Effect of Ultrasound on Lignocellulosic Biomass as a Pretreatment for Biorefinery and Biofuel Applications

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Effect of Ultrasound on Lignocellulosic Biomass as a Pretreatment for Biorefinery and Biofuel Applications

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Ⓢ *Supporting Information*

ABSTRACT: The conversion of lignocellulosic biomass for biofuels and biorefinery applications is limited due to the cost of pretreatment to separate or access the biomass's three main usable components, cellulose, hemicellulose, and lignin. After pretreatment, each component may be utilized via chemical conversion, hydrolysis, and/or fermentation. In this review we aim first, to identify the current status-quo of knowledge of the parametric effects of ultrasound, second, to evaluate the potential of ultrasound as a pretreatment and fractionation method of lignocellulose, and last, to identify the challenges that this technology faces. Ultrasound produces chemical and physical effects which were both found to augment the pretreatment of lignocellulose via delignification and surface erosion. The magnitudes of these effects are altered when the ultrasonic field is influenced by parameters such as solvent, ultrasonic frequency, and reactor geometry and type. Therefore, the implementation of ultrasound for the pretreatment of lignocellulose must consider the variation of ultrasonic influences to capitalize on the key effects of ultrasound. Currently the literature is dominated by low frequency ultrasonic treatment, coupled with alkaline solutions. High frequency ultrasound, oxidizing solutions, and use of combined alternative augmentation techniques show promise for the reduction of energy consumed and synergistic enhancement of ultrasonic treatment. Furthermore, feedstock characteristics, reactor configuration, kinetics, and the ultrasonic environment should be considered.

1. INTRODUCTION

As concerns increase over climate change and the limitations of the global supply of oil there is a move toward alternative, renewable fuels and chemical sources. Currently ethanol for biofuel is fermented from carbohydrates from corn grain, sugar cane, and beets.[1] The majority of competitive ethanol production processes divert what could otherwise be crops for food into crops for fuel. Given the imminent global food shortage new technologies are required to make biofuels from other sources such as agricultural waste, forestry wastes, and energy crops.[1] These sources are known as lignocellulosic biomass and are composed mainly of cellulose, hemicellulose, and lignin. In order to fully utilize the lignocellulosic material, the biomass can concurrently be used in a biorefinery as an alternative feedstock for the chemical industry[2] (Figure 1). The concept of a biorefinery is similar to that of a petrorefinery except instead of crude oil, biomass is the starting material.[3] A biorefinery may produce commodities such as fuels, solvents, chemicals, and plastics. In the case of a lignocellulosic biorefinery the aim is to utilize the lignin, cellulose, and hemicellulose for further modification into building block chemicals.

Conversion of lignocellulosic materials for biofuels or in biorefineries comprises of three key steps: 1) pretreatment of material, 2) conversion of cellulose and hemicellulose into fermentable sugars, and 3) fermentation of sugars into raw biofuels.[4,5] Sugars can also be converted to fuels or feedstock chemicals such as ethanol, butanol, acetone, lactic acid, itaconic acid, and amino acid using microbial processes.[3] The conversion of lignocellulosic biomass presents numerous technological challenges, especially in the pretreatment step. Pretreatment methods aim to improve the enzymatic hydrolysis
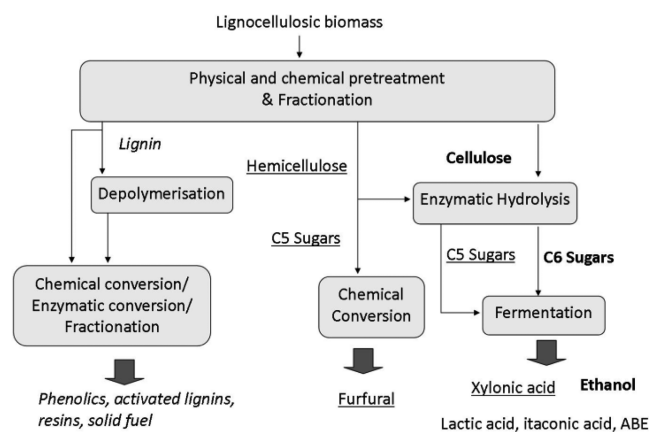
Figure 1. A flowchart of conceptual biorefinery options for lignocellulosic biomass.

of cellulose by reducing the effect of the limiting factors. The limiting factors for the hydrolysis of cellulose are the degree of polymerization, crystallinity of the cellulose, available surface area, lignin content, and moisture content.[5] Some pretreatment methods do not make full use of the available sugars in the biomass as they were traditionally aimed at ethanol production via fermentation of glucose.

The main pretreatment options historically explored are hydrothermal, acidic, alkaline, wet oxidation, ammonia fiber

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explosion, organosolv, and, more recently, ionic liquid pretreatment and were reviewed elsewhere.[4,5] A comparative summary of these treatments is presented in Table S1. Thermal pretreatment[5] aims at solubilizing the hemicellulose and the lignin at high temperatures. Desirable temperatures of thermal treatment are below 200 °C. This is because thermogravimetric analysis showed at 200 °C the thermal degradation of polysaccharides commences, and above 250 °C it becomes very significant.[6]

Organic solvents[7] and ionic liquids show promise for biorefineries due to their ability for separation of different biomass components.[8] Organic solvents are used with or without a catalyst to break down the lignin and hemicellulose bonds prior to further hydrolysis and solubilization of lignin and hemicellulose. Acidic pretreatment is achieved with either concentrated or dilute forms of an acid to hydrolyze the hemicellulose to xylose and solubilize the lignin, thus improving the accessibility and hence digestibility of the cellulose. Alkaline treatment[9,10] initially swells the biomass as well as degrades the hemicellulose and lignin increasing the accessibility of cellulose. Some alkaline solvents such as ammonia[11] and lime[9,10] show potential due to their recyclability. Oxidative pretreatments work via different mechanisms dependent on the conditions involved. Treatment options include the use of oxygen or ozone, wet oxidation, and the use of oxidizing solvents such as hydrogen peroxide and peracetic acid.[12−20] Oxidative treatments can be unselective, and the formation of inhibitors may impede subsequent hydrolysis.

Current pretreatment options are expensive and energy intensive and utilize chemicals which require special disposal, handling, or production methods. When considering biofuel production it is counterproductive to incorporate energy intensive, wasteful processes. Therefore new technologies must look toward methods with low environmental and economic impacts and high efficiency.[20]

Ultrasonic treatment of solutions is a new emerging technology that has potential as an alternative pretreatment technology. Ultrasound produces radicals in a solution and enhances mass transfer through streaming within the solution; however, it also requires significant additional energy input. Ultrasound for pretreatment of lignocellulose was examined in conjunction with other methods; however, the mechanisms of the ultrasonic assistance were not fully evaluated. In this review the principals of ultrasound and the composition of lignocellulosic materials are examined. Then evidence is collected from previous investigations into ultrasound and lignocellulosic biomass. The evidence is weighed against current pretreatment options and used to evaluate the necessary considerations for the implementation of ultrasound as a pretreatment alternative.

2. PRINCIPLES OF ULTRASOUND

Ultrasonic waves create pressure differences within a solution for the enhancement of physical (mechanoacoustic) and chemical (sonochemical) processes. This occurs at frequencies beyond the audible range, typically between 20 and 1000 kHz.[21] Ultrasound is generated by either piezoelectric or magnetostrictive transducers. Piezoelectric transducers are more commonly used today and manipulate the piezoelectric property of some ceramics. The piezoelectric material will respond to an alternating current with mechanical vibrations to produce ultrasound of a characteristic frequency. It is due to this characteristic frequency of transducers that currently limits

a lot of research into the properties of ultrasound. When the transducer is attached to a vessel filled with a sonication solution, the mechanical vibrations of the piezoelectric material create a pressure wave through the solution.

The pressure wave that travels through the liquid medium has regions of high pressure (compression) and low pressure (rarefaction). The rarefaction of the cycle can stretch the liquid molecules apart and create cavities also known as bubbles. As the wave cycles through the liquid, the bubbles expand and contract with the rarefaction and compression of the wave, respectively, drawing more liquid molecules into the bubbles as they grow. The bubbles either continue to expand and then float to the surface, are subject to coalescence due to Bjerknes forces,[22] or collapse during compression of the wave (Figure 2).
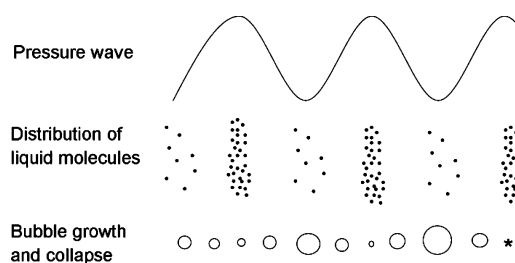
Figure 2. A schematic of a pressure wave traveling through a solution, adapted from Mason.[21] The bubble collapses as continual growth causes it to become unstable in the compression part of the pressure wave.

This collapse is almost adiabatic and can result in localized temperatures of around 5000 K and pressures of 1000 atm. The collapse results in the formation of radicals through dissociation of the molecules within and around the bubbles, luminescence due to excited molecules formed losing energy and microjets shooting out of the bubbles of speeds in the realms of hundreds of km hour^{-1}.

2.1. Ultrasonic Reactors. An ultrasonic reactor normally comprises of three main components, namely, an ultrasonic frequency generator, a transducer, and a reactor. The ultrasonic frequency is generated from the electric current by a sinus wave generator whose signal is amplified by a power amplifier. This signal is then turned into a pressure wave via an ultrasonic transducer and delivered into the reactor space filled with a solution to be sonicated. The pressure wave is normally delivered to the solution through either an ultrasonic bath, transducer plate system, or a horn.[21] The ultrasonic bath is commonly used for cleaning at low frequencies and can produce low intensity cavitation in the solution. A horn will sit in the solution, a few centimeters from the top, and produces high intensity ultrasound near the tip of the horn, in the order of several hundred W cm^{-2}. The power is often variable, but the frequency is fixed at around 20−40 kHz. Cavitation induced by the horn occurs at the tip of the horn, and this can cause problems of erosion to the horn tip. The transducer plate can be singular or in an array and produces ultrasound throughout the solution. Ultrasonic plate systems can work at higher frequencies and give a cavitation zone more widely distributed than the horn, as demonstrated by sonoluminescence imagery.[23] A schematic of a laboratory, Meinhardt Ultraschalltechnik multifrequency system that can operate at 376, 995, and 1179 kHz is shown in Figure 3. The system is designed so that the key operating parameters can be varied and investigated and the solution can have continuous flow and
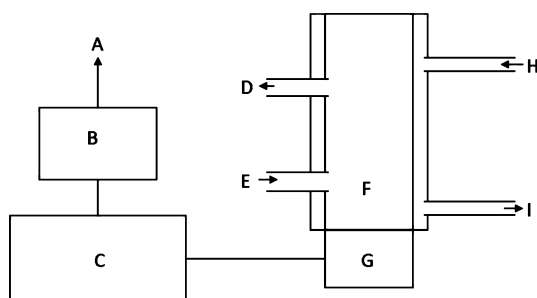
Figure 3. Schematic of a multifrequency sonicator. **A** - power source, **B** - sinus wave generator, **C** - power amplifier, **D** - outlet to reaction, **E** - inlet to reaction, **F** - reaction vessel, **G** - ultrasonic transducer, **H** - cooling water in, **I** - cooling water out.

allows for periodic sampling. Reactor design and scaling were reviewed extensively.[24] The review highlighted important considerations such as power dissipation, flow behavior, and reactor configuration for maximal sonochemical and/or mechanoacoustic effects.

