into value-added products has dramatically increased. In this sense, this review covers theoretical aspects, promising applications, challenges and perspectives about US and its use for biomass treatment. The combination of US energy with a suitable reaction time, temperature and solvent contributes to the destruction of recalcitrant lignin structure, allowing the products to be used in thermochemical and biological process. The main mechanisms related to US propagation and impact on the fragmentation of lignocellulosic materials, selectivity, and yield of conversion treatments are discussed. Moreover, the synergistic effects between US and alternative green solvents with the perspective of industrial applications are investigated. The present survey analysed the last ten years of literature, studying challenges and perspectives of US application in biorefinery. We were aiming to highlight value-added products and some new areas of research.

1. Introduction

Biomass is considered an alternative source for the production of fuels, solvents, chemical building-blocks, and biopolymers. The biomass processing enables a reduction of petroleum dependence, which may supply the inputs necessities for the industry activities with a decrease of environmental impacts [1]. Biomass is a common industrial residue from food processing, wasted husks, leaves, and seeds, which have been reported as low-cost carbon sources for biorefinery. Moreover, the use of these residues as feedstock does not represent a competition with human food, being an attractive alternative considering the population growth [2,3].

The biomass processing can be performed by thermochemical, biochemical, chemical, and physical-chemical processes [4]. Several alternatives have been proposed to ensure efficient protocols aiming biomass conversion, as well as to ensure the economic viability of the biorefinery process when compared to conventional routes using non-renewable raw materials. In thermochemical routes, the production of biochar, or the so-called bio-crude, is considered as a potential alternative to most of crude oil derivatives [5]. For biochemical process, food residues and lignocellulosic wastes have been described as viable feedstocks for the production of fermentable sugars and ethanol. The use of

chemical agents that generates a selective degradation of biomass fractions for value-added products has also been described as an important advance for biorefinery activities [6]. The use of lignocellulosic wastes (e.g., discarded husks, leaves, and seeds) as feedstocks has been widely studied to the extraction of value-added products, which came together with the growing demand for circular economy-friendly processes [7,8].

Despite the advances in biomass processing, several drawbacks are still an open issue affecting the competitiveness of biomass conversion. The heterogeneity of biomass composition, the inefficient pretreatment steps, the lack of adequate reactors, the dependence on high temperatures and elevated pressures, the need of toxic reagents in high amount, and the loss of calorific power owing to inorganic contaminants, are considered critical issues for the development of alternative technologies for biomass processing [9].

Ultrasound (US) energy is considered a valuable technology for industrial process intensification. The application of US in biomass pretreatments, lignin degradation, cellulose conversion, and increase of sugar production by biochemical routes are some successful examples of the use of this technology for biomass valorization [9]. When US energy is used for assisting the biomass treatment, the main observed effects are associated with the increase of convective forces, acoustic cavitation,

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and the production of highly reactive radicals [9,10]. In the following sections an overview on theoretical aspects, promising applications, challenges and perspectives about US and its use for biomass treatment is discussed.

2. Theoretical aspects of ultrasound energy

US is classified as an acoustic wave with mechanical nature that oscillates at frequencies above 16 kHz [11]. When US propagates in liquid medium, cycles of compression and rarefaction can be observed [12]. During the compression cycle the molecules of the solvent are pushed together, whereas rarefaction cycles pull them apart [11,12]. If the rarefaction cycle has enough energy to overcome the solvent intermolecular bound, a cavity is formed, which tends to be filled by the solvent vapor and the dissolved gas present in the medium [13,14].

The application of the US wave in a liquid medium can induce physical (heating, acoustic streaming, acoustic cavitation, and nebulization), and chemical phenomena (radicals formation). A schematic representation about these mentioned phenomena is presented in Fig. 1. Among them that might happen while US propagates in a liquid medium, acoustic cavitation deserves a special attention.

Acoustic cavitation is observed when the US waves propagates at specific energy and frequency in a liquid medium, where the compression and rarefaction cycles generate microbubbles containing gas and liquid vapor [15]. When the bubbles collapse, dramatic chemical and physical effects occur in the medium [10]. The bubble collapse can be classified as an adiabatic compression process, which increases the temperature in a rate of 10^{10} °C/s with local pressures up to 2000 atm [16]. Depending on the conditions when bubble is created and collapsed, the acoustic cavitation can occur in different ways, generating stable or transient cavitation. In stable cavitation, the bubbles lifetime is longer. In general, the bubbles are filled with gas, and them oscillate around an equilibrium size during their growth at higher frequency [10,15,16]. With regard to transient cavitation, the bubbles lifetime is shorter. The bubbles are formed faster than one cycle of high intensity

US, and the bubble collapse releases a high amount of energy (localized high temperature and pressure) which contributes to chemical and mechanical effects [10,15,16].

Taking into account the effects of acoustic cavitation, the main physical effects observed due to the bubble collapse can be summarized as micro jets, shockwaves, and micro flow that intensified the fluids transport and further the dissolution of solid particles [17]. Chemical effects, for instance, are attributed to the radical species generated during bubble collapse, as a consequence of the hotspots generated by cavitation phenomena [18]. The bubble collapse, under specific frequency and energy conditions, can generate reactive radicals ($\bullet\text{H}$ and $\bullet\text{OH}$) that enable the use of US energy to reagents [19]. In general, when chemical reactions are sonicated, a local increase of the reaction temperature and an improved reaction rate are observed.

Taking into account biomass treatments assisted by US, bubble collapse have been related to the reduction of the crystallinity degree of lignocellulosic material and, consequently, making easier the lignocellulosic separation, as presented throughout this review.

3. Ultrasound-assisted biomass pretreatments

Lignocellulosic materials comprise the major source of carbon present in the surface of the earth [20]. This is the main reason that biomass has been considered a promise alternative source for producing liquid fuels, building blocks, and fine chemical products, in an enough amount for complying with the actual demand of energy with moderate environmental impact. Most of biomass valorization processes are associated with catalytic and biological conversions, pyrolysis, and hydrothermal treatments [21]. Although different conversion process are available, all the processes used for the biomass valorization need a pretreatment step to ensure the selectivity conversion with good yields [22].

The biomass pretreatments are physical, chemical, or biological steps that aim to the separation of lignin, hemicellulose, cellulose, and inorganic compounds for further processing and valorization [23]. Conventionally, cellulose and hemicellulose fractions are used as

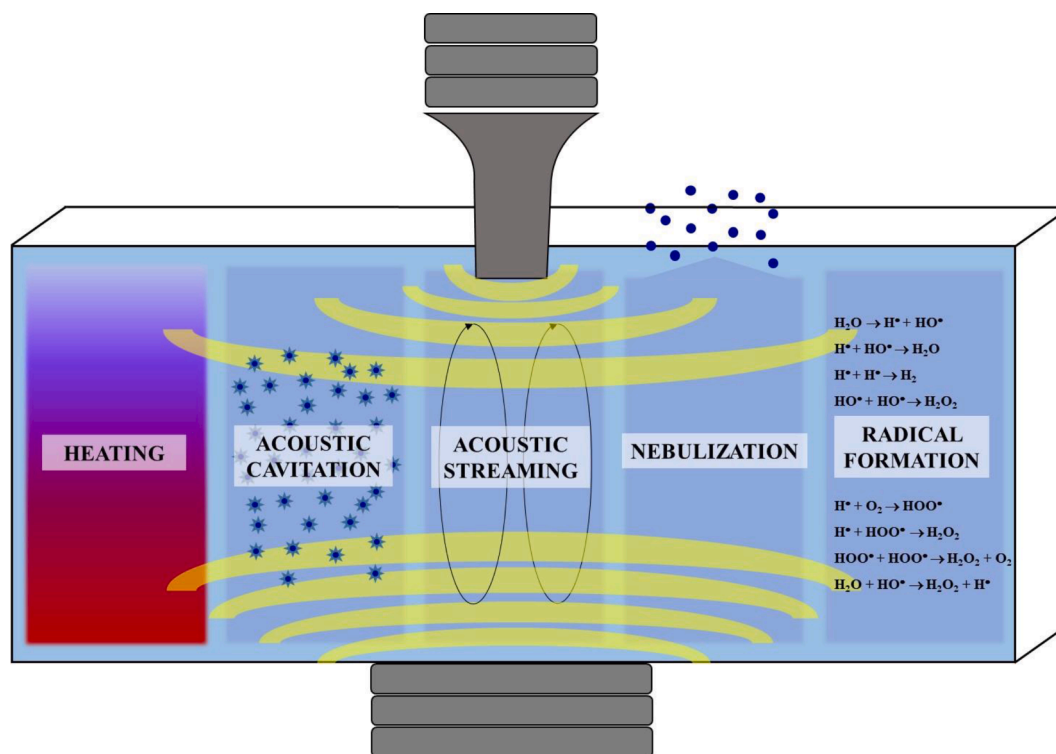


Fig. 1. Schematic representation about the main physico-chemical phenomena observed when a liquid medium is directly or indirectly sonicated. All the phenomena are graphically separated for making their comprehension easier.

feedstocks to biorefinery activities (e.g., fermentation) [24]. Lignin, for instance, is considered a sub-product that has been used as low energy fuel in industrial process. Some drawbacks affected the full exploitation of lignin, among them the inhomogeneous composition and the high energy consumption for selectively conversion/hydrolysis [24,25].

The current pretreatments are generally based on alkaline/acid hydrolysis, biomass extrusion, and biological treatments [26]. In alkaline hydrolysis, the increase of the pH, contribute to the saponification of intermolecular ester bonds between lignin, hemicellulose and cellulose [27,28]. Acid hydrolysis, in turn, tends to solubilize the hemicellulose fraction as xylose. In acidic medium lignin can be degraded to organic acids, increasing the availability of the cellulose fraction for any further process [27,28]. The biomass extrusion combines a mechanical effect with an increase of temperature, which improves the cellulose and hemicellulose fragmentation and increases the sugar recovery [27,28]. The biological protocols are considered the most specific among the other pretreatments [27,28]. They can be used simultaneously or sequentially with other pretreatments to increase the xylose and glucose recovery from hemicellulose and cellulose fractions, respectively [27,28].

Although the majority of the pretreatments described can present a satisfactory efficiency, the use of large amount of reagents, long pretreatment times and hard conditions (e.g., high pressure and/or temperature) is still a current challenge from the environmental and economic point-of-view. On this aspect, US energy has been widely investigated as an alternative technology to increase the efficiency of pretreatment steps. The efficiency of US-assisted pretreatments can be attributed to physical effects such as turbulence, micro jets, micro level mixing, and shock waves that makes the biomass more suitable for the subsequent process steps [29].

The major part of the studies available in the literature are dealing with the use of US for biomass pre-treatments with horn-based systems (direct application) operating at frequencies lower than 50 kHz. In these works, the US effects are mainly attributed to the existence of physical phenomena, such as shock waves, increase the mass transfer and turbulence [29–31]. When the lignocellulosic material is sonicated the accessibility and/or solubility of biomass increase in comparison to the processes in silent conditions [29,30]. The size diameter of lignocellulosic materials tends to be reduced in sonochemical processes, increasing the contact with the solvent and speeding up the conversion [31].

Despite the physical effects, sonochemical treatments are associated with radicals formation ($\bullet\text{H}$ and/or $\bullet\text{OH}$) as the consequence of the implosion of the cavitation bubbles. At low frequency (20 kHz), the cavitation bubbles are less numerous, but larger in diameter, which means a more intense collapse with higher mechanical energy delivered, whereas at around 300 kHz radical formation is more intense [32]. In biomass pretreatments, these effects are not deeply investigated owing to the reduced penetration potential of the cavitation bubbles formed at low frequencies [33]. In other words, the energy released from the bubbles collapse is retained on the surface of the lignocellulosic material making it difficult to separate the lignocellulosic fractions.

Among the pretreatments assisted with US, it is possible to observe that the lignin removal has been the focus of several studies [29,31]. The lignin structure is responsible for the stabilization and self-sustaining of the lignocellulosic material. It is present in a more external part of lignocellulosic material (behaves as a natural protection of hemicellulose and cellulose), being generally the fraction that comes in direct contact with the solvent [29–31]. Since the physical effects of US are predominant in the biomass pretreatment, the lignin removal becomes the first step in any separation process of lignocellulosic materials [29–31]. It is important to emphasize that lignin removal assisted with US tends to be highly efficient with reduced time and temperature when compared to conventional processes [29–31].

Few studies proposed the simultaneous separation of lignin, cellulose and hemicellulose fractions. Some alternatives such as the use of ozone,

permanganate, and sono-Fenton methods have been reported but with long processing times or high operational costs, being not feasible for industrial applications [34–36]. Alternatively, hybrid systems assisted by US-energy (e.g., sonication at elevated pressure, and US-autoclaving) are reported to increase the efficiency of pretreatment step. Considering the literature, hybrid processes can be interesting alternatives to biomass pretreatments [37]. A synergic effect might be observed when US was used to acid hydrolysis process, which increased the diffusion of sugar molecules from biomass matrix when compared to conventional procedures for acid hydrolysis, without application of US [37].

As a consequence of sonication of the lignocellulosic biomass, the crystallinity of cellulose fraction can be also reduced. When US waves interact with cellulose fraction a weakening (or even delinking) of intermolecular hydrogen bonds was observed. This reduces the organization of cellulose sheets and makes the hydrolytic process easier by improving the accessibility, hydrophilicity, and reactivity of this fraction [38,39]. However, if the delivered US is further increased, despite the reduction in the crystallinity of the cellulose, its amorphous regions starts to improve the polymerization degree thus leading to a more stable structure [40]. Although controversial, it shows that US might be used as a tool for the fragmentation and reorganization of the cellulose fraction. Although it can be considered a clear evidence of the versatility and potential applicability of this US, it also represents a situation that the use of US must be carefully evaluated. Otherwise the expected effects associated with US should not be observed.

Although the pretreatment step assisted with US has been strongly related with separation of lignocellulosic fractions, the concept of biomass pretreatment tends to cover a wide range, not only associated with this aspect [29–31,38–40]. In recent years, potential alternative feedstocks from food raw-materials have been extensively studied. The so called “second generation feedstocks” are wastes or sub-products of conventional routes, such as food industry waste, agricultural waste, peels, and straws (all of them with very low acquisition costs) [41]. Up to few years ago, these residues were not of industrial interest, and equipment for harvest were not satisfactorily development. As a consequence, lignocellulosic materials contaminated with metals, soil, and ash emerged and became problems owing pipe clogging, incrustation and corrosion of industrial reactors [42,43]. Considering thermochemical processes, the biomass contaminated with inorganic materials can reduce the available calorific energy, resulting in a less energetic process with lower efficiency [42,43].

For minimizing such problems, a step of inorganic materials removal can be applied prior to biomass conversion. This type of process normally is associated with the use of inorganic or organic acids, and long extraction times at relatively high temperatures [44,45]. If the step related to the removal of soil residues, silica, ash, and metals is not carefully performed, the demineralization process can degrade the biomass, making unfeasible any further conversion [44,45]. The potential of US energy for inorganic compounds removal is widely known, mainly when it is used at lower frequencies (e.g., lower than 50 kHz) and higher delivered power (e.g., 692 W L^{-1}) [46]. This approach has been already used for metals extraction from fuels, tanned waste, and carbonatite rocks [46–48]. In spite of this valuable application, the biomass demineralization was poorly investigated so far, and it is expected as valid alternative for industrial applications.

The main features of US-assisted biomass pretreatments can be summarized as time reduction, lower process temperatures (even at room temperature), and the possibility of working using reactor operating at atmospheric pressure (Fig. 2). The use of hybrid systems (US combined with conventional treatments) may be a feasible alternative for increasing the efficiency of pretreatment steps. It is worth mentioning that a few studies reported the use of hybrid systems for scaling the process up. It makes evident that many developments are still necessary for allowing US-assisted pretreatment as routine in industrial applications. Table 1 summarizes the main operational conditions and reagents used for the US-assisted biomass pretreatment of several

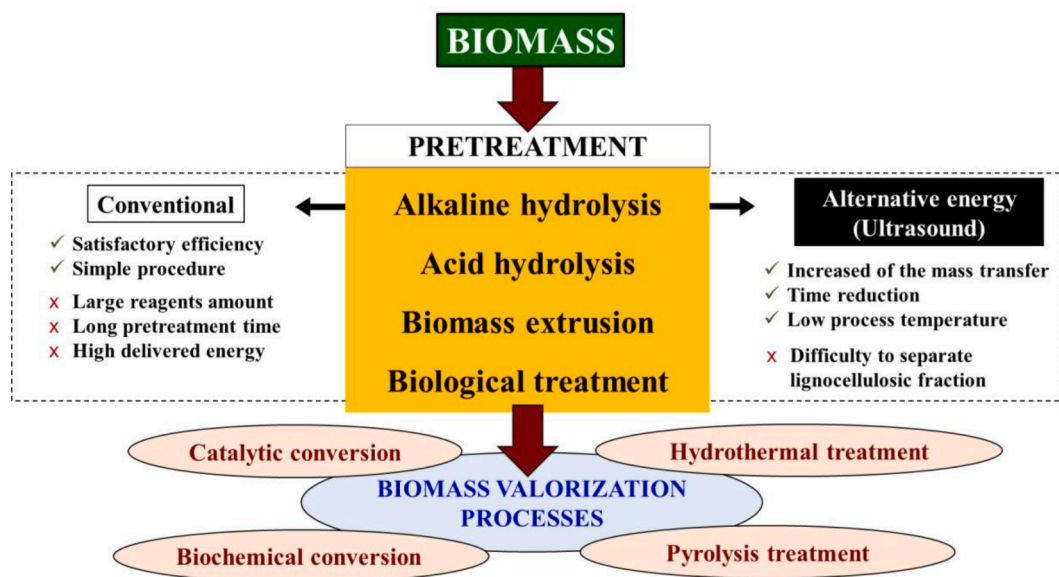


Fig. 2. Schematic representation about biomass conversion and the main features of US energy.

Table 1

Selected works using US-assisted pretreatments from biomass feedstocks.

Biomass	US details (frequency, nominal power and type)	Experimental conditions	Main features	Ref.
Bacterial cellulose and plant cellulose	37 kHz, 150 W, bath	60 min, 25 °C, alkaline solution	reduction of molecular weight and crystallinity	[49]
<i>Bombogori</i>	30 kHz, 100 W, horn	100 min, 35 °C, CaOH at 2% (v v ⁻¹)	65% of lignin removal	[50]
<i>Arecanuthusk</i>	37 kHz, [a], bath	120 min, 60 °C, 10% of NaOH (v v ⁻¹)	cellulose after US treatment possess greater cross-linker content judging by the loss of the cellulose fibril structure	[51]
Cellulose from sugarcane bagasse	20 kHz, 50 W, horn	20 min, 110 °C, using 1-butyl-3-methylimidazolium chloride as solvent	decrease in cellulose dissolution time	[52]
Chili post-harvest residue	80 kHz, [a], bath	30 min, 25 °C, 2% NaOH (wt%)	44.3% of sugars	[53]
Corn stover	20 kHz, 50 W, horn	180 min, 50 °C, 0.8 mol L ⁻¹ Na ₂ CO ₃ + 1.2 mol L ⁻¹ H ₂ O ₂	glucose yield of 3 mg mL ⁻¹ of hydrolysate	[54]
<i>Crotalaria juncea</i>	50 kHz, [a], bath	300 min, 2% H ₂ O ₂ (wt%)	85% of lignin removal	[55]
<i>Crotalaria juncea</i>	20 kHz, 500 W, horn	10 min, 121 °C, 1% NaOH (wt%)	67% of lignin removal	[56]
Grass	25 kHz, 260 W, horn	30 min, 35 °C, 1% HCl (wt%)	increase of sugar production	[57]
Kenaf core fiber	24 kHz, 35 W, horn	180 min, 25 °C, 2 g L ⁻¹ TiO ₂ + 0.1 mol L ⁻¹ H ₂ O ₂ + 0.1 mol L ⁻¹ FeSO ₄	60% of lignin removal	[58]
Microcrystalline cellulose	21–23 kHz, 800 W, horn	150 min (cycles of 2 s on/4 s off), 25 °C, 0.6 mL of H ₂ O ₂ + 0.01 g of FeSO ₄ ·7H ₂ O	84.8% of lowest crystallinity of cellulose	[59]
Newspaper waste	20 kHz, 100 W, horn	70 min, 80 °C, 1 mol L ⁻¹ NaOH	80% of lignin removal	[60]
<i>Partheniumhysterophorus</i>	20 kHz, 500 W, horn	15 min, 30 °C, 1.5% NaOH (w v ⁻¹)	64% of lignin removal	[61]
Rice hull	20 kHz, 500 W, horn	30 min, 90 °C, 2 mol L ⁻¹ NaOH	84.7% of lignin removal	[62]
Rice straw	22 kHz, 200 W, horn	180 min (cycles of 2 s on/4 s off), 25 °C, 0.88 mol L ⁻¹ H ₂ O ₂ + 0.2 mol L ⁻¹ FeSO ₄	sugars yield of 7 g L ⁻¹ of hydrolysate	[35]
Spent coffee waste	47 kHz, 310 W, bath	20 min, 25 °C, 4% KMnO ₄ (wt%)	46% of lignin removal 98% of cellulose removal	[34]
Sugar cane bagasse	24 kHz, 400 W, horn	47 min, 70 °C, 3% NaOH (wt%)	82% of lignin removal	[63]
Sugar cane bagasse	24 kHz, 200 W, horn	45 min, 50 °C, 2% H ₂ SO ₄ (wt%)	70% of theoretical glucose yield 81% of theoretical pentose yield	[64]
Sugar cane bagasse	22 kHz, 50 W, horn	5 min, ozone + 0.1 mol L ⁻¹ NaOH	39.1% of glucose yield	[65]
Sugar cane bagasse	24 kHz, 400 W, horn	60 min, 75 °C, 1% H ₂ O ₂ (wt%)	79% of lignin removal	[66]
Sugar cane bagasse	24 kHz, 400 W, horn	75 min, 60 °C, 1.5% H ₂ O ₂ (v v ⁻¹) + FeCl ₃ (solid: liquidratioof 1:100)	cellulose recovery of 79% 94% of lignin removal	[36]
Sugar cane tops	23–45 kHz, [a], horn	30 min (60 s cycles on/off), 35 °C, 2% surfactant (wt%)	66.1% of sugars	[67]
Wheat straw	20 kHz, 650 W, horn	30 min, 50 °C, 15% NH ₄ OH (wt%)	92% of theoretical sugar yield	[68]
Wood waste	40 kHz, 200 W, bath	[a], 30 °C, filamentous fungi	68% of lignin removal	[69]

[a] data no available in the selected publication.

feedstocks.