2.2. Mechanoacoustic Effects. Mechanoacoustic effects are caused by the pressure differentials which augment mixing processes and the microjets from the bubble collapse. The formation of microjets[25] occurs when the cavitation takes place near a solid boundary of larger size than the bubble (Figure 4).
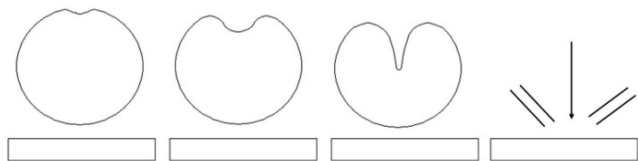
Figure 4. Formation of microjets near a solid boundary, adapted from Suslick.[25] The asymmetrical liquid motion near the boundary distorts the normally spherical cavitation.

The normally spherical cavitation is distorted by the asymmetrical liquid motion near the boundary. The microjets produced are responsible for cleaning applications of ultrasound due to the erosion capabilities. Additionally, microjets have the ability to break cell walls and increase the available surface area in heterogeneous systems.
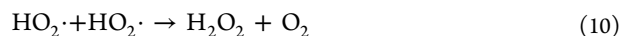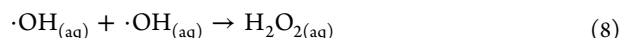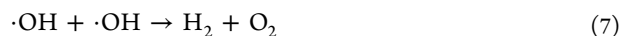
Ultrasound enhances mixing of a solution due to the pressure wave traveling through the solution causing acoustic streaming, microstreaming, and shock waves.[22] Shock waves occur after the collapse of the bubbles and have enough force to distribute molecules from around the bubbles to other areas in the solution. Microstreaming occurs around a small object, such as a bubble in a sound field and will create flow patterns within the solution dependent on the amplitude of the pressure wave and the viscosity of the solution. Microstreaming creates hydrodynamic shear stresses and is capable of inducing change, damaging biological cell walls, contributing to polymer degradation and enhancing mass transfer. Acoustic streaming occurs due to the attenuation of the pressure wave as the wave travels through the solution. The attenuation of the wave creates a pressure difference in the solution causing a flow in the direction of the sound field. Generally at higher frequencies the momentum of the wave is subject to higher absorption, and hence acoustic streaming is more evident.

Mechanoacoustic effects in a heterogeneous mixture of biomass and liquid can enhance the accessibility of the biomass
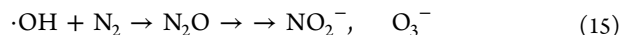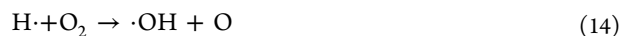
through microjet erosion, cell wall collapse, and mass transfer augmentation within the mixture. These effects all have the potential to enhance treatment of biomass in the heterogeneous solid−liquid environment

2.3. Sonochemical Effects. Ultrasound is also used to enhance chemical reactions or to choose a certain reaction pathway. These pathways are normally radical driven processes. Reaction augmentation via ultrasound often results in faster reactions at lower temperatures than otherwise possible and can reduce the amount of chemicals required in a process.[21]

Water undergoing sonochemistry initially cleaves the hydrogen−oxygen (H−O) bond in the molecule to produce hydroxyl radicals and hydrogen, which then continue on reacting to produce hydrogen peroxide, hydrogen gas, oxygen gas or recombine to produce water. Further radical reactions occur in the gas or aqueous phase producing more radicals or oxidizing species as outlined by a series of reactions below.[21,26]

$$H_2O +))) \rightarrow H\cdot + \cdot OH \tag{1}$$

$$\cdot OH + \cdot OH \rightarrow O + H_2O \tag{2}$$

$$\cdot OH + H_2O \rightarrow H_2O_2 + O \tag{3}$$

$$H\cdot + \cdot OH \rightarrow H_2O \tag{4}$$

$$H\cdot + H\cdot \rightarrow H_2 \tag{5}$$

$$2O \rightarrow O_2 \tag{6}$$

$$\cdot OH + \cdot OH \rightarrow H_2 + O_2 \tag{7}$$

$$\cdot OH_{(aq)} + \cdot OH_{(aq)} \rightarrow H_2O_{2(aq)} \tag{8}$$

$$HO_2\cdot + H\cdot \rightarrow H_2O_2 \tag{9}$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{10}$$

$$H\cdot + O_2 \rightarrow HO_2\cdot \tag{11}$$

$$O_2 \rightarrow 2O \tag{12}$$

$$O_2 + O \rightarrow O_3 \tag{13}$$

A species in the solution is likely to react with the generated radicals and hydrogen peroxide. Furthermore when the solution is saturated with gas, the composition of the gas affects the sonochemical degradation products. The degradation products from air saturation, represented by the introduction of nitrogen and oxygen, are shown in reactions 10−16.[27]

$$H\cdot + O_2 \rightarrow \cdot OH + O \tag{14}$$

$$\cdot OH + N_2 \rightarrow N_2O \rightarrow \rightarrow NO_2^-, \quad O_3^- \tag{15}$$

$$O + N_2 \rightarrow N_2O, \quad NO, \quad N \rightarrow \rightarrow NO_2^-, NO_3^- \tag{16}$$

There is potential for the use of the sonochemical properties of ultrasound on an industrial scale as a standalone technology or combined with other technologies. Ultrasound was viewed as a viable option for a variety of physical and chemical applications coupled with other chemicals and technologies such as microwave processing and ultraviolet photolysis.[26,28]

2.4. Operating Parameters. The operating parameters affect the severity and incidence of cavitation and hence the degree of sonochemical and mechanoacoustic influence. Generally an increase in viscosity, decrease in temperature and increase in external pressure applied will increase the lower cavitational threshold (the minimum power for transient

cavitation to occur).[21] Similarly an increase in power will increase the amplitude of the ultrasonic wave and increase the occurrence and severity of cavitation. An increase in temperature increases the vapor pressure of a liquid so cavitation becomes more facile;however, the effects of the bubble collapse are also reduced. Thus, in a given system there will be an optimal temperature for the desired ultrasonic effect. An increase in pressure of a system will require an increase in power to achieve the same amount of cavitation as a higher amplitude will be required in the rarefaction of the cycle to create a transient bubble. The effects of the parameters stem from the Rayleigh-Plesset equation, explored by Leighton[22] and more recently adapted from single bubble theory.[29] However, the effects of the parameters such as frequency, solvent, gas saturation, geometry, and reactor configuration are more complex. A complete understanding of these parameters is yet to be developed, and the current status in literature is summarized below.

Frequency. Studies looking for mass transfer improvement generally opt for the lower frequency range, and higher frequencies are used for increased sonochemical activity.[30,31] Frequency effects of different studies are summarized in Table S2. At lower frequencies (under 100 kHz) the bubbles have more time to grow, and, therefore, the cavitational collapses are more violent. At higher frequencies more bubbles are produced which collapse, producing more radicals. The inverse effects of frequency were demonstrated with ultrasonic treatment of polyphenylene ether[32] and through iodide dosimetry.[33] At even higher frequencies, as in the megahertz range, the rarefaction of the wave becomes too short for cavitation to occur. For example, at a comparable power, the yield of peroxide at 1056 kHz was less than 25% of the yield at 355 and 647 kHz.[30] These trends were supported by data from the present authors' work where hydrogen peroxide yield was maximized at 376 kHz. Experiments were carried out in an ultrasonic reactor (Meindhart Ultraschalltechnik) at frequencies 376, 995, and 1179 kHz with 300 mL of a 0.1 M KI (Ajax Finechem) sonication solution. Ultrasound was introduced using a 5 cm piezoelectric transducer plate. The yield of iodine was measured after 30 min of sonication as per standard iodide dosimetric techniques.[34] The absorption of iodine was measured on a Hewlett-Packard 8453 ultraviolet−visible spectrophotometer at 351 nm. Calibration curves were constructed each day of measurement using solutions of iodine standardized against sodium thiosulfate (Ajax Finechem). The results of these studies are summarized in Table S2.

There is general agreement that radically driven processes are maximized at high frequencies and physical effects are maximized at low frequencies. When considering a heterogeneous system such as biomass in solution, it is important to consider which frequency effects are more desirable and effective, the mechanical erosion or the chemical attack.

Solvent Effects. Chemicals in solution also influence the ultrasonic effects, and we consider this in an aqueous, ionic, and organic solvent environment. The solvent will affect the physical properties of the solution, such as surface tension and viscosity, which govern the severity of the cavitational collapse and subsequent ultrasonic effects, as previously mentioned. Furthermore the chemical behavior of the solution will influence the overall outcomes of ultrasonic irradiation.

In an aqueous solution, hydrophobic solutes influence the ultrasonic effects. Solutes which are hydrophobic will gather at the bubble interface and can either act as radical scavengers in the hot region surrounding the bubble or reduce the maximum temperature reached during bubble collapse, quenching sonoluminescence.[35,36] The mechanisms of quenching occur through the evaporation of the solutes into the oscillating bubble and subsequent degradation reactions within the bubble. The degradation products remain in the bubble and over numerous oscillations will accumulate, quenching sonoluminescence and maximum temperatures achieved by the bubble. The more volatile the solute the more it is able to quench the sonoluminescence due to the increased ability of evaporation into the bubble.[35,36] Ionized species in an aqueous solution do not have this effect during the bubble collapse, as demonstrated in the irradiation of organic acids and bases at a range of pHs.[37] However, the ionized acids and bases with hydrophobic tails have the ability to gather at the interface and undergo proton transfer reactions in the hot interfacial region around the bubble.[38] These observations do not always hold for low frequency situations.[39,40] Therefore quenching is believed to be more influential on stable cavitation, where the solutes are able to reach near equilibrium absorption conditions rather than in transient cavitation fields. These observations highlight the potential effects of solutes within an aqueous system.

In an organic solvent degradation products were produced from the solvent. In organic solvents the volatility of the solvent can influence the effects since the volatility is governed by vapor pressure which determines the ease of evaporation into the cavity. An increase in volatility decreases the intensity of the cavitational collapse which in turn decreases the maximum temperatures and reaction rates.[41]

Ionic liquids have very little vapor pressure; however, sonochemical effects are still observed within them, as are the degradation products of the liquid. This is explained by the hot spot theory, which describes a hot region around the bubble interface during the cavitational oscillations. The temperatures in the interfacial region are hot enough for the degradation of the ionic liquid salts.[42]

Dissolved Gas. Cavitation occurs at crevices of dissolved gas in a liquid so when a liquid is saturated with a gas, the gas molecules act as cavitation sites and influence the reaction. Influences of gases on reaction rates are summarized in Table S3. The extent of the effect of a gas on the mass transfer and chemical enhancements is dependent on the saturation level, solubility, and properties of the gas.[21] Saturating a solution with gas will decrease the lower cavitational threshold which therefore increases reaction rates when the reaction is sonochemically enhanced. For example, the degradation rate of phenol was nearly doubled in an air-saturated environment compared to a degassed environment.[43]

The effects of the gas dissolved are influenced by shockwave intensity, polytropic ratio, and thermal conductivity. The intensity of a shockwave will be reduced by a cushioning effect of dissolved bubbles; however, an increase of gas in the cavitational bubble can lead to an increase in the intensity of the shockwave. Noble gases or gases with a larger polytropic ratio will have larger sonochemical effects;[44] however, the thermal conductivity of the gas in solution will also affect the heat transferred into the bulk solution during bubble collapse. The rate of phenol degradation under different gas atmospheres was demonstrated to be increased with an addition of argon to air[43] (Table S3). However the mixture had an optimum value at 73/27 air/argon attributed to a possible balance of the polytropic ratio and the thermal conductivity of the gas mixture.

Geometry. The geometry of an ultrasonic reactor can be altered according to the type of sonication as well as the size and shape of the solution. A 2011 review found geometry affected power dissipation, ultrasonic flow, and mass transfer within a sonicated solution.[24] The review recommended the use of tubular or hexagonal reactors in order to minimize the energy consumption. The treatment of lignocellulose with ultrasound mainly involved the use of the two common laboratory ultrasonic reactors, the horn and the plate transducer (Table S7). Here, some additional comparisons of geometric effects of the horn and plate reactor systems on sonochemical activity are summarized (Table S4). No difference in sonochemical activity was found when the bath versus horn system was evaluated at 20 kHz, with two horns of different diameters.[45] However when the sonication zone was altered by changing the diameter of a 200 kHz reaction vessel the yield was directly affected.[46] The sonochemical effects were attributed to the migration of active bubbles to the outer solution, outside of the sonication zone. The active bubbles would then dissolve, decreasing the yield of radicals in solution.

The path length of the ultrasonic wave controlled by the height of the solution in the reactor and was found to directly affect the sonochemical efficiency and yield.[47,48] Maximal sonochemical activity was found at different liquid heights for different frequencies.[47] A reason suggested for the different effects of height was attenuation of the ultrasonic wave versus standing wave formation. The formation of standing waves is known to increase sonochemical efficiency in a reactor. However in other works on the effects of liquid heights in the near and far zones in the reactor were attributed to the observed trends in sonochemical activity.[48] In the near zone the reflection of the wave reaches a maximum, and ca. 90% of the acoustic energy is concentrated in a cone shape, diverging from the transducer base.[49] In the far zone the wave attenuates and loss of energy occurs. This theory does not extend to the previous investigation by Asakura et al.,[47] where they found maxima in the far zones at lower frequencies (45 and 128.9 kHz) and in near and far zones in the higher frequencies (231 and 490 kHz) as identified in Table S4. The maxima in the different zones may be attributed to the reflection maxima in the near zone, maximizing the standing wave and maxima in the far zone related to the optimal degree of acoustic streaming for radical production in that reactor. However in both studies the inner diameter of the reactor is wider than the transducer diameter, which, as previously identified by Nanzai et al.,[46] would affect the ultrasonic field and hence sonochemical yield.

As evidenced above, contradictory results exist for the geometric influences on ultrasound. The consideration of geometry, liquid height, and wave attenuation is also important when considering a heterogeneous system such as biomass as the biomass may act as a reflector of the ultrasonic wave and effectively change the sonication region.

Batch versus Flow Systems. Previous reports involving measurements of sonochemical activity under the influence of flow have found conflicting results (Table S5). At low frequencies (below 100 kHz) the mass transfer effects of ultrasound dominate and the introduction of flow in reactors at these frequencies enhanced the sonochemical yield.[50] However at higher frequencies, both an increase and a decrease in sonochemical activity were observed. At 500 kHz the sonochemical degradation rate of pentachlorophenol was decreased with an increase in flow rate,[51] the degradation of chlorinated hydrocarbons at 100 kHz was also decreased with

an increase in flow rate,[52] and at 133.2 kHz the rate constant of potassium iodide oxidation was maximized without flow in the reactor.[53] However a study at 490 kHz found an overhead stirrer increased the sonochemical efficiency.[54] At lower frequencies bubbles are bigger as they have more time to grow; when these bubbles coalesce they become too large for sonochemical activity. The coalescence caused by the secondary Bjerknes forces was believed by Hatanaka et al.[50] to be prevented by the flow introduced into their reactor leading to an increased number of bubbles of active sizes. They then predicted at higher frequencies, where the secondary Bjerknes force is lower, the coalescence of small, nonactive bubbles is prevented and sonochemical activity is reduced. The different geometries of the reactors in these studies make them difficult to compare, since sonochemical activity is also influenced by geometry.[45−47] In order for ultrasound to be considered on an industrial scale for pretreatment of lignocellulose, the effects of flow in a heterogeneous sonication solution need to be elucidated.

2.5. Ultrasound in Heterogeneous Systems. Ultrasound is able to augment processes in homogeneous liquids and in heterogeneous mixtures such as solid−liquid systems.[55] Ultrasound in homogeneous systems is often used for sonochemical effects such as bond-breakage and radical formation which leads to chemical reactions. Conversely in heterogeneous systems ultrasound is utilized for the enhancement of mass transport, erosion, and mixing. High power ultrasound enhances mixing for immiscible liquids such as in biodiesel production.[56] The cavitational and streaming forces are able to overcome the surface tension to enhance mixing of the immiscible liquids (Figure 5). Ultrasound for mass transfer is generally maximized
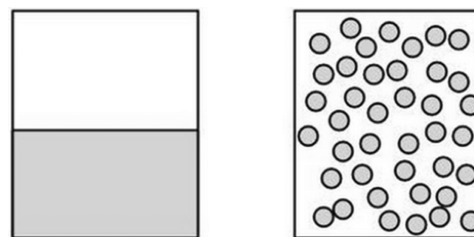

Figure 5. Immiscible liquids before (left) and after (right) high power ultrasound treatments. The ultrasonic effects of cavitation and acoustic streaming enhance mixing of the two liquids.

at lower frequencies such as 20−40 kHz and was developed for the pretreatment of wastewater sludge.[57] Ultrasound is used to break down cell walls and release the cell contents within the sludge to improve overall digestibility. Additionally, augmentation of rates and yields are also explained by a chemical effect of the ultrasound in heterogeneous systems.[31] Furthermore when ultrasound was used for the modification of wheat straw for paper making it was suggested the oxidants produced by ultrasound may have influenced the depolymerization of the lignin macromolecule.[58]

The pretreatment of biomass also benefits from the chemical degradation of lignin. The homolytic cleavage of bonds in lignin observed with ultrasonic treatment demonstrates that ultrasound plays a chemical as well as a physical role. In order to fully realize the industrial potential of ultrasound in heterogeneous systems the sonochemical effects as well as the mechanoacoustic effects must be considered.

3. LIGNOCELLULOSIC MATERIALS

Lignocellulosic biomass consists mostly of the interlinked polymers, cellulose, hemicellulose, and lignin (Figure 6).
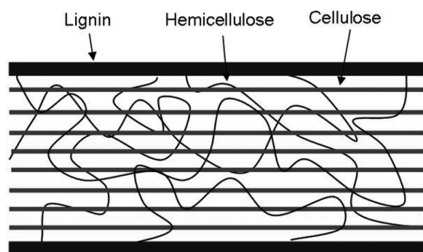

Figure 6. A schematic of lignocellulose in biomass. The hemicellulose, cellulose, and lignin are interlinked, and the pretreatment step aims to either separate these or improve the accessibility of the cellulose and hemicellulose for enzymatic hydrolysis (adapted from the USDA Agricultural Research Service).

Pretreatment aims at separating these components so the sugar monomers may be fermented or chemically converted into biofuels or feedstock chemicals. In order to comprehend the potential effects of ultrasound, the structure, inter- and intramolecular linkages of the major components of lignocellulosic biomass are described. Ultrasound produces sonochemical and mechanoacoustic effects which will affect the chemical and physical composition of lignocellulose. The mechanoacoustic influences can alter the surface structure of the biomass, and the sonochemical production of oxidizing radicals can lead to chemical attack of the components of lignocellulose. The following section identifies the components and structure of lignocellulosic material as well as identifying potential reactive sites.

3.1. Composition. Wood and lignocellulosic materials[59] consist mainly of the three polymeric compounds that make up cell walls. This can be up to 99% of the composition of the wood material. Of these polymeric compounds the most abundant is cellulose, followed by hemicelluloses and lignin. In woods, cellulose makes up about half of the wood content, whereas in agricultural residues this is usually less, with about 30 to 40% cellulose. Composition varies between biomass types as well as species and growing conditions; some typical values are shown in Table S6.