4. Ultrasound-assisted biomass conversion into value-added products

The use of US has been considered an emerging field for the biomass conversion to high value-added products, such as chemical platforms, building blocks, fuels, etc [6]. This scenario is reinforced by the prevision about crude oil and coal reservoirs decrease, which comes associated with the need for reducing the emissions related with greenhouse gases [70]. In this way, renewable biomass has emerged as a promising alternative for fossil-based fuels, as well for polymers, and solvents production. Recently, the focus in biomass conversion has been reported for producing chemical platforms that can generate several products of industrial interest, such as ethanol, lactic acid, and levulinic acid [24].

Among the technologies used to biomass conversion, the thermochemical processes have being widely employed owing the reduction of conversion time, and the “one-pot” production of several interesting industrial products [25,71]. Some examples of thermochemical processes are pyrolysis, liquefaction, torrefaction, and gasification [25,71].

Biomass pyrolysis is based on biomass cracking in the absence of oxygen at high temperatures (from 300 up to 1000 °C) [72]. Lignin, cellulose, and hemicellulose are converted into gases and volatile compounds [73]. Depending on the reactor residence time, they can be also converted into condensable hydrocarbons. The liquefaction processes produce high-quality bio-oil at high H₂ pressures, and controlled temperatures (from 250 up to 450 °C) [74]. The low oxygen content of bio-oil contributes to their higher heating value, improving several fuel properties [74]. Torrefaction is considered a milder pyrolysis to produce a more energy-dense product with properties similar to coal [75]. Biomass gasification consists of a combination of pyrolysis, steam gasification, and partial oxidation [76]. The gasification generates several products of industrial interest, such as fuels, solvents, and polymers derivatives, leading to extremely versatile biomass conversion [76].

Another technology used to biomass conversion is the transesterification reaction, widely used for biodiesel production from vegetable oils [77]. In this process, triglycerides from vegetable oil react with short chain alcohol (up to 4 carbons, being methanol and ethanol the most used) for producing fatty acid alkyl esters (biodiesel) [78]. The feasibility for producing biodiesel depends on the availability of a wide range of feedstocks, low production costs, and viability of large-scale production [77,78]. It is important to emphasize that the protocols

used for oil extraction tend to use large amounts of toxic solvents, requiring its separation prior to use, or replacement, to reduce the environmental impact.

In spite of the several applications described in this section, the thermochemical processes and biodiesel production demand a high consumption of energy. High temperature, and pressure, requirements and also the heterogeneity or seasonality of biomass are some challenges that need to be overcome. In this sense, the US energy can be a viable alternative for the intensification of biomass conversion. Table 2 presents some examples of biomass conversion into high value-added chemical products, or biofuels, assisted with US energy.

As shown in Table 2, the conversion yields are strongly affected when the medium is sonicated. The increase in the degradation rate promotes high yield of bio-oil for some conventional pretreatments steps, such as those based on acid or alkaline treatments. On this aspect, the use of US might help for degrading lignin structure, promoting a partial breaking of the glycosides bonds, even using lower reagents amount and reduced sonication time [80–83]. When US wave pass through reaction medium it generates shock waves, turbulence, and increase in the mass transfer, which can explain the high efficiency observed when US energy was applied to prior to pyrolysis [79,88].

4.1. Building blocks and chemical platforms

It has been reported the synergic effects between US energy and acid hydrolysis for producing compounds from furanic platforms [81,83]. US energy has shown its potential for the process intensification of biomass conversion, contributing for environmental friendly synthetic routes [90]. The use of a cup horn system as US-applicator, in an acid hydrolysis reaction with diluted acid, lead to promising yields for the synthesis of these compounds [81,83]. In the same way, the use of ionic liquids shown a potential alternative to toxic mineral acids in the furanic platform synthesis [80]. These studies reported some advances in the furanic platforms synthesis assisted by US energy [80]. The reuse of ionic liquids and the use of even more diluted mineral acids are challenges in each research field, even without US. Although some studies describe the beneficial effects of US for the intensification of conventional processes, the use of US energy aiming biomass conversion to high added value products has been not yet completely elucidated, with enough space additional research.

Table 2

Selected works using US-assisted conversion from biomass feedstocks to high-value-added chemical products or biofuels.

Biomass	US details (frequency, nominal power and type)	Experimental conditions	Main features	Ref.
Cedar wood	40 kHz, 150 W, bath *pyrolysis pre-treatment	120 min, 80 °C, distilled water	hydrocarbon yield of 80% (wt%)	[79]
Glucose, cellulose and local bamboo	20 kHz, 500 W, horn	3 min, 140 °C, 2% of ionic liquid (wt%)	Hydroxymethylfurfural yield of 43% (wt%) of glucose initial	[80]
Microcrystalline cellulose	20 kHz, 750 W, cup horn	60 min, 30 °C, 4 mol L ⁻¹ HNO ₃	furfural yield of 22% (wt%)	[81]
Non-edible oils	35 kHz, 35 W, bath	60 min, 59 °C, alcohol:oil molar ratio of 11.68:1	biodiesel yield of 92% (wt%)	[82]
Rice husk, sugar cane straw, yerbamate, grass and wood waste	20 kHz, 750 W, cup horn	60 min, 30 °C, 4 mol L ⁻¹ HNO ₃	furfural yield of 7.2% (wt%) of grass initial	[83]
Sawdust	40 kHz, 50 W, liquefaction reactor	20 min, 98% (wt%) + PEG 400 + glycerol	liquefaction yield of 91% (wt%)	[84]
Soybean oil	21.5 kHz, 600 W, pilot flow reactor	80:20 M ratio of alcohol/oil Step 1: 30 min at 45 °C (mechanical stirring) Step 2: 35 min at 45 °C (US)	a flow rate of 55 mL min ⁻¹ brought the reaction to completion	[85]
Soybean oil	20 and 28 kHz, 200 W, dual horn	initial temperature of 25 °C, alcohol: oil molar ratio of 8:1, catalyst content 1.8%	biodiesel yield of 96% (wt%)	[86]
Waste cooking oil	20 kHz, 100 W, horn	5 min, methanol:oil molar ratio of 6:1	biodiesel yield of 90% (wt%)	[87]
Wood chips	170 kHz, 1000 W, bath, step 1 40 kHz, 1000 W, bath, step 2 * pyrolysis pretreatment	30 min, distilled water (step 1) 90 min, distilled water (step 2)	increase of 12% in bio-oil yield compared to untreated wood	[88]
Zahidi seeds	24 kHz, 300 W, horn	5 min, 60 °C, 1% (wt%) of NaOH with methanol:oil molar ratio of 6:1	biodiesel yield of 96.4% (wt%)	[89]

4.2. Extraction of vegetable oils and biofuels production

US energy has been also used to assist the production of biofuels [91]. Concerning biodiesel production, several studies have reported that the US irradiation contributes for increasing the interaction between alcohol and fatty acids, since it improves the mass transfer in a such biphasic reaction [92]. Among the evaluated frequencies, the range from 25 to 45 kHz has been reported as the most promising for the biofuels production, mainly when US is directly delivered in the reaction medium by means of a horn-applicator. The positive effect of US for biofuels production has been understood as a matter of interaction of sound wave and reaction medium. When reaction medium is sonicated, the observed phenomena of shock-waves, micro-convection, and acoustic cavitation can contribute for improve the homogenization, dispersion and/or emulsification of catalysts and feedstocks [91]. Another effect related to the use of US, is the activation of chemical, physical or biological catalysts, once the erosion and leaching of biofuels catalysts leads to a reduction of activation energy and reaction time improving biofuels production [91].

The extraction of vegetable oil is considered another critical step for industrial processes. The use of large amounts of toxic organic solvents, such as hexane or methanol, associated with protocols that tends to be performed at high pressure and elevated temperatures, are considered industrial challenges [91,92]. On this aspect, US energy has been also applied in vegetable oils extraction for further biofuels production [91,92]. Several studies reported that US energy lead to an increase in oil yield based on faster approaches, operating at relatively milder operational conditions of temperature, pressure, and solvents amount when compared with processes without assistance of US energy [91,92]. The main mechanisms related to the use of US, which might contribute for increasing the extraction procedure, are related to making easier the migration of vegetable oil from vegetable tissue to extraction solvent, such as sonoporation, sonocapillarity, and vegetal surface erosion [93].

The production of biofuels with the assistance of US has been reported for the production at pilot scale [90–93]. Some works have pointed that the US reactor design is the main aspect for allowing an efficient scale up with assistance of US [91,94]. Industrial reactors require the quantitative prediction of acoustic power dissipation, mass transfer, and acoustic cavitation prediction [95]. The use of a single transducer, even able to deliver high amount of localized energy, is not considered a suitable arrangement [96]. Sound waves tend to present a divergent behaviour while propagating, becoming less energetic when moving away from the transducer. It represents a non-appropriate condition for scaling up due to the formation of non-uniform cavitation fields, which increase the dead ends of acoustic streaming [91,96]. Moreover, since high delivered energy is required to sonicate a pilot-scale, the use of a single transducer represents a condition of high transducer erosion, being a challenge for designing pilot-scale reactor [97]. As an alternative, the use of several transducers of low-output energy has demonstrated the efficiency of US propagation, and consequently high acoustic density [96]. These beneficial effects can be associated with the superposition of US field (constructive interference phenomenon), resulting in an uniform cavitation field due to consecutive reflections and reverberation of sound wave inside reactor, thus resulting in the required energy efficiency [91,96,97].

Although several works have reported the use of US for biomass conversion, its contribution for improving selectivity or yields was not deeply elucidated. The use of alternative solvents (with emphasis on those considered greener solvents) or milder operational conditions already represent advances in the biomass conversion [90–95]. Despite this, more studies are required for proving the mechanisms with enough evidence about the US effects, as well as the scaling up feasibility. On the other hand, the US-assisted biofuels production can be considered a successful example of scaling up attempt. The challenges in this research area are associated to process intensification and costs reduction [90–95].

5. Extraction of value-added products from biomass

The use of lignocellulosic wastes as feedstocks to the extraction of value-added products has been widely studied, which came together with the growing demand for circular economy-friendly processes [98]. Essential oils, polyphenols, flavonoids, and anthocyanins are examples of value-added products for industrial activities [99–101]. The lignocellulosic waste can be further valorized, thus reducing the process cost, and generating “renewable products”. Among the process applied to high added-values extraction from biomass it is possible to highlight the use of conventional solid-liquid extraction, accelerated solvent, supercritical CO₂ and subcritical water [102]. The main features of the extraction protocols are presented in Fig. 3.

The conventional solid-liquid extraction consists of using organic solvents for increasing the extraction temperature in order to enable the extraction of high-value-added products [103–105]. Usually, this procedure is applied using methanol or ethanol as organic solvent, which normally demands a high amount of solvents for efficient extraction [103–105]. In industrial activities solid-liquid extraction is applied to the extraction of several products, but the costs associated with solvents, and the process ecotoxicity are considered a crucial drawback for extraction method [103–105].