Cellulose is a polymeric, linear molecule made up exclusively of β-D-glucose units linked by 1,4-β-glucosidic bonds (Figure 7). It is the main structural component of cell walls with a high
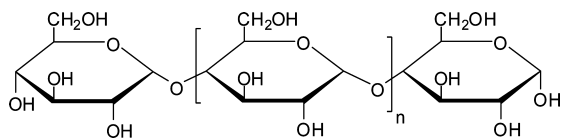

Figure 7. A chemical structural model of cellulose (adapted from Fengel and Wegener[59]).

degree of crystallinity. Hemicelluloses are made from five and six carbon sugars (hexoses and pentoses). Hemicelluloses are more prolific in hardwoods than in softwoods, and the sugar composition varies from species to species. Hemicelluloses differ from cellulose as they have side groups and shorter chains and are in some cases branched. The hemicellulose sugars are held together by glycosidic linkages and are more accessible to chemical and physical attack. Lignin is an amorphous

component of the cell wall and is a strengthening constituent, penetrating the fibrils during development, and it is more prolific in softwoods than hardwoods. The components of the cell wall are interlinked by hydrogen bonds and glycosidic linkages; therefore, separation requires chemical treatment.[59]

The separation of lignocellulosic components was initially developed for the pulping processes. Thus, high temperature and pressure effects on biomass were investigated with the aim at pulp delignification.[60] Lignocellulosic materials were investigated in supercritical fluids using a range of solvents and complementary thermogravimetric analysis.[6] The thermograms were replicated by the authors using 15 mg of a wheat straw sample, ground to fit through a 20 mesh sieve, under nitrogen (60 mL min^{-1}) on a Thermogravimetric Analyzer (TA Instruments SDT Q600) with a heating rate of 20 °C min^{-1} (Figure 8). The thermograms demonstrate at 200 °C the
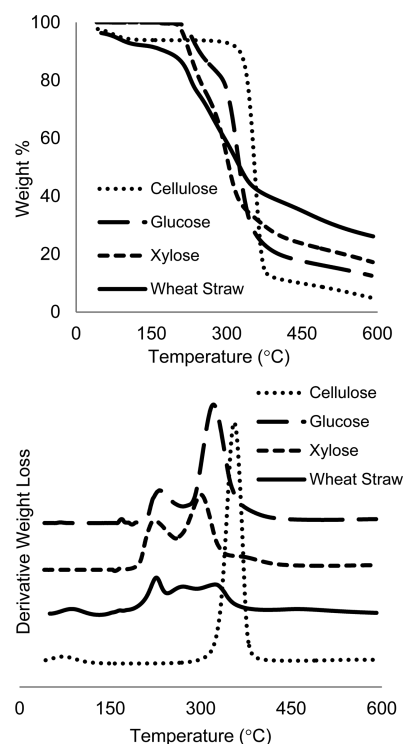
Figure 8. Thermograms (top) and derivative weight loss (bottom), dW/DT, plots of biomass components.

thermal degradation of polysaccharides commences and above 250 °C becomes very significant. Furthermore, the results indicated nonreactive supercritical fluids were unsuccessful at delignification indicating chemical interactions are needed for delignification to occur.[6] The oxidizing species produced from ultrasound have the potential to aid in the chemical interactions required for delignification.

3.2. Carbohydrate Reactivity. The polysaccharides, hemicellulose, and cellulose have three main reactive sites, namely, reducing end groups, glycosidic linkages, and hydroxyl groups.[61] The end groups of the polysaccharides are partially converted to function as an open chain aldehyde when in solution and can be reduced and oxidized. The glycosidic linkages are subject to hydrolysis in acidic, alkaline, and oxidative conditions. The hydroxyl groups on the cellulose and hemicellulose units are susceptible to oxidation and can undergo further degradation such as dehydration and cleavage

of the glycosidic linkages. The reactivity of carbohydrates depends largely on the accessibility of the reactive site and varies under different conditions.

Degradation. In acidic mediums the glycosidic linkages in the polysaccharides are hydrolyzed to form sugar monomers. The hydrolysis precedes further dehydration, condensation, and degradation reactions to produce furans and phenolic compounds. The nonglucose units of the hemicellulose are generally more reactive than the glucose, and acidic treatments were used to selectively remove the hemicellulose.[5,61] Alkali mediums give rise to the cleavage of glycosidic linkages of polysaccharides as well as endwise degradation, also known as peeling, which produces carboxylic acid derivatives. The endwise peeling in alkaline solutions can be stabilized with divalent cations which impede the peeling process.[61] Hemicelluloses are subject to physical as well as chemical changes in alkaline environments, such as swelling due to the solvation of the hydroxyl groups by hydroxyl ions. Oxidative degradation of hemicelluloses and celluloses are similar, with hemicelluloses in biomass being more accessible so they are more likely to undergo degradation. The types of degradation reactions in an oxidative environment are likely to occur at the reducing end group, the hydroxyl group, and at the anomeric position (C1). The reducing end groups are readily oxidized to an acid moiety which does not undergo peeling in alkaline conditions. When the anomeric site is attacked, glycosidic cleavage results, and an acid moiety is produced. The nature of the oxidation occurring at the hydroxyl groups is known to vary depending on the type of oxidants and substrates.[61] Ultrasound produces oxidizing radicals, which, coupled with mechanoacoustic effects, are able to degrade the carbohydrates.

3.3. Lignin Structure and Reactivity. The lignin polymer is formed through enzymatic dehydrogenation of phenylpropanes followed by radical coupling.[61] Lignin is derived from three monomer units, *trans*-coniferyl, *trans*-sinapyl, and *trans*-*p*-coumeryl alcohols (Figure 9). These three units are linked
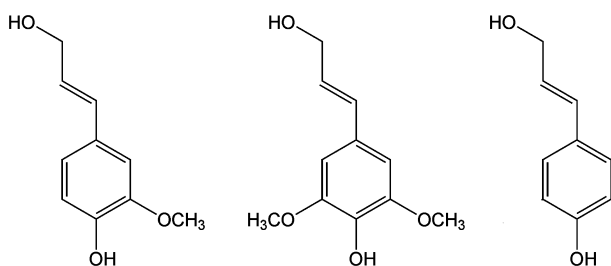
Figure 9. Lignin precursor units, coniferyl alcohol, sinapyl alcohol, and *p*-coumeryl alcohol.[61]

randomly mostly through ether linkages at α and β positions to construct the lignin macromolecule. Due to the random linkages the structure of a lignin in any given plant varies, and composition of different species can range from 10 to 30%.

Reactive Sites. The reactive sites in lignin are mainly the ether linkages and functional groups since the carbon–carbon linkages are generally resistant to chemical attack. The areas of lignin susceptible to chemical attack are the hydrolyzable ether linkages (β-aryl, α-aryl, and α-alkyl), phenolic and aliphatic hydroxyl groups, ester groups, methoxyl groups, the unsaturated groups, and uncondensed units. Lignin is amorphous and tends to form hydrogen bonds influencing the accessibility of the groups which in turn affects the levels of reactivity.[61]

Lignin-Carbohydrate Linkages. There are three possible types of lignin-carbohydrate linkages, ester, ether, and glycosidic (Figure 10), which due to the difficulty in separating
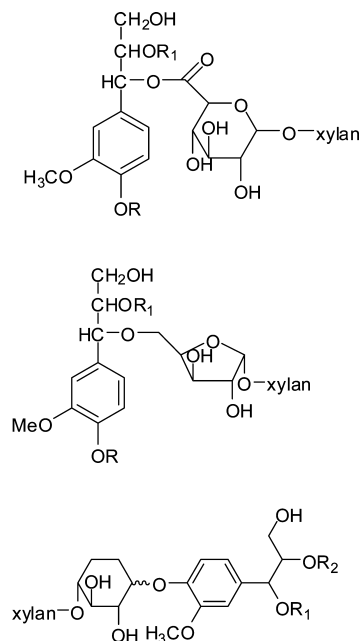
Figure 10. Possible lignin-carbohydrate linkages; from top to bottom; ester linkages, ether linkages, and glycosidic linkages.[61]

the carbohydrate and the lignin are believed to exist. The ester linkages can be readily hydrolyzed in alkali media, unlike the ether linkages which are relatively stable under mild alkaline conditions.[61]

Lignin Degradation. The chemical mechanism of lignin degradation depends on the environment whether it is acidic, alkaline, oxidative, or a combination of these.[61] In acidic environments benzyl oxygen can be protonated initiating acid degradations of α- and β-ether lignin units. The protonation is followed by α-ether elimination of the phenol or alcohol giving a benzylic carbonium ion intermediate which can undergo further degradation enabling depolymerization of the lignin compound. Alkaline and oxidative environments were used extensively for delignification in the bleaching of pulp in the Kraft process[60] and were looked at as pretreatment options. In alkaline and alkaline-oxidative environments lignin degrades through the cleavage of the α- and β-aryl ether linkages to yield fragmentation units. However in oxidative environments, unlike in pulping, degradation is driven by the cleavage of carbon–carbon linkages and the formation of acidic groups from ring degradations such as carboxylic acids. Side chains within the lignin may be displaced or cleaved in oxidative reactions through electrophilic substitution at an unsubstituted ring position and α–β-cleavage of the carbon chain.[61] These three main chemical methods of lignin degradation were the basis for many chemical pretreatments to enhance the enzymatic digestibility of cellulose in lignocellulosic biomass. The pretreatments are not always selective and can sometimes be counterproductive due to the loss of carbohydrates in the process.

4. ULTRASONIC EFFECTS ON LIGNOCELLULOSIC BIOMASS

In order to evaluate the potential of ultrasound as a pretreatment option, for lignocellulose, previous investigations into ultrasonic effects on lignocellulosic biomass were explored and are summarized in Table S7.[58,62−117] The effect of hydrodynamic and ultrasonic cavitation on lignocellulosic biomass was reviewed with the aim at pretreating wheat straw.[118] The review highlighted the dominance of physical effects of ultrasound in the enhancement of delignification and recommended the use of low frequency ultrasound. Furthermore the combination of conventional techniques with ultrasound and the use of noble gases were cited as methods to enhance delignification. With these concepts in mind the literature was reviewed with the aim to increase the understanding on the interaction of ultrasound and lignocellulosic biomass in different environments. First, pretreatment of lignocellulose for improved hydrolysis is discussed. Second, the use of ultrasound for lignin extraction from lignocellulose and finally the use of ultrasound for the extraction of polysaccharides will be examined. Within these three key areas, an understanding of common ultrasonic interactions with lignocellulose and the components within is developed.

4.1. The Mechanisms of Ultrasonic Pretreatment of Lignocellulose. *Ultrasound for the Pretreatment of Lignocellulose.* Ultrasonic pretreatment of various lignocellulosic materials was able to enhance subsequent treatments. Both enzymatic and acid hydrolyses were enhanced and ethanol yield increased following ultrasonic pretreatment of lignocellulose. Enzymatic hydrolysis of sugar cane bagasse was improved with ultrasonic pretreatment, with an increase in glucose yield by 21.3%.[63] The increase in glucose yield was almost linear with an increase in sonication time, linking the ultrasonic pretreatment to improved hydrolysis. Further improvements of enzymatic hydrolysis with ultrasonic pretreatment were reported in dilute acid,[68] alkaline solutions,[69,70] and in ionic liquids[66] for sugar cane bagasse and for rice hulls in water.[65] Ultrasound was shown to increase the enzymatic hydrolysis yields and reduce necessary times of pretreatment and saccharification. Similarly, acid hydrolyses of sugar cane bagasse[72] and oil palm empty fruit bunch[73] were improved by ultrasonic pretreatment in an alkaline solution and an acidic solution, respectively. The ultrasonic pretreatment of oil palm empty fruit bunch, more than doubled the subsequent xylose yields from 22 to 52%. Furthermore, ethanol yield from hydrolyzed sorghum bagasse was increased by 4.5% from ultrasonic pretreatment.[62] In conclusion, hydrolysis of lignocellulosic biomass was improved by ultrasonic pretreatment for a variety of materials. Ultrasound was able to increase yields of glucose, xylose, and ethanol in downstream processing as well as reduce the treatment times required, attributed to enhanced accessibility and delignification.

Enhanced Accessibility and Delignification of Lignocellulose. The efficacy of ultrasonic pretreatment for improved processing was attributed partly to mechanoacoustic effects. The mechanoacoustic effects, described in Section 2.2, improved mass transfer and enhanced the accessibility of the biomass for subsequent processing. For instance, the enhancement of enzymatic hydrolysis of rice hull was coupled with improved accessibility and particle surface erosion.[65] Similarly, the improvement of enzymatic hydrolysis of Kenaf biomass was attributed to the physical, rather than chemical effects.[71] In addition, an improvement of acid hydrolysis yields was attributed to the increased accessibility from the removal of silica from the surface of oil palm fibers.[73] Further evidence of the mechanoacoustic effects in the treatment of lignocellulose were observed from an increase in pore size and improved liquefaction. The micropore and macropore volume of sunflower husks was increased after ultrasound from 9.5 to 11% and 14 to 16%, respectively.[78] Liquefaction times of various lignocellulosic materials were improved by 72−89% with ultrasound,[81] and dissolution times of holocellulose in 1-butyl-3-methylimidazolium chloride were more than halved after ultrasonic pretreatment, from 750 to 360 min.[108] Improved liquefaction times demonstrated mass transfer was improved under the influence of ultrasound. The observed increases of surface erosion, solubilization, and accessibility under the influence of ultrasound all contribute to the improvement of subsequent processing of lignocellulose.

Delignification of lignocellulose enhances hydrolysis yields of cellulose. Ultrasonic pretreatment tended to augment delignification, which coupled with improved hydrolysis yields. The success of enzymatic hydrolysis of rice hull with a control, ultrasound, and hydrogen peroxide pretreatment step followed the most efficient delignification pretreatment. Hydrogen peroxide, followed by ultrasound, removed more lignin than the control, and subsequently the hydrolysis yields were highest for the hydrogen peroxide pretreated biomass, followed by the ultrasound and control pretreatments.[65] Similarly, improved acid hydrolysis[72] and enzymatic hydrolysis[69,70] of sugar cane bagasse was coupled with the increased removal of lignin in ultrasonic pretreatment. Furthermore ultrasonic pretreatment of corn stover improved hydrolysis yields, alongside a decrease in lignin content.[64] Delignification with ultrasound was observed for different lignocellulosic materials in a variety of solvents. Delignification in the fractionation of olive tree prunings was improved with ultrasound in water and acetic acid but not in soda solution.[74] However, other ultrasonic treatments in a basic environment were able to improve delignification.[69,70,75−77] Furthermore the lignin content of sunflower husks[78] and pulped wheat straw[58] was decreased by ultrasonic treatment in water. Overall, the reported delignification ranged from an increase in lignin content by 8.9% in a soda solution[74] to a decrease in lignin by 90.6% in 2% NaOH.[70] The variety of conditions and lignocellulosic feedstock over which delignification was enhanced by ultrasound led to a wide range of delignification yields. Furthermore delignification was nearly always accompanied by a loss of carbohydrates. Hence the purpose of the ultrasonic treatment must also be considered. If the ultrasonic treatment is to enhance hydrolysis yields, or includes further use of carbohydrates in downstream processing, carbohydrate loss is undesirable.

Ultrasound improved pretreatment for subsequent enzymatic and acid hydrolysis of lignocellulose. The augmentation of hydrolysis yields was observed to occur for a range of experimental conditions, such as solvent, feedstock, and reactor configuration. However two key mechanisms appeared to be effective for successful pretreatment. First, enhanced accessibility of the biomass through surface erosion and, second, delignification during pretreatment. Ultrasonic delignification of lignocellulose is a result of sonochemical and mechanoacoustic effects.

4.2. The Mechanisms for the Extraction of Lignin from Lignocellulose with Ultrasound. *Lignin Extraction with Ultrasound.* Ultrasound was used to enhance the extraction of

lignin from lignocellulose and for lignin modification[83−94] (Table S7). Ultrasound improved the yields of the lignin extract and increased the purity while retaining the molecular structure. However treatment had varied effects on the molecular weight of the extracted lignin, and longer times were not always optimal. For instance, the yield of lignin extracted from sugar cane bagasse with ultrasound (91.2%) was achieved in a shorter time and at lower hydrogen peroxide concentration than the maximum yield without ultrasonic pretreatment (90.6%).[86] Furthermore, sonication of increasing time allotments, up to 35 min, increased the yield of lignin extracted from wheat straw by 5[84] and 11%.[83] Similarly, sonication for up to 50 min of ball milled bamboo in 95% ethanol increased the lignin yield by up to 23%. Although sonication of the liquor from pretreated olive tree residues saw an increase in lignin after 15 min of sonication (61 to 67%) but an overall decrease in lignin extracted after 120 min (63%).[90] These reports demonstrated lignin extraction yields were enhanced by ultrasound; however, the overall yield can decrease in prolonged sonication treatments.

Alongside the improved yields of the lignin extractions, the purity also tends to be increased by ultrasound. Lower amounts of associated polysaccharides in the lignin extractions were observed in ultrasonic-assisted extractions of wheat straw.[83,84]

The structure of lignin extracted with ultrasound tended to be the same as nonultrasonic extractions, despite improved yields and purity. While the trend was for lignin to retain the molecular structure, differences in molecular weight were observed between ultrasonic and nonultrasonic extractions.[83,84,88] The lignin fractions isolated from wheat straw, with ultrasound in an alkaline methanol−water solution, had a lower molecular weight than the lignin fraction isolated without ultrasound.[83] Conversely a higher molecular weight average was observed for ultrasonic-assisted extractions when wheat-straw lignin was extracted in an aqueous potassium hydroxide solution.[84] Furthermore, no ultrasonic effect on the molecular weight and yields of lignin was observed when bamboo lignin was extracted in ethanol with ultrasound.[87] The different responses of molecular weight to ultrasound are likely to be due to competing depolymerization and condensation reactions.

Ultrasonic Depolymerization, Separation, Degradation, and Condensation of Lignin. Depolymerization and separation of lignin occurs under the influence of ultrasound. These phenomena will contribute to the increased lignin extraction yields with ultrasound; however, ultrasound also degrades lignin components. Separation of lignin with ultrasound occurs via cleavage of the lignin-hemicellulose linkages (Figure 10). Cleavage of the linkages was evidenced in the increased purity of lignin and hemicellulose extractions with ultrasonic treatment.[83,84,86,95−98]

Depolymerization of lignin occurs through the homolytic cleavages of the phenyl ether β-O-4 and α-O-4 bonds described in Section 3.3. Homolytic cleavage of the phenyl ether β-O-4 and α-O-4 bonds in lignin was established by electron spin resonance spectroscopy (ESR). Moreover, the β-O-4 bond underwent cleavage more than the α-O-4 bond.[91] In addition, evidence of β-O-4 cleavage within lignin was found when wheat straw was sequentially treated, including a low frequency sonication step, to obtain purified lignin. However, the cleavage was not observed to occur in significant amounts under the conditions of treatment.[83,84]

Degradation of ultrasound can occur through hydroxyl attack on the lignin structure. The hydroxyl attack on model lignin compounds under ultrasound was found to mostly (75−85%)

occur on the aromatic ring.[119] This led to hydroxylated, demethoxylated, and side chain eliminated products. The remaining 25−15% of hydroxyl attack occurred on the side chains leading to the formation of dimers and the oxidation of aromatic aldehydes to carboxylic acids. Additionally, an increased production of hydroxyl radicals, from the combination of ultrasound with TiO_2 and the Fenton reagent, coincided with an increased lignin degradation.[71] Further evidence of oxidative attack was found in the increased number of nonconjugated carbonyls in sonicated pulp fibers under high frequency irradiation.[117]

For the purpose of lignin extraction, separation and depolymerization can augment yields, whereas degradation was also observed. In regards to the pretreatment of biomass for utilization of the carbohydrates and/or the lignin component, lignin depolymerization and separation enhance pretreatment. However, the competing condensation reactions, responsible for the change in molecular weights observed, must also be considered.

Alongside the cleavage of interunitary bonds within the lignin and lignin-hemicellulose bonds evidence for condensation of lignin in the presence of ultrasound was observed. Condensation was observed in the ultrasonic-enhanced hydrogenolyis of lignin[93] and the extraction of humic acids from tobacco dust.[94] Furthermore lignin condensation was shown to occur during lignin extraction[84,90] and in the treatment of lignocellulosic biomass.[74,78] Lignin condensation mechanisms without ultrasound depend on the chemical environment, as with the degradation mechanisms, discussed in Section 3.3. However, with ultrasound, the conditions can favor the accumulation of species at the bubble interface,[120] depending on the solvent properties. This accumulation may enable proton transfer[38] or promote radical scavenging[36] in the hot interfacial region, which would in turn promote recondensation and repolymerization reactions. The behavior of phenol at the bubble interface supports this possible mechanism of recondensation of lignin. Ashokkumar et al.[36] presented evidence phenol scavenges hydroxide radicals at the bubble surface in aqueous solutions, and this will also occur in the presence of phenol derivatives due to the similarity of types of decomposition products observed.[36] However it is important to note that the behavior would depend on the exact nature of the solvent used and the sonochemical field.