In view of the need for changes to the conventional solid-liquid extraction, the accelerated solvent extraction method emerged as a suitable alternative to the extraction protocols. When using accelerated solvent extraction systems the organic solvent is pressurized (10 to 15 mPa), which allows a temperature increase up to the range of 200 °C, without significant losses of high value-added products [105–107]. Additionally, the amount of organic solvent is reduced, and a conventional extraction in “one-step” is substituted for several-steps with solvents recycle [105–107]. With the increase in the extraction pressure and temperature the solvent viscosity is reduced and the diffusivity between solvent and lignocellulosic material increase, which results in higher extraction yields [105–107].

Despite the advances in accelerated solvent extraction, the use of organic solvents is still a challenge for extraction processes. The use of supercritical CO₂ for extraction process has been reported as an alternative for the extraction of high added-value products [105,108,109]. The lower thermal degradation, associated with the absence of organic solvents, results in an eco-friendly extraction method [105,108,109]. Although supercritical CO₂ enables selective and efficient extraction of apolar compounds, the high investment required and the elevated pressure limit to few specific industrial applications [104,107,108].

Similarly, the use of subcritical water has been pointed out as a viable alternative to the extraction of high value-added products from biomass. In subcritical conditions, the hydrogen bonds and the dielectric constant of water are reduced, and consequently, the water properties become similar to those of organic solvents [105,110,111]. The main advantage of using subcritical water for extraction protocols is the production of water as extraction waste. So far the lack of suitable industrial reactors hamper the diffusion [104,109,110].

In all extraction methods presented in Fig. 3, the US energy could increase the extraction yield. Among the US assisted applications for adding value to lignocellulosic biomass, the US assisted extraction is considered one of the most easily applicable. Table 3 presents some examples for US application in several extraction procedures from different biomass feedstocks.

US-assisted extraction showed reduced process time, even when performed at low temperature [93,126]. The use of low US frequencies (from 20 to 100 kHz) have been associated with the increase in the extraction yield [93,103]. In this range of US frequencies, the physical effects are more evident, and the reduction of diameter size make easier the extraction process [93,103].

The mechanisms US-assisted extraction process, are associated with erosion, shear forces, sonoporation, fragmentation, capillary effect and detexturation [93]. The implosion of cavitation bubbles on the vegetable

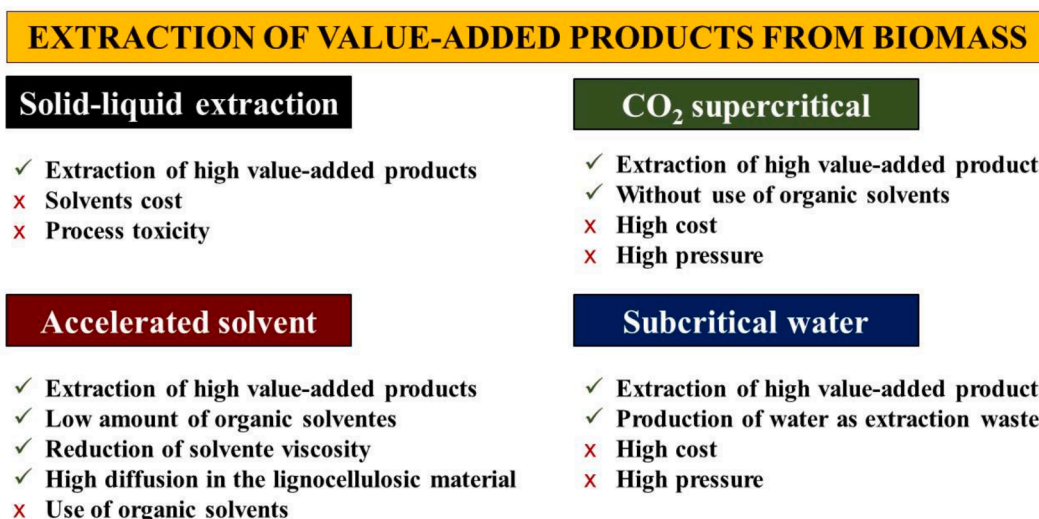


Fig. 3. Main features related to the extraction protocols without assistance of US.

surface induces the erosion of structures which increases the accessibility of solvent with the vegetable materials, leading to an efficient solubilization and consequently an increase in the extraction efficiency [93,127]. Shear forces generates deformations and microfractures in the vegetable structures, which increase the contact between the solvent and the solid material [93,127].

The sonoporation is the US effect associated with the increase in the permeability of cellular membranes [128]. At lower US frequencies, the diffusion of solvent into cellular membrane of lignocellulosic materials is more effective leading to higher extraction yields [128]. Some studies reported that near to the bubble collapse the micro jets and micro flow might modify the diffusion in cellular membranes [128].

Capillarity is an effect generated when the depth and speed of solvent penetration in the lignocellulosic material increases during the US application [129]. The diffusion of extracting product from cellular membranes of lignocellulosic materials tends to be more effective due to the higher solvent penetration rate [129]. Another important effect is the detexturation that consists in the destruction of vegetable cells during the US propagation which promotes the solvation and extraction efficiency [93,127].

It is important to highlight that erosion, shear forces, sonoporation, fragmentation, capillary effect and detexturation associated with sonication, do not cover all extraction mechanisms associated with US [93]. A full understanding of mechanisms that contribute to increase the extraction efficiency depends on the operational and physicochemical conditions employed [93,127]. In most studies, the main limitation for increasing the extraction efficiency are the properties of lignocellulosic materials, and how the value-added products are linked to it.

For scaling up extraction systems, the use of continuous process, or serial reactors, are good alternatives for industrial applications. Ultrasonic baths, for instance, are applied to a large amount of feedstock, but these systems normally require mechanical agitation [93,130]. Taking into account the use of US in extraction procedures, it is considered the most promising research area looking for industrial applications in relatively short time. US-assisted protocols are associated with the reduced extraction times, as well as the possibility of working at relatively milder condition of temperature when compared to protocols in the absence of US [92,125].

Regarding to green food processing, the use of US energy in degassing, demoulding, and cutting are described as valid alternatives for industrial applications [131]. The use of US for degassing enables the removal of dissolved oxygen, nitrogen or carbon dioxide at atmospheric pressure, and without increment in the temperature, which is desirable for the production of carbonated beverages and beers [131]. Some

authors have reported that the US vibration in demoulding procedures ensure a complete removal of residual materials from the industrial moulds, thus reducing the necessity of cleaning steps [131]. In cutting procedures, the US leads to the minimization of maintenance costs and reduction of food wastes. The main applications of US-cutting are associated to overcome problems related to handle of fragile and heterogeneous food [131].

Although the feasibility of using US-assisted extraction for biomass valorization, the overall process is strongly dependent on the availability of lignocellulosic materials. Several studies have also discussed the effects of US energy for biomasses not considered as a waste of any industrial process. However, the extraction protocols for biomass valorization are only feasible for lignocellulosic material already considered as waste from industrial process. Additionally, the amount of generated waste must be enough for allowing its reuse towards circular economy strategies [131,132]. The so-called “coproduction”, or “coextraction” processes are going to be increasingly common for the biomass valorization [132,133]. Additionally, the proposal of using a single lignocellulosic material to produce several products has become the main challenge in biomass valorization.

6. Developments based on the use of alternative “green” solvents

Recently, the use of ionic liquids (IL), deep eutectic solvents (DES), and natural deep eutectic solvents (NADES) have been widely studied as an alternative to the use of organic solvents to biomass valorization [134,135]. Ionic liquids are salt, composed of a small anion and a large organic cation that are liquids at environmental conditions [134,135]. The interest in these alternative solvents is increasing due to negligible vapor pressure, allowing exploring several biomass valorization processes [134,135]. Another class of solvent is the DES, which have similar physical properties of ionic liquids, but are mixtures of compounds that present a lower melting point when compared to the individual components (due to the presence of hydrogen bonds) [134,135]. The most used reagents for producing IL and DES are amides, carboxylic acids, alcohols, choline chloride, and quaternary ammonium salts. The main advantage of DES in comparison with IL are associated with solvent production [134,135]. For DES the production comprises a reduced number of process steps, absence of solvents, and low associated cost. These aspects, associated with the high purity of the obtained product, make this solvent a potential reagent for industrial applications [134,135].

Despite advantages of these alternative “green” solvents, the use of

Table 3

Some examples of US-assisted extraction of high-value-added chemical products from biomass feedstocks.

Biomass	US details	Experimental conditions	Main observations	Ref.
Olive leaves	24 kHz, 400 W, horn	15 min, ~70 °C, 50% ethanol (v v ⁻¹) with a solid:liquid ratio of 1:20	30.7 g of gallic acid equivalent per g of biomass	[112]
Fresh purple sweet potato	45 kHz, 178 W, bath	40 min, 80 °C, 58% ethanol (v v ⁻¹) with a solid:liquid ratio of 1:20	3.877 mg of polyphenols per g of feedstock 0.293 mg of anthocyanins per g of feedstock	[113]
Pomegranate peel	23.1–30.8 kHz, 480–640 W, horn	25 min, 70 °C, 10 MPa, water as solvent	61.72 mg of polyphenols per g of feedstock	[114]
Fresh olives	100 kHz, 240 W, bath	30 min, 50 °C, 80% methanol (v v ⁻¹) of methanol as solvent with a solid:liquid ratio of 1:22	7.01 mg of polyphenols per g of feedstock	[115]
Spent coffee grounds	20 kHz, 244 W, horn	34 min, 40 °C, 100% ethanol (v v ⁻¹) as solvent with a solid:liquid ratio of 1:17	34 mg of polyphenols per g of feedstock	[116]
Flax	30 kHz, 400 W, bath	60 min, 25 °C, 0.2 N NaOH with a solid:liquid ratio of 1:20	24.01 mg of secoisolariciresinol diglucoside per g of feedstock	[117]
Eggplant peel	33.88 kHz, [a], bath	45 min, 55 °C, 55% of methanol (v v ⁻¹) with a solid:liquid ratio of 1:10	240 mg of anthocyanins per g of feedstock	[118]
Jaboticaba peel	25 kHz, 150 W, bath	10 min, 30 °C, 46% of ethanol (v v ⁻¹) with a solid:liquid ratio of 1:20	92.8 mg of anthocyanins per g of feedstock	[119]
Mango peel	20 kHz, 750 W, horn	20 min, 30 °C, 50% of ethanol (v v ⁻¹) with a solid:liquid ratio of 1:25	The US increased than 50% of pectin extraction yield	[120]
Grape pomace	24 kHz, 200 W, horn	6 min, 10 °C, 50% of ethanol (v v ⁻¹) with a solid:liquid ratio of 1:10	US energy load to shorter extraction time (conventional extraction 60 min)	[121]
Grape skin	20 kHz, 1000 W, horn	9 min, 30 °C, 50% of ethanol (v v ⁻¹) with a solid:liquid ratio of 1:10	Reduction of 51 min in extraction time	[122]
Citrus peel	60 kHz, 360 W, bath	60 min, 15 °C, 80% of methanol (v v ⁻¹) with a solid:liquid ratio of 1:20	Efficiently extraction of 7 phenolic compounds of industrial interest	[123]
Coconut shell powder	25 kHz, 150 W, bath	50 min, 30 °C, 50% of ethanol (v v ⁻¹) with a solid:liquid ratio of 1:35 43 min, 40 °C, acid water as	406 mg of polyphenols per extract liter	[124] [125]

Table 3 (continued)

Biomass	US details	Experimental conditions	Main observations	Ref.
Maritime pine sawdust waste	25 kHz, 150 W, horn	solvent with a solid:liquid ratio of 1:10	342 mg of catechin equivalent per 100 g of dry basis	

synthetic compounds is considered a crucial issue for the development of the eco-friendly process [134–136]. On this aspect, NADES have been studied as an alternative to the use of synthetic compounds [137]. As reported, the use of organic acids, amino acids, sugars, and urea ensure the solvent efficiency with reduced toxicity and lower waste generation.