Ultrasound tended to enhance the purity and yield of lignin extraction. The ability of ultrasound to enhance the cleavage of linkages between hemicellulose and lignin increased the separation and purity of the extracts. Furthermore, ultrasound influenced the molecular weight of the lignin extracted. The influence on molecular weight was not uniform attributed to competing separation, degradation, and recondensation reactions. The condensation reactions of lignin are theorized to occur in the interfacial region around the collapsing bubble, hence depending on the nature of the treatment solution.

4.3. The Mechanisms for the Extraction of Carbohydrates from Lignocellulose with Ultrasound.

Carbohydrate Extraction with Ultrasound. Ultrasound was also utilized for hemicellulose and cellulose extraction and modification[95−116] (Table S7). Similarly to lignin, the overall trends from the implementation of ultrasound were the improved purity and yield with few differences observed in the molecular structure. The purity of hemicellulose[95,96] and cellulose[106] extracted from wheat straw was increased with a decrease in associated lignin with ultrasonic treatment. The

reduction of associated lignin with ultrasound follows on from the ultrasound-enhanced cleavage of the hemicellulose-lignin linkages, previously discussed.

Ultrasonic-assisted hemicellulose extraction also enhanced the yield and decreased treatment severities. The solubilization of hemicellulose from wheat straw was enhanced by up to 1.8%[95] and 9.2%[96] with 35 min of ultrasound. Similarly the yield of hemicellulose from sugar cane bagasse was increased with ultrasound.[97,107] Additionally, the yields of hemicellulose from various alkaline extractions of buckwheat hulls were all improved by a factor of 1.2−1.5 with 5 or 10 min ultrasound.[98] Furthermore, the total time for comparative extraction of hemicellulose from almond shells was reduced from 60 to 10 min with ultrasound.[104] These studies have demonstrated the ability of ultrasound to improve treatment times and severities for the extraction of cellulose and hemicellulose from lignocellulosic biomass.

Ultrasonic-assisted extraction of hemicellulose tended to induce minor changes on the structure, and different responses of molecular weight were observed. The ultrasonic-assisted extraction of hemicellulose from wheat straw in alkaline methanol−water solution produced lower molecular weight hemicellulose with decreased thermal stability.[96] Similarly, the molecular weight of the cellulose extracted from wheat straw decreased with an increase in sonication time.[106] However, extraction of hemicelluloses from wheat straw in an aqueous potassium hydroxide solution saw an increase in molecular weight and a slightly higher thermal stability from ultrasonic extraction.[95] Minor differences in structure were noted in the sugar compositions of hemicellulose. The hemicellulose extractions from wheat straw tended to be less acidic and had increased linearity.[95,96] This was evidenced by an increase in relative xylan in the hemicellulose but a decrease in the side chain structures of arabinose, glucose, galactose, and uronic acids. Additionally, minor or no differences were observed from the use of ultrasound for the extraction of hemicellulose from buckwheat hulls[98] and for the dissolution of holocellulose.[108] The different responses of molecular weight to ultrasound, without altering the backbone structure of the extracts, were attributed to the modes of ultrasonic interaction with polymers.

Ultrasonic Depolymerization, Separation, Degradation, and Condensation of Carbohydrates. Ultrasound effects the separation, depolymerization, and degradation of cellulose and hemicellulose from mechanoacoustic and sonochemical effects. This occurred via a cumulative effect of the hydroxyl radicals, shear forces, and pyrolytic degradation of hydrophobic polymers in the hot region around the collapsing bubbles, as discussed in a 2001 review.[121] The separation of lignin and carbohydrates was enhanced by cleavage of the hemicellulose-lignin linkages under ultrasound, as previously discussed.

Depolymerization of polysaccharides in solution is non-random. This was found by the two-stage response of viscosity from the ultrasonic treatment of water-soluble corn hull xylan. Initially the viscosity decreased rapidly, followed by a slower decrease.[113] Similarly the average molecular weight from cellulose modification decreased by 64% in the first 10 min of ultrasonic treatment of cellulose, then leveled, after longer treatment times.[116] This indicates two types of depolymerization mechanisms, the initial scission in the midsection of large polymer chains followed by depolymerization of smaller molecular structures. Various types of depolymerization were also observed in the depolarization of other polysaccharides. The molecular weight distribution of the degradation products

of some water-soluble polymers was reproduced with Gaussian probability,[122] and the ultrasonic degradation of dextran at 20 kHz followed similar trends with molecular masses decreasing with sonication time.[123] Additionally, a comparison of two glucose polymers, amylose and cellulose, highlighted the macromolecular structural effects of ultrasound.[124] Amylose differs from cellulose, with α linkages compared to β linkages, yet the amylose was degraded ultrasonically to a limiting length five times smaller than cellulose. Moreover, larger polymers were found to generally degrade faster than smaller polymers, and scission occurs near the middle of the chain.[124] Depolymerization may also be followed by degradation and repolymerization of monomer units in solution.

Evidence of degradation and repolymerization under ultrasound was also found. The formation of oligomers was observed to occur from ultrasonic treatment of water-soluble corn hull xylan.[113] This was attributed to radical recombination as the spectroscopic characterization indicated that new unsaturated structures with enolic and/or unsaturated α/β carbonyl groups were formed. The degradation of cellulose in solution was also observed. Cellulose extracted from wheat straw and sugar cane bagasse produced a lower viscosity solution when ultrasound was used. The viscosity was lowered from the destruction of cellulose[105,106] from either depolymerization or degradation.

4.4. The Potential of Ultrasound as a Pretreatment. Pretreatment using ultrasound enhanced the hydrolysis yields from lignocellulosic biomass. The augmentation coincided with decreases in lignin content and increased accessibility of the biomass. Ultrasonic interactions with lignocellulose for delignification and lignin modification demonstrated the key ultrasonic effects on lignocellulose. First, ultrasound increased the cleavage of bonds within lignin as well as the bonds between lignin and hemicellulose. The cleavage reactions were enhanced by radicals produced by ultrasound. Additionally, the shear forces from ultrasonic mixing augmented polymer degradation. Furthermore, lignin and lignin compounds were degraded via hydroxide attacks generated from ultrasound. However ultrasound also increased degradation and depolymerization of hemicellulose and cellulose. Degradation of polysaccharides is important when considering ultrasound as a pretreatment option for biofuels and biorefinery applications as it will lead to loss in yield. Lignin is the most accessible component of the lignocellulose and will be degraded preferentially. However the mechanisms and parametric effects of ultrasound on biomass need to be understood at a deeper level before it can be implemented either as a sole pretreatment alternative or as a mechanism to enhance current pretreatment options.

5. PRACTICAL CONSIDERATIONS FOR ULTRASOUND AS A PRETREATMENT OPTION

The literature demonstrated that ultrasound has potential for pretreatment in biofuel and biorefinery applications. However in view of trends found in the literature, there are several considerations to be made. Here the discussion on these considerations was separated into six main sections: feedstock characteristics, solvent, ultrasonic environment, kinetics, reactor configuration, and scale-up considerations.

5.1. Feedstock Characteristics. The initial feedstock is an important consideration as the physical properties as well as the chemical composition will determine the efficacy of ultrasonic treatment. Previously the interaction of ultrasound with a

heterogeneous system was developed for treatment of wastewater sludge.[57] However, generally with sludge the particle size is in the micrometer range and is able to be treated as a single feedstock type. Scanning electron microscopy images demonstrate that ultrasound has the capacity to modify the surface structure of lignocellulose;[64] however, the effects of solid size, density, and concentration on the ultrasonic pressure wave is not as well documented. When considering the treatment of biomass we must consider the interaction with larger particles, loading, and a range of feedstock types.

Type of Biomass. Different types of lignocellulose will respond differently to ultrasonic treatment under the same conditions. Various responses to ultrasound were found for different biomass types as well as for different agricultural residues and different wood types. Two biomass types, sage leaves[99] and valerian roots,[100] were exposed to the same two step treatment plan. First, the medicinal tinctures were extracted with and without ultrasound, followed by extraction and isolation of the polysaccharides. However the yields of the polysaccharides were much lower in the case of the valerian root isolation as they were dissolved in the initial treatment. Additionally, different responses to ultrasound were observed from ultrasonic treatment of similar biomass types. For example, the comparison of two agricultural residues, with and without ultrasound, showed improvements at different stages of the hydrolysis treatment. After the first hour of hydrolysis of corn stover, the glucose yields were improved by 32%; however, with sugar cane bagasse, glucose yields were improved by 17% in the first hour which increased to 20.6% after eight hours.[63] Moreover, the optimization of conditions for delignification of acacia nut husks, bon bogori trunks, and moj trunks found the same conditions were optimal for the trunks, but the nut husks required a longer pretreatment time (180 min compared to 120 min).[75] Furthermore, the reduction in liquefaction times with ultrasound for different wood types was varied (65−100 min), although the reduction percentages were in a similar range (72−89%).[81] Woods generally contain more cellulose than agricultural residues, and hemicellulose and lignin compositions can vary in different biomass types (Table S6). Ideally an ultrasonic pretreatment process would be useful for all types of lignocellulosic biomass. However the literature indicates that for a variety of goals, such as polysaccharide extraction, delignification, glucose hydrolysis, and liquefaction, optimal conditions vary significantly between biomass types. Therefore ultrasonic treatment of lignocellulose could only be practical for a single biomass type or for a homogenized sample.

Particle Size. Particle size affects the efficacy and economics of treatment. Optimization of particle size range tends to favor the smaller particle size; however, ultrasonic pretreatment was also effective at larger particle size ranges. The optimization of the pretreatment of sugar cane bagasse was conducted for both alkaline and acidic pretreatment. The alkaline pretreatment was optimized for reducing sugar production and delignification efficacy. The particle size range was 0.27−0.91 mm, and the optimal particle size was 0.27 mm for both delignification and sugar production.[69] Similarly, the optimization of acidic ultrasonic pretreatment of sugar cane bagasse found the smallest size range (<0.18 mm) was most efficient for sugar production. This was compared to the other ranges of 0.5−0.18 mm, 1−0.5 mm, and >1 mm.[68] In both cases particle size was found to be a significant factor on the effect of the pretreatment of sugar cane bagasse. The majority of ultrasonic treatment in the literature deals with biomass screened to smaller than 1

mm. However, grinding to a small size is an energy intensive and expensive step in the consideration of pretreatment on a larger scale. Therefore it is important to consider the efficacy of ultrasound for larger particle sizes. There were few studies involving a larger biomass size range via shredding and screening to sizes over 1 mm. The hydrolysis of shredded oil palm empty fruit bunch was improved with ultrasound[73] as was the hydrolysis of sugar cane bagasse screened to 5 mm.[66] Furthermore, the fractionation of olive tree prunings was successfully improved by ultrasound over their particle size range of 1−8 mm,[74] and liquefaction times of lignocellulose screened to 2 mm were improved with ultrasound.[81] These studies demonstrate that ultrasound can be effective over a range of particle sizes, although optimization indicates that higher yields are achieved for lower particle sizes. Therefore, although, the smaller size range can increase yields, for consideration of the scale-up of ultrasonic treatment a cost-benefit analysis of grinding to smaller particle size would need to be considered.

Loading. The optimal biomass loading depends on the feedstock and purpose of treatment. A range of loadings were investigated for pretreatment, hydrolysis, and pulp delignification. The pretreatment of a range of biomass types investigated loadings of 1/10, 1/20, and 1/30 (g/g of lime solution) and found that for delignification, the optimal loading was 1/20 (g/g).[75] However, biomass loading was found to be the least influential parameter as compared to lime loading and ultrasonic treatment time. Optimization of the pretreatment of sugar cane bagasse over the loading range of 1/10 (g/mL) to 1/20 (g/mL) found 1/25 (g/mL) to be the most effective loading for delignification and reducing sugar yield. Although, the calculated optimal value was outside of the experimental range.[69] The hydrolysis of pretreated sugar cane bagasse with solid to liquid ratios of 1/10, 1/15, 1/20, and 1/25 (g/mL) found 1/20 g/mL was the optimal loading for hydrolysis, although inhibitory compounds were formed.[72] A lower range of solid to liquid ratio was investigated in the ultrasonic treatment of pulped wheat straw.[58] The lignin content was reduced to 2.4, 4.2, and 4.8% in the 1/70, 1/105, and 1/140 (g/mL) loadings, respectively, compared to 5.4% in straight pulp. Delignification of the pulped biomass decreased with an increase in loading. However the range of loadings used were outside of the loading ranges considered for pretreatment and hydrolysis. The three optimizations of raw and pretreated sugar cane bagasse suggest that a suitable loading would be 1/20 g/mL for pretreatment and hydrolysis. The lower loading was recommended as it is more beneficial to process higher amounts of biomass at the same time. However, the optimizations were all for a similar feedstock, and hence when other biomass types are considered a different loading may be optimal.

There was substantial evidence to demonstrate the treatment of lignocellulosic biomass is influenced by the biomass type, particle size, and loading. The different response of lignocellulosic materials to ultrasonic treatment supports the use of singular biomass types in ultrasonic pretreatment. Although it would be of interest to investigate the combined processing of multiple types of lignocellulose compered to monotype feedstock. Lower particle sizes are more susceptible to ultrasonic degradation; however, the cost and benefit of additional grinding should be considered. The optimal loading for pretreatment of sugar cane bagasse was 1/20 g/mL,

although these findings should be evaluated for alternative feedstock types.

5.2. Solvent. Solvents successful at pretreatment of lignocellulose coupled with ultrasound were organized in three categories: aqueous, organic liquid, and ionic liquid. Chemicals within the ultrasonic solution will change the viscosity of the solution which in turn will affect the cavitational threshold and physical properties such as augmentation of mass transfer and presence of shear forces of the solution. The chemical species also have the potential to partake in the bubble collapse and produce different radicals and species available to interact with the lignocellulose in the solution. The need to use ultrasound combined with other treatments is likely, and these effects have the potential to increase selectivity and performance in the biorefinery industry.

Alkaline and Acidic Pretreatment. In aqueous solutions, chemicals are generally added to improve delignification. However the addition of chemicals should be done with care as high concentrations lead to undesirable degradation reactions. For instance, a comparison of three aqueous solvents, acetic acid, water, and soda, for the fractionation of olive tree prunings[74] looked at the remaining lignin, cellulose, and hemicellulose. The water and acetic acid had a similar effect on lignin reduction, whereas the soda treatment increased the remaining lignin content. Previously (Section 4.2), evidence was presented for the recondensation of lignin in alkaline solution which is likely to account for this increase. Conversely, pretreatment of sorghum bagasse produced a decrease in lignin content with alkaline pretreatment and an increase in lignin content with acidic pretreatment.[62] However the pretreatments were conducted under different ultrasonic conditions so a direct comparison was not possible. Additionally in other studies, alkaline solutions such as sodium hydrate, hydroxide solutions, and lime were successful at delignification without an increase in lignin content (Table S7). The concentration of the alkaline solution has ranged up to 12% sodium hydroxide,[62] and optimization of pretreatment with 0.25−3.25% sodium hydroxide found the highest concentration was most effective for delignification.[66] Alkaline treatments also have the potential to degrade the carbohydrates, cellulose, and hemicellulose, and so some studies opt for milder alkaline solutions such as lime where the loading of lime (0.25−0.75 g/g of biomass) increased the delignification (64−68%); however, no adverse effect on the sugar molecules was observed.[75]

Fewer studies have combined acidic treatment with ultrasound, probably due to the known carbohydrate degradations that can occur under acidic conditions.[5,61] The loss of carbohydrates under acidic conditions was demonstrated when a 2% sulfuric acid solution was used to treat and hydrolyze oil palm empty fruit bunch. The xylose yield was increased in the first 45 min of treatment; however, treatment for longer than 45 min reduced the yield.[73] Furthermore, pretreatment of sugar cane bagasse with 0−5% sulfuric acid found 3% sulfuric acid was optimal for sugar production. At higher acid concentrations, inhibitory compounds were formed, most likely from the degradation of carbohydrates. In both acidic and alkaline conditions, milder treatments are recommended to reduce the overall loss of usability of the biomass. The loss may occur through degradation of biomass components and/or formation of compounds which inhibit downstream processing.

Organic Solvents and Ionic Liquids for Pretreatment. Ultrasound has the potential to augment pretreatment in organic solvents and ionic liquids. The treatment of biomass was enhanced by ultrasound in a variety of organic solvents. For example, the liquefaction of woods in a diethylene glycol/glycerol mixture,[81] phenol extraction in 50% ethanol,[79] and lignin extraction in 0.5 M NaOH in 60% methanol:water,[83] 95% ethanol,[89] and 60% ethanol.[90] However the extraction of lignin from bamboo using an ultrasonic pretreatment in 95% ethanol did not produce any difference in lignin yield or molecular weight with ultrasound time[87]although the carbohydrate content of the ethanol extraction of bamboo with lignin in another case was decreased with an increase in treatment time.[89]

Ionic liquids are also reported to have successful enhancement with treatment combined with ultrasound. N-Methylmorpholine-N-oxide (NMMO) improved the conversion efficiencies of sugar cane bagasse cellulose when used in combination with ultrasound,[66] and the dissolution of sugar cane bagasse holocelulose was improved with ultrasound in 1-butyl-3-methylimidazolium chloride.[108] Ionic liquids are either used to dissolve cellulose which is then recovered with an antisolvent such as water or ethanol[125] or for the extraction of lignin followed by enzymatic hydrolysis of the xylose and cellulose.[126] Although ionic liquids and organic solvent pretreatments are augmented by ultrasound, there are still cost issues to overcome. Both solvents are relatively expensive and would need to be recycled to improve the process economics. Furthermore ultrasound was shown to degrade solvents such as organic and ionic liquids which must be minimized.

Oxidizing Pretreatments. There are a lack of investigations into the combination of ultrasound with oxidizing pretreatments. Oxidizing pretreatments may be performed under milder conditions, suitable to ultrasonic processing. The promotion of hydroxyl radicals with ultrasound was found to increase lignin degradation.[71] However, under the same conditions, with increased hydroxyl radical production, delignification of lignocellulose was not promoted. Although enzymatic saccharification yields were improved. Pretreatment with hydroxide can be unselective and degrade other components of the biomass.[14] However, addition of an alkaline to hydrogen peroxide for the delignification of rye straw suggested that the separation occurred mainly through cleavage of the hemicellulose-lignin linkages, rather than degradation of the phenolic ring structures.[15] Ultrasound is known to augment oxidization reactions,[21] hence there is potential for ultrasound to be combined synergistically with oxidizing pretreatments, perhaps with a necessary addition of alkaline.

Combined Solvent and Ultrasonic Effects. The ultrasonic effects of cleavage and separation occur in a variety of solvents; however, condensation behavior is altered by solvent use. The effect of the solvent and chemical environment on the known interactions between ultrasound and biomass should also be considered. Evidence for the cleavage of lignin and hemicellulose was cited in organic mixtures[83,90] and aqueous solutions,[84,86] which suggests that use of ultrasound enhanced this cleavage over a range of environments.

Lignin condensation reactions were not ubiquitous over a range of solvents. In a 0.5 M NaOH methanol:H_2O (60:40) mixture, a reduction in lignin condensation was reported;[83] however, in a 60:40 ethanol−water mixture condensation reactions were likely due to a peak in acid insoluble lignin yield after 15 min.[90] Furthermore condensation reactions were reported in aqueous soda,[74] water,[78] and dilute potassium

hydroxide.[84] The occurrence of condensation in a range of environments supports the theory that the condensation reactions take part at the bubble interface. Furthermore in Sections 2.4 and 5.2 evidence suggested the condensation reaction may be manipulated by additives in solution and alteration of ultrasonic parameters. In the literature, condensation occurred in alkaline solutions but was reduced by methanol but still observed in an ethanol solution. Since condensation hinders subsequent accessibility to the biomass, further works with model lignin compounds should be undertaken to understand the condensation reactions in the presence of ultrasound and different additives.

The literature demonstrates that a range of solvents are effective in combination with ultrasound and the treatment of lignocellulosic biomass. Addition of acid and alkaline to aqueous treatment solutions should be done with care to avoid degradation reactions. Given the success in aqueous solvents and the abilities of additives to improve ultrasonic treatments, cheaper, green solvents such as lime should be considered. The additional cost and chemical consumption of organic solvents and ionic liquids must be overcome with either an increase in productivity or efficient recycling before their implementation. Although organic solvents may be able to reduce lignin condensation which should be further investigated. Lastly the combination of ultrasound and oxidizing pretreatment should also be considered.

5.3. Ultrasonic Environment. *Gas Environment.* The gas present within the solution can influence the physical and chemical processes brought about by ultrasound. Ultrasound produces oxidizing radicals, and the presence of different gases will affect not only the rate of the formation of these radicals but also which reactive species are produced. This is important as some reactive gases such as ozone and oxygen were previously used to enhance alkaline pretreatments.[12] Noble gases are used to augment sonochemical processes, as discussed in Section 2.4. A noble gas atmosphere is able to increase the temperature reached during the collapse of a bubble and can hence enhance sonochemical reactions. This was evidenced when argon, krypton, and xenon dignified wheat straw pulp to 3.7, 1.2, and 0.8% content compared to 4.2% lignin without noble gas atmosphere.[58] However the use of noble gas is an expensive option, and the enhanced yields would need to be high enough to justify the additional cost. Therefore the consideration of the use of solutions saturated with cheaper gases may be considered for the pretreatment of lignocellulose with ultrasound.