For biomass valorization, the use of alternative “green” solvents can lead to biomass solubilization and high extraction efficiency of bioactive compounds [138]. The synergic effects of alternative solvents and US energy have shown a promising eco-friendly process for biomass valorization [137]. Some successful examples can be highlighted, as the production of furanic platforms in ionic liquids/US horn [80], the extraction of bioactive compounds from grape pomace in natural deep eutectic solvents/US horn [99], and the lignin removal from wheat straw in deep eutectic solvents/US bath [139,140].

Several green solvents and experimental conditions have been used for biomass treatments. The use of lower amounts of organic solvents associated with high efficiency in biomass solubilization generates favourable conditions for in the potential scaling up to industrial applications. Nevertheless the development of suitable purification procedures and solvents recycling remain a priority [99]. Solvents recovery, can be achieved by liquid–liquid extraction (using organic solvents), and solid–liquid extraction (using resins and adsorbents) [134,135,141]. A big effort is running in this direction for biomass valorization at industrial scale.

7. Challenges and perspectives

The modern lifestyle has demanded a growing amount of energy and chemical products as feedstocks for several industrial processes. Despite this growing trend being associated with industrialization patterns, it is dependent on non-renewable fossil fuels, which are gradually depleting the reservoirs. Residual biomass has been considered for gradually replacing the current industrial and energetic dependency on fossil fuels. However, this goal could be achieved only by means of highly efficient and economically sustainable conversion processes. In this way, residual biomass has become a very attractive alternative because the low cost, and the lack of ethical conflict with food availability. Unfortunately, the technology for biomass conversion is not ready to replace conventional protocols, based on finite feedstock. It happens because the conversion process of biomass is strongly dependent on its composition, physical characteristic, being normally able to convert only one defined kind of biomass.

Currently, US technology deserves a special attention due to the efficient and selective conversions observed. The advances in the US-assisted processing of several lignocellulosic materials improve their conversion to biofuels, fine chemicals, chemical building blocks, and solvents. The main responsible for increasing the efficiency in biomass valorization processes assisted by US are those effects related with acoustic cavitation (as microbubble implosion, local hotspots, high-speed microjets, and strong shockwaves). Additionally, sonoporation, sonocapillarity, and sonoerosion are also observed when lignocellulosic biomass is sonicated, which contributes for reducing cellulose crystallinity, solubilization of lignin, and the extraction protocols. Moreover, operational conditions (solvent concentration, solid/liquid ratio etc.) and reaction rates, can be dramatically improved by US-assisted processes.

Despite US has been mainly used in the pretreatment step, its application in the conversion process, alone or combined with other

technologies, has aroused interest in the scientific community. Sonochemical-assisted hydrolysis, pyrolysis, biochemical/hydrothermal conversion, among others, showed a higher efficiency. Although the industrial application of US is not yet fully exploited, the new advances in R&D developments represent a glimpse of the amazing potential.

CRedit authorship contribution statement

Erico M.M. Flores: Supervision, Writing - review & editing, Funding acquisition. **Giancarlo Cravotto:** Writing - review & editing, Funding acquisition. **Cezar A. Bizzi:** Project administration, Writing - review & editing. **Daniel Santos:** Writing - original draft. **Gabrielle D. Iop:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] A. Demirbas, Political, economic and environmental impacts of biofuels: A review, *Appl. Energy* 86 (2009) S108–S117, <https://doi.org/10.1016/j.apenergy.2009.04.036>.
- [2] M. Hoogwijk, A. Faaij, R. van den Broek, G. Berndes, D. Gielen, W. Turkenburg, Exploration of the ranges of the global potential of biomass for energy, *Biomass Bioenergy* 25 (2) (2003) 119–133, [https://doi.org/10.1016/S0961-9534\(02\)00191-5](https://doi.org/10.1016/S0961-9534(02)00191-5).
- [3] J. Valentine, J. Clifton-Brown, A. Hastings, P. Robson, G. Allison, P. Smith, Food vs. fuel: The use of land for lignocellulosic 'next generation' energy crops that minimize competition with primary food production, *GCB Bioenergy* 4 (2012) 1–19.
- [4] N. Sonil, A.K. Janusz, K.D. Ajay, Lignocellulosic biomass: A review of conversion technologies and fuel products, *Curr. Eng. J.* 3 (2016) 24–36.
- [5] Y.H. Chan, K.W. Cheah, B.S. How, A.C.M. Loy, M. Shahbaz, H.K.G. Singh, N. R. Yusuf, A.F.A. Shuhaili, S. Yusup, W.A.W.A.K. Ghani, J. Rambli, Y. Kansha, H. L. Lam, B.H. Hong, S.L. Ngan, An overview of biomass thermochemical conversion technologies in Malaysia, *Sci. Total Environ.* 680 (2019) 105–123, <https://doi.org/10.1016/j.scitotenv.2019.04.211>.
- [6] M. FitzPatrick, P. Champagne, M.F. Cunningham, R.A. Whitney, A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products, *Bioresour. Technol.* 101 (2010) 8915–8922.
- [7] N. Mirabella, V. Castellani, S. Sala, Current options for the valorization of food manufacturing waste: a review, *J. Cleaner Prod.* 65 (2014) 28–41, <https://doi.org/10.1016/j.jclepro.2013.10.051>.
- [8] D.A. Teigiserova, L. Hamelin, M. Thomsen, Review of high-value food waste and food residues biorefineries with focus on unavoidable wastes from processing, *Resour. Conserv. Recycl.* 149 (2019) 413–426, <https://doi.org/10.1016/j.resconrec.2019.05.003>.
- [9] A. Pandey, S. Negi, P. Binod, C. Larroche, Pretreatment of biomass: Processes and technologies, Elsevier, Amsterdam, 2015.
- [10] S. Kentish, M. Ashokkumar, The physical and chemical effects of ultrasound, in: H. Feng, G. Barbosa-Canovas, J. Weiss (Eds.), *Ultrasound technologies for food and bioprocessing*, Food engineering series, Springer, New York, 2011.
- [11] M. Gallo, L. Ferrara, D. Naviglio, Application of ultrasound in food science and technology: A perspective, *Foods* 7 (2018) 1–18.
- [12] C. Leonelli, T.J. Mason, Microwave and ultrasonic processing: Now a realistic option for industry, *Chem. Eng. Process.* 49 (2010) 885–900.
- [13] J. Luo, Z. Fang, R.L. Smith, X. Qi, Fundamentals of acoustic cavitation in sonochemistry, in: Z. Fang, J.L. Smith, X. Qi (Eds.), *Production of biofuels and chemicals with ultrasound*, Biofuels and Biorefineries, Springer, Dordrecht, 2015.
- [14] D. Chen, S.K. Sharma, A. Mudhoo, *Handbook on applications of ultrasound: Sonochemistry for sustainability*, 1st ed., CRC Press, USA, 2011.
- [15] T. Mason, D. Peters, *Practical sonochemistry: Power ultrasound uses and applications*, 2nd ed., Copyright, Woodhead, 2003.
- [16] T. Leong, M. Ashokkumar, S. Kentish, The fundamentals of power ultrasound - A review, *Acoust. Aust.* 39 (2011) 54–63.
- [17] J. Rooze, E.V. Rebrov, J.C. Schouten, J.T.F. Keurentjes, Dissolved gas and ultrasonic cavitation - A review, *Ultrason. Sonochem.* 20 (1) (2013) 1–11, <https://doi.org/10.1016/j.ultsonch.2012.04.013>.
- [18] T.Y. Wu, N. Guo, C.Y. Teh, J.X.W. Hay, Theory and fundamentals of ultrasound, in: T.Y. Wu, N. Guo, C.Y. Teh, J.X.W. Hay (Eds.), *Advances in ultrasonics technology for environmental remediation*, Springer, Dordrecht, 2013.
- [19] M. Ashokkumar, The characterization of acoustic cavitation bubbles - An overview, *Ultrason. Sonochem.* 18 (4) (2011) 864–872, <https://doi.org/10.1016/j.ultsonch.2010.11.016>.
- [20] R. Kumar, S. Singh, O.V. Singh, Bioconversion of lignocellulosic biomass: biochemical and molecular perspectives, *J. Ind Microbiol. Biotechnol.* 35 (5) (2008) 377–391, <https://doi.org/10.1007/s10295-008-0327-8>.
- [21] R.C. Brown, *Thermochemical processing of biomass: Conversion into fuels, chemicals and power*, 2nd ed., Copyright, USA, 2019.
- [22] M.H.L. Silveira, A.R.C. Morais, A.M. daCostaLopes, D.N. Oleksyszyn, R. Bogel-Lukasik, J. Andreas, L. PereiraRamos, Current Pretreatment Technologies for the Development of Cellulosic Ethanol and Biorefineries, *ChemSusChem* 8 (20) (2015) 3366–3390, <https://doi.org/10.1002/cssc.201500282>.
- [23] M. Badii, N. Asim, J.M. Jahim, K. Sopian, Comparison of Chemical Pretreatment Methods for Cellulosic Biomass, *APCBEE Procedia* 9 (2014) 170–174, <https://doi.org/10.1016/j.apcbpe.2014.01.030>.
- [24] F. Cherubini, The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, *Energy Convers. Manag.* 51 (2010) 1412–1421.
- [25] F. Cherubini, A.H. Stromman, Chemicals from lignocellulosic biomass: Opportunities, perspectives, and potential of biorefinery systems, *Biofuel. Bioprod. Bior* 5 (2011) 548–561.
- [26] A.M.R. Galletti, C. Antonetti, Biomass pretreatment: Separation of cellulose, hemicellulose, and lignin - existing technologies and perspectives, in: M. Aresta, A. Dibenedetto, F. Dumeignil (Eds.), *Biorefinery: From biomass to chemicals and fuels*, Walter de Gruyter, Germany, 2012.
- [27] T.W. Jeffries, in: *Physiology of Biodegradative Microorganisms*, Springer Netherlands, Dordrecht, 1991, pp. 163–176, https://doi.org/10.1007/978-94-011-3452-1_7.
- [28] M. Aresta, A. Dibenedetto, F. Dumeignil, *Biorefinery: From biomass to chemicals and fuels*, Walter de Gruyter, Germany, 2012.
- [29] M.J. Bussemaker, D. Zhang, Effect of Ultrasound on Lignocellulosic Biomass as a Pretreatment for Biorefinery and Biofuel Applications, *Ind. Eng. Chem. Res.* 52 (10) (2013) 3563–3580, <https://doi.org/10.1021/ie3022785>.
- [30] S.I. Mussatto, Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery, Elsevier, 2016.
- [31] S.S. Hassan, G.A. Williams, A.K. Jaiswal, Emerging technologies for the pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 262 (2018) 310–318, <https://doi.org/10.1016/j.biortech.2018.04.099>.
- [32] T.J. Mason, *Advances in sonochemistry*, Elsevier, 1996.
- [33] J.P. Lorimer, T.J. Mason, Sonochemistry. Part 1—The physical aspects, *Chem. Soc. Rev.* 16 (0) (1987) 239–274, <https://doi.org/10.1039/CS9871600239>.
- [34] R. Ravindran, S. Jaiswal, N. Abu-Ghannam, A.K. Jaiswal, Evaluation of ultrasound assisted potassium permanganate pre-treatment of spent coffee waste, *Bioresour. Technol.* 224 (2017) 680–687, <https://doi.org/10.1016/j.biortech.2016.11.034>.
- [35] Z.-Y. Xiong, Y.-H. Qin, J.-Y. Ma, L.i. Yang, Z.-K. Wu, T.-L. Wang, W.-G. Wang, C.-W. Wang, Pretreatment of rice straw by ultrasound-assisted Fenton process, *Bioresour. Technol.* 227 (2017) 408–411, <https://doi.org/10.1016/j.biortech.2016.12.105>.
- [36] G. Ramadoss, K. Muthukumar, Ultrasound assisted metal chloride treatment of sugarcane bagasse for bioethanol production, *Renewable Energy* 99 (2016) 1092–1102, <https://doi.org/10.1016/j.renene.2016.08.003>.
- [37] Y. Zheng, Z. Pan, R. Zhang, Overview of biomass pretreatment for cellulosic ethanol production, *Int. J. Agr. Biol. Eng.* 2 (2009) 51–68.
- [38] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapfel, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 96 (2005) 673–686.
- [39] P.F.H. Harmsen, W.J.J. Huijgen, L.M.B. López, R.R.C. Bakker, Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, in: *Wageningen UR-Food & Biobased Research* (2010).
- [40] M.S.U. Rehman, I. Kim, Y. Chisti, J.I. Han, Use of ultrasound in the production of bioethanol from lignocellulosic biomass, *Energy Ed. Sci. Technol. Part A: Energy Sci. Res.* 30 (2013) 1391–1410.
- [41] P. Ghisellini, C. Cialani, S. Ulgiati, A review on circular economy: The expected transition to a balanced interplay of environmental and economic systems, *J. Clean. Prod.* 114 (2016) 11–32.
- [42] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, *Fuel* 94 (2012) 1–33, <https://doi.org/10.1016/j.fuel.2011.09.030>.
- [43] B.M. Jenkins, L.L. Baxter, T.R. Miles Jr., T.R. Miles, Combustion properties of biomass, *Fuel Process. Technol.* 54 (1–3) (1998) 17–46, [https://doi.org/10.1016/S0378-3820\(97\)00059-3](https://doi.org/10.1016/S0378-3820(97)00059-3).
- [44] M. Asadiaraghi, W. Daud, Characterization of lignocellulosic biomass thermal degradation and physicochemical structure: Effects of demineralization by diverse acid solutions, *Energy Convers. Manag.* 82 (2014) 71–82.
- [45] L. Jiang, S. Hu, L.-S. Sun, S. Su, K. Xu, L.-m. He, J. Xiang, Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass, *Bioresour. Technol.* 146 (2013) 254–260, <https://doi.org/10.1016/j.biortech.2013.07.063>.

- [46] L.O. Diehl, T.L. Gatiboni, P.A. Mello, E.I. Muller, F.A. Duarte, E.M.M. Flores, Ultrasound-assisted extraction of rare-earth elements from carbonatite rocks, *Ultrason. Sonochem.* 40 (2018) 24–29, <https://doi.org/10.1016/j.ultsonch.2017.04.012>.
- [47] F.A. Duarte, P.A. Mello, C.A. Bizzi, M.A.G. Nunes, E.M. Moreira, M.S. Alencar, H. N. Motta, V.L. Dressler, E.M.M. Flores, Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process, *Fuel* 90 (6) (2011) 2158–2164, <https://doi.org/10.1016/j.fuel.2011.01.030>.
- [48] C.A. Bizzi, R.C. Zanatta, D. Santos, K. Giacobe, R.M. Dallago, P.A. Mello, E.M. M. Flores, Ultrasound-assisted extraction of chromium from residual tanned leather: An innovative strategy for the reuse of waste in tanning industry, *Ultrason. Sonochem.* 64 (2020) 104682, <https://doi.org/10.1016/j.ultsonch.2019.104682>.
- [49] S.-S. Wong, S. Kasapis, D. Huang, Molecular weight and crystallinity alteration of cellulose via prolonged ultrasound fragmentation, *Food Hydrocolloids* 26 (2) (2012) 365–369, <https://doi.org/10.1016/j.foodhyd.2011.02.028>.
- [50] S. Sasmal, V.V. Goud, K. Mohanty, Ultrasound Assisted Lime Pretreatment of Lignocellulosic Biomass toward Bioethanol Production, *Energy Fuels* 26 (6) (2012) 3777–3784, <https://doi.org/10.1021/ef300669w>.
- [51] I.A. Udoetok, L.D. Wilson, J.V. Headley, Ultra-sonication assisted cross-linking of cellulose polymers, *Ultrason. Sonochem.* 42 (2018) 567–576, <https://doi.org/10.1016/j.ultsonch.2017.12.017>.
- [52] W.U. Lan, C.F. Liu, F.X. Yue, R.C. Sun, J.F. Kennedy, Ultrasound-assisted dissolution of cellulose in ionic liquid, *Carbohydr. Polym.* 86 (2) (2011) 672–677, <https://doi.org/10.1016/j.carbpol.2011.05.013>.
- [53] R. Sindhu, P. Binod, A.K. Mathew, A. Abraham, E. Gnansounou, S.B. Ummalyma, L. Thomas, A. Pandey, Development of a novel ultrasound-assisted alkali pretreatment strategy for the production of bioethanol and xylanases from chili post harvest residue, *Bioresour. Technol.* 242 (2017) 146–151, <https://doi.org/10.1016/j.biortech.2017.03.001>.
- [54] K. Nakashima, Y. Ebi, M. Kubo, N. Shibasaki-Kitakawa, T. Yonemoto, Pretreatment combining ultrasound and sodium percarbonate under mild conditions for efficient degradation of corn stover, *Ultrason. Sonochem.* 29 (2016) 455–460, <https://doi.org/10.1016/j.ultsonch.2015.10.017>.
- [55] S. Baksi, S. Saha, C. Birgen, U. Sarkar, H.A. Preisig, S. Markussen, B. Wittgens, A. Wentzel, 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* 16 (2019) 662–676.
- [56] M. P. P. Saroj, N. Korrapati, Ultrasound-assisted alkaline pretreatment to intensify enzymatic saccharification of *Crotalaria juncea* using a statistical method, *Biomass Conv. Bioref.* 8 (3) (2018) 659–668, <https://doi.org/10.1007/s13399-018-0324-8>.
- [57] G. Yang, J. Wang, Ultrasound combined with dilute acid pretreatment of grass for improvement of fermentative biohydrogen production, *Bioresour. Technol.* 275 (2019) 10–18, <https://doi.org/10.1016/j.biortech.2018.12.013>.
- [58] K. Ninomiya, H. Takamatsu, A. Onishi, K. Takahashi, N. Shimizu, Sonocatalytic-Fenton reaction for enhanced OH radical generation and its application to lignin degradation, *Ultrason. Sonochem.* 20 (4) (2013) 1092–1097, <https://doi.org/10.1016/j.ultsonch.2013.01.007>.
- [59] M.-F. Zhang, Y.-H. Qin, J.-Y. Ma, L. Yang, Z.-K. Wu, T.-L. Wang, W.-G. Wang, C.-W. Wang, Depolymerization of microcrystalline cellulose by the combination of ultrasound and Fenton reagent, *Ultrason. Sonochem.* 31 (2016) 404–408, <https://doi.org/10.1016/j.ultsonch.2016.01.027>.
- [60] P.B. Subhedar, P.R. Gogate, Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material, *Ultrason. Sonochem.* 21 (1) (2014) 216–225, <https://doi.org/10.1016/j.ultsonch.2013.08.001>.
- [61] S. Singh, S.T.P. Bharadwaja, P.K. Yadav, V.S. Moholkar, A. Goyal, Mechanistic Investigation in Ultrasound-Assisted (Alkaline) Delignification of Parthenium hysterophorus Biomass, *Ind. Eng. Chem. Res.* 53 (37) (2014) 14241–14252, <https://doi.org/10.1021/ie502339q>.
- [62] N.D. Vu, H.T. Tran, N.D. Bui, C.D. Vu, H.V. Nguyen, Lignin and cellulose extraction from Vietnam's rice straw using ultrasound-assisted alkaline treatment method, *Int. J. Polym. Sci.* 1 (2017) 1–8.
- [63] R. Velmurugan, K. Muthukumar, Ultrasound-assisted alkaline pretreatment of sugarcane bagasse for fermentable sugar production: Optimization through response surface methodology, *Bioresour. Technol.* 112 (2012) 293–299.
- [64] R. Velmurugan, K. Muthukumar, Utilization of sugarcane bagasse for bioethanol production: Sono-assisted acid hydrolysis approach, *Bioresour. Technol.* 102 (2011) 7119–7123.
- [65] O.M. Perrone, F.M. Colombari, J.S. Rossi, M.M.S. Moretti, S.E. Bordignon, C.D. C. Nunes, E. Gomes, M. Boscolo, R. Silva, Ozonolysis combined with ultrasound as a pretreatment of sugarcane bagasse: Effect on the enzymatic saccharification and the physical and chemical characteristics of the substrate, *Bioresour. Technol.* 218 (2016) 69–76.
- [66] G. Ramadoss, K. Muthukumar, Mechanistic study on ultrasound assisted pretreatment of sugarcane bagasse using metal salt with hydrogen peroxide for bioethanol production, *Ultrason. Sonochem.* 28 (2016) 207–217, <https://doi.org/10.1016/j.ultsonch.2015.07.006>.
- [67] R. Sindhu, M. Kuttiraja, V. Elizabeth Preeti, S. Vani, R.K. Sukumaran, P. Binod, A novel surfactant-assisted ultrasound pretreatment of sugarcane tops for improved enzymatic release of sugars, *Bioresour. Technol.* 135 (2013) 67–72, <https://doi.org/10.1016/j.biortech.2012.09.050>.
- [68] C. Zhong, H. Jia, P. Wei, Enhanced saccharification of wheat straw with the application of ultrasonic-assisted quaternary ammonium hydroxide pretreatment, *Process Biochem.* 53 (2017) 180–187, <https://doi.org/10.1016/j.procbio.2016.11.004>.
- [69] Q.-F. Wang, L.-I. Niu, J. Jiao, N.a. Guo, Y.-P. Zang, Q.-Y. Gai, Y.-J. Fu, Degradation of lignin in birch sawdust treated by a novel Myrothecium verrucaria coupled with ultrasound assistance, *Bioresour. Technol.* 244 (2017) 969–974, <https://doi.org/10.1016/j.biortech.2017.07.164>.
- [70] D. Holmgren, Future scenarios: How communities can adapt to peak oil and climate change, *Chelsea Green Publishing*, 2012.
- [71] A.V. Bridgewater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94, <https://doi.org/10.1016/j.biombioe.2011.01.048>.
- [72] Y. Chhiti, M. Kemiha, Thermal conversion of biomass, pyrolysis and gasification: A review, *Int. J. Eng. Sci.* 2 (2013) 75–85.
- [73] C. Zhao, E. Jiang, A. Chen, Volatile production from pyrolysis of cellulose, hemicellulose and lignin, *J. Energy Inst.* 90 (6) (2017) 902–913, <https://doi.org/10.1016/j.joei.2016.08.004>.
- [74] A.A. Lappas, S. Bezerigianni, I.A. Vasalos, Production of biofuels via co-processing in conventional refining processes, *Catal. Today* 145 (1–2) (2009) 55–62, <https://doi.org/10.1016/j.cattod.2008.07.001>.
- [75] J.S. Tumuluru, S. Sokhansanj, C.T. Wright, J.R. Hess, R.D. Boardman, A review on biomass torrefaction process and product properties. Symposium on Thermochemical Conversion, Oklahoma State University, 2011.
- [76] H. Haykiri-Acma, S. Yaman, S. Kucukbayrak, Gasification of biomass chars in steam–nitrogen mixture, *Energy Convers. Manage.* 47 (7–8) (2006) 1004–1013, <https://doi.org/10.1016/j.enconman.2005.06.003>.
- [77] P. Vasudevan, S. Sharma, A. Kumar, Liquid fuel from biomass: An overview, *J. Sci. Ind. Res.* 64 (2005) 822–831.
- [78] V. Gude, G. Grant, P. Patil, S. Deng, Biodiesel production from low cost and renewable feedstock, *Open Eng.* 3 (2013) 595–605.
- [79] S. Karnjanakom, G. Guan, B. Asep, X. Du, X. Hao, J. Yang, C. Samart, A. Abudula, A green method to increase yield and quality of bio-oil: Ultrasonic pretreatment of biomass and catalytic upgrading of bio-oil over metal (Cu, Fe and/or Zn)/ γ -Al₂O₃, *RSC Adv.* 5 (2015) 83494–83503.
- [80] A. Sarwono, Z. Man, N. Muhammad, A.S. Khan, W.S.W. Hamzah, A.H.A. Rahim, Z. Ullah, C.D. Wilfred, A new approach of probe sonication assisted ionic liquid conversion of glucose, cellulose and biomass into 5-hydroxymethylfurfural, *Ultrason. Sonochem.* 37 (2017) 310–319, <https://doi.org/10.1016/j.ultsonch.2017.01.028>.
- [81] C.A. Bizzi, D. Santos, T.C. Sieben, G.V. Motta, P.A. Mello, E.M.M. Flores, Furfural production from lignocellulosic biomass by ultrasound-assisted acid hydrolysis, *Ultrason. Sonochem.* 51 (2019) 332–339, <https://doi.org/10.1016/j.ultsonch.2018.09.011>.
- [82] R.S. Malani, V. Shinde, S. Ayachit, A. Goyal, V.S. Moholkar, Ultrasound-assisted biodiesel production using heterogeneous base catalyst and mixed non-edible oils, *Ultrason. Sonochem.* 52 (2019) 232–243, <https://doi.org/10.1016/j.ultsonch.2018.11.021>.
- [83] D. Santos, U.F. Silva, F.A. Duarte, C.A. Bizzi, E.M.M. Flores, P.A. Mello, Ultrasound-assisted acid hydrolysis of cellulose to chemical building blocks: Application to furfural synthesis, *Ultrason. Sonochem.* 40 (2018) 81–88, <https://doi.org/10.1016/j.ultsonch.2017.04.034>.
- [84] Z. Lu, Z. Wu, L. Fan, H. Zhang, Y. Liao, D. Zheng, S. Wang, Rapid and solvent-saving liquefaction of woody biomass using microwave-ultrasonic assisted biotechnology, *Bioresour. Technol.* 199 (2016) 423–426, <https://doi.org/10.1016/j.biortech.2015.09.048>.
- [85] P. Cintas, S. Mantegna, E.C. Gaudino, G. Cravotto, A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel, *Ultrason. Sonochem.* 17 (6) (2010) 985–989, <https://doi.org/10.1016/j.ultsonch.2009.12.003>.
- [86] X. Yin, X. Zhang, M. Wan, X. Duan, Q. You, J. Zhang, S. Li, Intensification of biodiesel production using dual-frequency counter-current pulsed ultrasound, *Ultrason. Sonochem.* 37 (2017) 136–143, <https://doi.org/10.1016/j.ultsonch.2016.12.036>.
- [87] M.N. Hussain, I. Janajreh, Acousto-chemical analysis in multi-transducer sonochemical reactors for biodiesel production, *Ultrason. Sonochem.* 40 (2018) 184–193, <https://doi.org/10.1016/j.ultsonch.2017.07.009>.
- [88] L. Cherpozat, E. Loranger, C. Daneault, Ultrasonic pretreatment effects on the bio-oil yield of a laboratory-scale slow wood pyrolysis, *J. Anal. Appl. Pyrol.* 126 (2017) 31–38, <https://doi.org/10.1016/j.jaap.2017.06.027>.
- [89] H.A. Allami, M. Tabasizadeh, A. Rohani, H. Nayebezhadeh, A. Farzad, Effect of ultrasonic irradiation on the properties and performance of biodiesel produced from date seed oil used in the diesel engine, *Ultrason. Sonochem.* 60 (2020), 104672.
- [90] E. Calcio Gaudino, G. Cravotto, M. Manzoli, S. Tabasso, Sono- and mechanochemical processes in the catalytic conversion of biomass, *Chem. Soc. Rev.* (2020) in press - DOI: 10.1039/d1030cs01152e.
- [91] J. Luo, Z. Fang, R.L. Smith Jr., Ultrasound-enhanced conversion of biomass to biofuels, *Prog. Energy Combust. Sci.* 41 (2014) 56–93, <https://doi.org/10.1016/j.pecs.2013.11.001>.
- [92] J.M. Marchetti, Z. Fang, *Biodiesel, Blends, properties, and applications*, Nova Science Publishers (2011).
- [93] F. Chemat, N. Rombaut, A.-G. Sicaire, A. Meullemiestre, A.-S. Fabiano-Tixier, M. Abert-Vian, Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review, *Ultrason. Sonochem.* 34 (2017) 540–560, <https://doi.org/10.1016/j.ultsonch.2016.06.035>.