Temperature. Temperature increase will improve pretreatment of lignocellulose. However cavitation effects in aqueous solvents are maximized at lower temperatures, hence the use of higher temperatures requires alternative solvents. Temperature increase over the range of 30−70 °C increased the effect of ultrasonic extraction of corn bran hemicellulose.[111] Similarly ultrasonic treatment in aqueous solvents generally opts for temperatures below 60 °C. However, higher temperatures were used in various nonaqueous solvents. Liquefaction times were improved with ultrasound at 160 °C in a diethylene, glycol/glycerol mixture. The ultrasonic effects were demonstrated by the reduction of the average size of the biomass particles and by depolymerization.[74] The conversion of sugar cane bagasse was improved with ultrasound in an ionic liquid at 90 °C,[66] and dissolution times of holocellulose in another ionic liquid were improved at 110 °C.[108] Furthermore, in supercritical conditions ultrasound was able to enhance extraction of ginger.[127] A test

with aluminum foil demonstrated that cavitation occurred under the supercritical conditions. Hence, although ultrasonic effects are maximized at lower temperatures, cavitation effects are still significant at higher temperatures, in nonaqueous solvents. Therefore, if higher temperatures are required, nonaqueous solvents need to be used. This would incur higher costs of energy and solvent production.

5.4. Kinetics and Time. Ultrasound increased reaction rates and decreased necessary processing time. However as treatment time is increased the effect is not always accumulative. For example, 120 min rather than 180 min was the optimum treatment for delignification of bon bogori and moj trunks,[75] and the lignin content of sunflower husks decreased with ultrasonic treatment up until 15 min, after which it increased.[78] These observations were probably due to recondensation reactions of the lignin occurring with ultrasonic treatment. Furthermore the sonication of pretreatment liquor was found to decrease the hemicellulose content after 60 min but then to increase the hemicellulose content after 120 min. Meanwhile, the acid insoluble lignin was increased after 15 min of ultrasound, after which the lignin content gradually decreased.[90] These observations were explained by hemicellulose and lignin degradation reactions, lignin condensation reactions, alongside the cleavage of the lignin-hemicellulose complex. Other factors, such as ultrasonic power[73] and lime loading,[75] can have a more significant effect than time, on the yields achieved. Given these factors it is understandable that there are few who have tackled the complex problem of the kinetics involved in ultrasonic treatment of lignocellulose. Although Baxi et al.[76] have elucidated the kinetics of the delignification of saw dust in a sodium hydroxide solution, the delignification was found to have a third-order rate equation, which was theorized to indicate that the acoustic cavitation mechanism reacts differently with the three building blocks of lignin: coniferyl alcohol, sinapyl alcohol, and *p*-coumeryl alcohol. This does not agree with the first-order kinetics observed for the degradation of pure lignin under oxidative conditions.[71] However, under the same oxidative conditions the response of lignin degradation from lignocellulose did not follow the same trend. This would indicate that the kinetics of pure lignin degradation are not always mirrored in the degradation of lignin within lignocellulose. This is most likely due to the complex intermolecular linkages between lignin and carbohydrates. More work on the kinetics of lignin removal from lignocellulose could lead to the capitalization of the preferential degradation of a specific lignin building block for more effective pretreatment. The elucidation of these mechanisms will be able to pave the way for a fuller understanding and subsequent kinetic models for the implementation of ultrasound technology.

5.5. Reactor Configuration. *Frequency and Power.* The frequency and power settings influence the nature and the severity of the ultrasonic effects. High frequency conditions promote more oxidizing radicals, and low frequency conditions promote physical effects of ultrasound; however, both physical and chemical effects are present across the frequency range generally used in ultrasound. An increase in ultrasonic power was reported to increase the ultrasonic effects on liquefaction,[75] dissolution times,[93,108] and hydrolysis yields.[73,78] However the pretreatment of sugar cane bagasse at different powers was optimal at the second highest input power of 120 W compared to 50, 80, and 200 W.[68] The majority of the reviewed studies have opted for high power, low frequency treatment (below

100 kHz), except for treatment of thermomechanical pulp at 610 kHz[117] which found evidence for the oxidation of surface fibers. Further evidence of a chemical interaction of ultrasound with lignocellulose was exemplified by the homolytic cleavage of lignin, previously discussed. Low frequency ultrasound tends to emit an irritating high pitch noise due to the attenuation of the wave in the sonication solution. Therefore it would be desirable to investigate the interaction of higher frequencies at high powers with lignocellulosic biomass as a consideration for pretreatment of lignocellulose.

Reactor Design. Reactor design such as geometry, batch versus flow, and the method of ultrasound delivery will influence the efficacy and viability of the treatment. A majority of biomass treatments reviewed have utilized some form of ultrasonic horn or probe as they tend to be effective for high powers at low frequencies, rather than a bath or transducer system. An ultrasonic horn was compared to the bath system with different volumes of saw dust mixture.[76] For treatments with comparable volumes, the horn was more effective for delignification than the bath. However the power rating for the horn was double that of the bath, and so the results are difficult to compare. Moreover, with an increase in volume, delignification was improved for the bath but not the horn. Alteration of the reactor geometry via liquid height and reactor diameter was found to influence the sonochemical yield and hence the ultrasonic pressure wave properties, most likely responsible for the observed differences.

Scale-up of ultrasonic treatment would need to consider the effect of flow in a reactor. Stirring combined with ultrasound was successful in improving enzymatic hydrolysis,[63] delignification,[76] and liquefaction,[81] at low frequencies. At lower frequencies, where heterogeneous systems were mostly considered, the introduction of flow increased the sonochemical yield. Although stirring tends to allow for ultrasonic augmentation of biomass processing, the effects of flow type and speed should be considered. Consideration of the reactor geometry highlights the challenges which must be overcome for the scale-up of ultrasonic pretreatment of lignocellulose.

5.6. Energy, Cost, and Scale-up. The additional energy use with ultrasound presents a challenge for the scale-up process. An increase in power generally increased the efficacy of the ultrasonic treatment. Clearly, the additional use of ultrasonic energy benefits the overall treatment of lignocellulose. For example, the delignification achieved in 180 min with ultrasound was comparable to the delignification yields achieved in 8 weeks in another study.[75] However a thorough cost-benefit analysis would need to be conducted prior to scale-up. Initial energy comparisons show promise for ultrasonic treatment compared to alternative treatments. The energy requirements calculated for pretreatment in an autoclave, steam explosion, and ultrasound were 23.3×10^4 J/g, 9.9×10^4 J/g, and 7.2×10^4 J/g, respectively.[70] Similarly, ultrasound was preferable to a heat pretreatment for the production of ethanol from cassava chips.[110] The energy consumption for ultrasound was 11 kJ compared to 22 kJ for heat pretreatment. Although ultrasound is recognized as a viable alternative on a laboratory scale, there lacks a comprehensive cost implementation such as those completed for advanced oxidative processes.[128] The costs were significantly reduced when ultrasound was combined with other technologies, such as, ultraviolet radiation, ozone addition, and hydrogen peroxide addition. In regards to a cost analysis of ultrasonic pretreatment of lignocellulose, first the optimal operating parameters should be fully considered.

Ultrasonic processing on a larger scale must first be optimized on a small scale to identify the key operating parameters in order for the technology to be developed. Various reviews[24,28] have dealt with some of the challenges for the implementation of ultrasonic processing in industry. Successful scale-up was achieved for ultrasonic applications such as sewage sludge disruption, nanoparticle coating, and ultrasonic crystallization. Power dissipation was identified as one of the major challenges in the up-scale of acoustic fields due to the necessary inclusion of energy loss due to reactor walls, ambient air, and bulk liquid.[24] Novel designs such as self-focusing reactors,[129] transducers with reflection,[130] and power transducers[131] were developed to enhance the ultrasonic field. Additional custom-design reactors such as hexagonal multi-transducers and rotating horns were outlined by Gogate et al.[24] The technology necessary to scale-up treatment of lignocellulose can only be developed once the key operating parameters are determined and optimized.

6. FINAL COMMENTS

Ultrasound technology is considered a green technique for use in chemical processes as it can reduce reaction times and chemical loading. It is evident that ultrasound has the potential to enhance the separation and hydrolysis of lignocellulosic materials for the use in biofuel production and biorefineries whether the enhancement be from physical or chemical mechanisms. Ultrasound provides physical augmentation via shear forces, mass transfer, and surface erosion as well as chemical effects of producing oxidizing radicals. These effects facilitated homolytic cleavage within the lignin macromolecule, to enhance the cleavage of linkages between the lignin and the hemicellulose and degrade model lignin compounds through hydroxyl attack of the phenolic ring. Furthermore the ultrasonic effects tended to aid in the separation and depolymerization of polysaccharides. However, alongside separation and depolymerization, degradation and condensation can occur. The determination of the relative contribution of the concurrent mechanoacoustic and sonochemical effects will enable appropriate parameter selection. If the contributions of the physical effects are dominant, then low frequencies should be selected. Alternatively cavitation mechanisms which require lower energy input, such as hydrodynamic cavitation, should be considered. However, if oxidizing radicals are necessary, then the ultrasonic effects on lignocellulose at high frequencies warrant investigation. Similarly, the combination of ultrasound with complementary oxidative species such as peroxide and ozone has the potential to synergistically enhance ultrasonic pretreatment. This would also reduce necessary energy requirements.

Various solvents can also be used to tailor the ultrasonic treatment. Alkaline solvents tend to augment delignification; however, in some cases lignin condensation was observed. The addition of organic solvents such as methanol shows promise for the prevention of condensation. Moreover, other operating parameters should be considered for optimal treatment, such as particle size, biomass loading, treatment time, and reactor configuration. Once an optimal setting of ultrasonic treatment is found the scale-up challenges, costs, and benefits of sonoprocessing must be considered.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The accompanying tables provide information referred to in the review. There is a comparative table of different pretreatment

options previously investigated for lignocellulose and some examples of compositions of lignocellulosic biomass. Additionally there are data tables to summarize the results described in Section 2.4 with regards to ultrasonic effects of frequency, geometry, flow, and gas atmospheres. Lastly there is a comprehensive review table summarizing current literature on ultrasonic treatment of lignocellulosic biomass. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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