- [94] L.T. Thanh, K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, H. Bandow, Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process, *Bioresour. Technol.* 101 (2) (2010) 639–645, <https://doi.org/10.1016/j.biortech.2009.08.050>.
- [95] V.S. Sutkar, P.R. Gogate, Design aspects of sonochemical reactors: Techniques for understanding cavitation activity distribution and effect of operating parameters, *Chem. Eng. J.* 155 (2009) 26–36.
- [96] V.S. Sutkar, P.R. Gogate, L. Csoka, Theoretical prediction of cavitation activity distribution in sonochemical reactors, *Chem. Eng. J.* 158 (2) (2010) 290–295, <https://doi.org/10.1016/j.cej.2010.01.049>.
- [97] P.R. Gogate, V.S. Sutkar, A.B. Pandit, Sonochemical reactors: Important design and scale up considerations with a special emphasis on heterogeneous systems, *Chem. Eng. J.* 166 (2011) 1066–1082.
- [98] A. Arevalo-Gallegos, Z. Ahmad, M. Asgher, R. Parra-Saldivar, H.M.N. Iqbal, Lignocellulose: A sustainable material to produce value-added products with a zero waste approach-A review, *Int. J. Biol. Macromol.* 99 (2017) 308–318.
- [99] M. Panic, V. Gunjevic, G. Cravotto, I.R. Redovnikovic, Enabling technologies for the extraction of grape-pomace anthocyanins using natural deep eutectic solvents in up-to-half-litre batches extraction of grape-pomace anthocyanins using NADES, *Food Chem.* 300 (2019), 125185.
- [100] D.F. Ferreira, J.S. Barin, A. Binello, V.V. Veselov, G. Cravotto, Highly efficient pumpkin-seed extraction with the simultaneous recovery of lipophilic and hydrophilic compounds, *Food Bioprod. Process.* 117 (2019) 224–230, <https://doi.org/10.1016/j.fbp.2019.07.014>.
- [101] G. Grillo, L. Boffa, A. Binello, S. Mantegna, G. Cravotto, F. Chemat, T. Dizhbite, L. Lauberte, G. Telysheva, Cocoa bean shell waste valorisation; extraction from lab to pilot-scale cavitation reactors, *Food Res. Int.* 115 (2019) 200–208, <https://doi.org/10.1016/j.foodres.2018.08.057>.
- [102] F. Chemat, M. Abert-Vian, A.S. Fabiano-Tixier, J. Strube, L. Uhlenbrock, V. Gunjevic, G. Cravotto, Green extraction of natural products. Origins, current status, and future challenges, *TrAC, Trends Anal. Chem.* 118 (2019) 248–263, <https://doi.org/10.1016/j.trac.2019.05.037>.
- [103] K. Vilku, R. Mawson, L. Simons, D. Bates, Applications and opportunities for ultrasound assisted extraction in the food industry — A review, *Innovative Food Sci. Emerg. Technol.* 9 (2) (2008) 161–169, <https://doi.org/10.1016/j.ifset.2007.04.014>.
- [104] M.I. Zaretskii, V.V. Rusak, E.M. Chartov, Extraction of phenols from industrial mixtures: A review, *Coke Chem.* 56 (3) (2013) 110–112, <https://doi.org/10.3103/S1068364X13030095>.
- [105] F. Chemat, M. Abert Vian, A.-S. Fabiano-Tixier, M. Nutrizio, A. Rezek Jambak, P. E.S. Munkata, J.M. Lorenzo, F.J. Barba, A. Binello, G. Cravotto, A review of sustainable and intensified techniques for extraction of food and natural products, *Green Chem.* 22 (8) (2020) 2325–2353, <https://doi.org/10.1039/C9GC03878G>.
- [106] E.A. Abourashed, J.R. Vanderplank, I.A. Khan, High-Speed Extraction and HPLC Fingerprinting of Medicinal Plants – I. Application to Passiflora Flavonoids, *Pharm. Biol.* 40 (2) (2002) 81–91, <https://doi.org/10.1076/phbi.40.2.81.5844>.
- [107] L. Wang, C.L. Weller, Recent advances in extraction of nutraceuticals from plants, *Trends Food Sci. Technol.* 17 (6) (2006) 300–312, <https://doi.org/10.1016/j.tifs.2005.12.004>.
- [108] B. Díaz-Reinoso, A. Moure, H. Domínguez, J.C. Parajó, Supercritical CO₂ Extraction and Purification of Compounds with Antioxidant Activity, *J. Agric. Food Chem.* 54 (7) (2006) 2441–2469, <https://doi.org/10.1021/jf052858j>.
- [109] C.G. Pereira, M.A.A. Meireles, Supercritical Fluid Extraction of Bioactive Compounds: Fundamentals, Applications and Economic Perspectives, *Food Bioprocess Technol* 3 (3) (2010) 340–372, <https://doi.org/10.1007/s11947-009-0263-2>.
- [110] E. Ibañez, A. Kubátová, F.J. Señoráns, S. Caverro, G. Reglero, S.B. Hawthorne, Subcritical Water Extraction of Antioxidant Compounds from Rosemary Plants, *J. Agric. Food Chem.* 51 (2) (2003) 375–382, <https://doi.org/10.1021/jf025878j>.
- [111] A.G. Carr, R. Mammucari, N.R. Foster, A review of subcritical water as a solvent and its utilisation for the processing of hydrophobic organic compounds, *Chem. Eng. J.* 172 (1) (2011) 1–17, <https://doi.org/10.1016/j.cej.2011.06.007>.
- [112] José.C. Martínez-Patiño, B. Gullón, I. Romero, E. Ruiz, M. Brncić, J.Šic. Žlabur, E. Castro, Optimization of ultrasound-assisted extraction of biomass from olive trees using response surface methodology, *Ultrason. Sonochem.* 51 (2019) 487–495, <https://doi.org/10.1016/j.ultsonch.2018.05.031>.
- [113] Z. Zhu, Q. Guan, M. Koubaa, F.J. Barba, S. Roohinejad, G. Cravotto, X. Yang, S. Li, J. He, HPLC-DAD-ESI-MS² analytical profile of extracts obtained from purple sweet potato after green ultrasound-assisted extraction, *Food Chem.* 215 (2017) 391–400, <https://doi.org/10.1016/j.foodchem.2016.07.157>.
- [114] B.R. Sumere, M.Corrêa. de Souza, M.Pacifico. dos Santos, Rosângela.M. N. Bezerra, D.T. da Cunha, J. Martinez, M.A. Rostagno, Combining pressurized liquids with ultrasound to improve the extraction of phenolic compounds from pomegranate peel (*Punica granatum L.*), *Ultrason. Sonochem.* 48 (2018) 151–162, <https://doi.org/10.1016/j.ultsonch.2018.05.028>.
- [115] J. Deng, Z. Xu, C. Xiang, J. Liu, L. Zhou, T. Li, Z. Yang, C. Ding, Comparative evaluation of maceration and ultrasound-assisted extraction of phenolic compounds from fresh olives, *Ultrason. Sonochem.* 37 (2017) 328–334, <https://doi.org/10.1016/j.ultsonch.2017.01.023>.
- [116] N.A. Al-Dhabi, K. Ponnuragan, P. Maran Jeganathan, Development and validation of ultrasound-assisted solid-liquid extraction of phenolic compounds from waste spent coffee grounds, *Ultrason. Sonochem.* 34 (2017) 206–213, <https://doi.org/10.1016/j.ultsonch.2016.05.005>.
- [117] C. Corbin, T. Fidel, E.A. Leclerc, E. Barakzoy, N. Sagot, A. Falguières, S. Renouard, J.-P. Blondeau, C. Ferroud, J. Doussot, E. Lainé, C. Hano, Development and validation of an efficient ultrasound assisted extraction of phenolic compounds from flax (*Linum usitatissimum L.*) seeds, *Ultrason. Sonochem.* 26 (2015) 176–185, <https://doi.org/10.1016/j.ultsonch.2015.02.008>.
- [118] F. Dranca, M. Oroian, Optimization of ultrasound-assisted extraction of total monomeric anthocyanin (TMA) and total phenolic content (TPC) from eggplant (*Solanum melongena L.*) peel, *Ultrason. Sonochem.* 31 (2016) 637–646, <https://doi.org/10.1016/j.ultsonch.2015.11.008>.
- [119] S. Rodrigues, F.A.N. Fernandes, E.S. de Brito, A.D. Sousa, N. Narain, Ultrasound extraction of phenolics and anthocyanins from jaboticaba peel, *Ind. Crops Prod.* 69 (2015) 400–407, <https://doi.org/10.1016/j.indcrop.2015.02.059>.
- [120] B. Bárbara.V. Guandalini, N.P. Rodrigues, L.D.F. Marczak, Sequential extraction of phenolics and pectin from mango peel assisted by ultrasound, *Food Res. Int.* 119 (2019) 455–461, <https://doi.org/10.1016/j.foodres.2018.12.011>.
- [121] C. Carrera, A. Ruiz-Rodríguez, M. Palma, C.G. Barroso, Ultrasound assisted extraction of phenolic compounds from grapes, *Anal. Chim. Acta* 732 (2012) 100–104, <https://doi.org/10.1016/j.aca.2011.11.032>.
- [122] T.W. Caldas, K.E.L. Mazza, A.S.C. Teles, G.N. Mattos, A.I.S. Brígida, C.A. Conte-Junior, R.G. Borguini, R.L.O. Godoy, L.M.C. Cabral, R.V. Tonon, Phenolic compounds recovery from grape skin using conventional and non-conventional extraction methods, *Ind. Crops Prod.* 111 (2018) 86–91, <https://doi.org/10.1016/j.indcrop.2017.10.012>.
- [123] Y.-Q. Ma, J.-C. Chen, D.-H. Liu, X.-Q. Ye, Simultaneous extraction of phenolic compounds of citrus peel extracts: Effect of ultrasound, *Ultrason. Sonochem.* 16 (1) (2009) 57–62, <https://doi.org/10.1016/j.ultsonch.2008.04.012>.
- [124] S. Rodrigues, G.A.S. Pinto, Ultrasound extraction of phenolic compounds from coconut (*Cocos nucifera*) shell powder, *J. Food Eng.* 80 (3) (2007) 869–872, <https://doi.org/10.1016/j.jfoodeng.2006.08.009>.
- [125] A. Meullemiestre, E. Petitcolas, Z. Maache-Rezzoug, F. Chemat, S.A. Rezzoug, Impact of ultrasound on solid-liquid extraction of phenolic compounds from maritime pine sawdust waste. Kinetics, optimization and large scale experiments, *Ultrason. Sonochem.* 28 (2016) 230–239, <https://doi.org/10.1016/j.ultsonch.2015.07.022>.
- [126] G. Chatel, K.D. Vigier, F. Jerome, Sonochemistry: What potential for conversion of lignocellulosic biomass into platform chemicals? *ChemSusChem* 7 (2014) 2774–2787.
- [127] B. Khadhraoui, M. Turk, A.S. Fabiano-Tixier, E. Petitcolas, P. Robinet, R. Imbert, M.E. Maïtaoui, F. Chemat, Histo-cytochemistry and scanning electron microscopy for studying spatial and temporal extraction of metabolites induced by ultrasound. Towards chain detexturation mechanism, *Ultrason. Sonochem.* 42 (2018) 482–492, <https://doi.org/10.1016/j.ultsonch.2017.11.029>.
- [128] S. Ohta, K. Suzuki, S. Miyagawa, Y. Ogino, M. Villacorte, Y. Wada, G. Yamada, Sonoporation in developmental biology, in: N. H. (Ed.), *Electroporation and sonoporation in developmental biology*, Springer, Tokyo, 2009.
- [129] N.V. Malykh, V.L. Petrov, G. Sankin, On sonocapillary effect, in: Proceedings of the 5th World Congress on Ultrasonics (WCU), Paris, 2003, pp. 1343–1346.
- [130] A.A. Kiss, R. Geertman, M. Wierschem, M. Skiborowski, B. Gielen, J. Jordens, J. J. John, T. Van Gerven, Ultrasound-assisted emerging technologies for chemical processes: Ultrasound-assisted emerging technologies for chemical processes, *J. Chem. Technol. Biotechnol* 93 (5) (2018) 1219–1227, <https://doi.org/10.1002/jctb.5555>.
- [131] F. Chemat, N. Rombaut, A. Meullemiestre, M. Turk, S. Perino, A.-S. Fabiano-Tixier, M. Abert-Vian, Review of Green Food Processing techniques. Preservation, transformation, and extraction, *Innovative Food Sci. Emerg. Technol.* 41 (2017) 357–377, <https://doi.org/10.1016/j.ifset.2017.04.016>.
- [132] H.M.A. Barbosa, M.M.R. de Melo, M.A. Coimbra, Cláudia.P. Passos, C.M. Silva, Optimization of the supercritical fluid coextraction of oil and diterpenes from spent coffee grounds using experimental design and response surface methodology, *The Journal of Supercritical Fluids* 85 (2014) 165–172, <https://doi.org/10.1016/j.supflu.2013.11.011>.
- [133] X. Jia, B. Xi, M. Li, Y. Yang, Y. Wang, Biodegradation of Potamogeton pectinatus biomass by hydrogen and methane coproduction: Effect of different pretreatments and parallel factor analysis, *Int. J. Hydrog. Energy* 42 (2017) 18315–18324.
- [134] Y.H. Choi, J. van Spronsen, Y. Dai, M. Verberne, F. Hollmann, I.W.C.E. Arends, G.-J. Witkamp, R. Verpoorte, Are Natural Deep Eutectic Solvents the Missing Link in Understanding Cellular Metabolism and Physiology? *Plant Physiol.* 156 (4) (2011) 1701–1705, <https://doi.org/10.1104/pp.111.178426>.
- [135] A.K. Kumar, S. Sharma, E. Shah, A. Patel, Technical assessment of natural deep eutectic solvent (NADES) mediated biorefinery process: A case study, *J. Mol. Liq.* 260 (2018) 313–322, <https://doi.org/10.1016/j.molliq.2018.03.107>.
- [136] Y. Liu, J.B. Friesen, J.B. McAlpine, D.C. Lankin, S.N. Chen, G.F. Pauli, Natural deep eutectic solvents: Properties, applications, and perspectives, *J. Nat. Prod.* 81 (2018) 679–690.
- [137] T. Bosiljkov, F. Dujmic, M.C. Bubalo, J. Hribar, R. Vidrih, M. Brncic, E. Zlatic, I. R. Redounkavic, S. Jokic, Natural deep eutectic solvents and ultrasound-assisted extraction: Green approaches for extraction of wine lees anthocyanins, *Food Bioprod. Process.* 102 (2017) 195–203.
- [138] M. Mora-Pale, L. Meli, T.V. Doherty, R.J. Linhardt, J.S. Dordick, Room temperature ionic liquids as emerging solvents for the pretreatment of lignocellulosic biomass, *Biotechnol. Bioeng.* 108 (6) (2011) 1229–1245, <https://doi.org/10.1002/bit.23108>.

- [139] A.K. Kumar, B.S. Parikh, L.Z. Liu, M.A. Cotta, Application of natural deep eutectic solvents in biomass pretreatment, enzymatic saccharification and cellulosic ethanol production, *Mater. Today* 5 (2018) 23057–23063.
- [140] A.K. Kumar, S. Sharma, Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review, *Bioresour. Bioprocess.* 4 (1) (2017), <https://doi.org/10.1186/s40643-017-0137-9>.
- [141] K.M. Jeong, M.S. Lee, M.W. Nam, J. Zhao, Y. Jin, D.-K. Lee, S.W. Kwon, J. H. Jeong, J. Lee, Tailoring and recycling of deep eutectic solvents as sustainable and efficient extraction media, *J. Chromatogr. A* 1424 (2015) 10–17, <https://doi.org/10.1016/j.chroma.2015.10.083>.