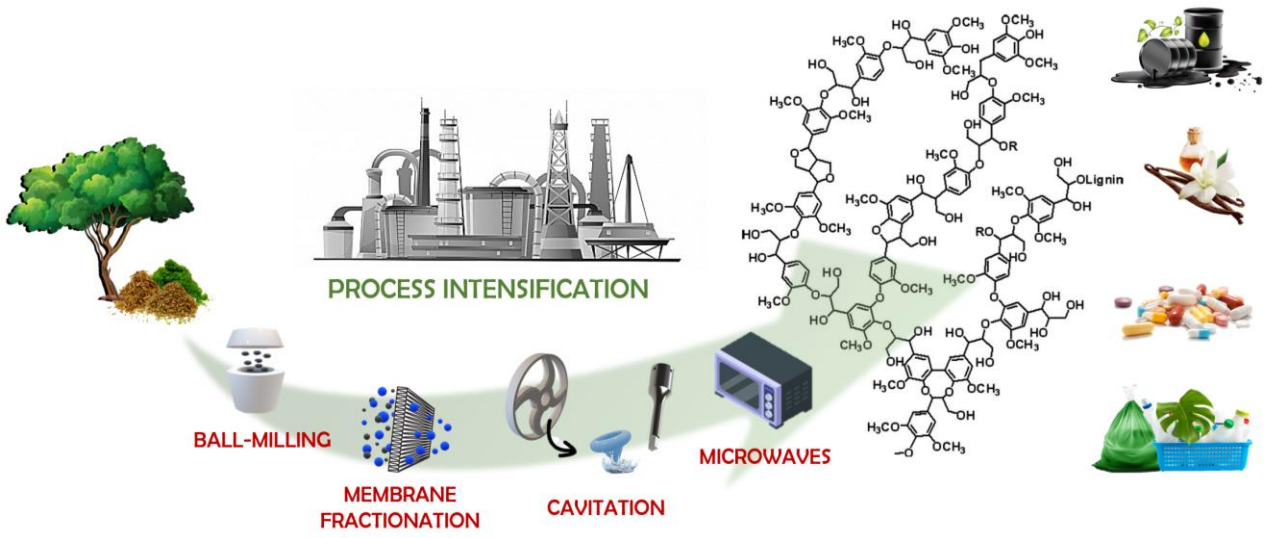
Process intensification strategies for lignin valorization

Process intensification strategies for lignin valorization



Keywords: lignin, microwave, hydrodynamic cavitation, ultrasound, membrane separation

Abstract

Nowadays, the increasing concern about the declining fossil fuel reserves and the environmental impact derived from their use has put considerable interest in lignocellulose exploitation as a renewable source of biofuels and biomaterials, according to the biorefinery concept.

Several processes and technologies have been extensively studied in order to optimize biomass treatments aiming to enhance the recovery of its main products: cellulose, hemicelluloses and lignin. Lignin is, in fact, considered a valid substitute to petroleum as a source of aromatics, thanks to its abundance in nature. However, its complex and highly resistant structure limits its further applications, therefore, lignin upgrading is considered extremely challenging: various processes have been developed in recent years, but their feasibility at industrial scale still represents a bottleneck.

Recently, process intensification has gained considerable attention in the design of sustainable procedures for lignin valorization. In particular, non-conventional technologies such as Ball milling, Ultrasounds (US) and Microwaves (MW) have recently shown promising results in biomass exploitation, thanks to their ability in

generating specific high-energy microenvironments which could enhance process efficiency: mechanochemical and US activation have been mostly applied to biomass pre-treatment, in order to separate its components and enhance lignin extraction yield, while MW have been exploited as a means for lignin depolymerization, achieving higher yields of aromatics in milder reaction conditions. However further efforts should be done to improve profitability through new processes, aiming to reduce the cost associated to bio-derived products.

In the present review, recent approaches to lignin valorization are discussed, focusing on new alternative methodologies for process intensification, besides their challenges and feasibility at industrial scale.

1. Introduction

The decline of fossil resources, the rising cost of fuel energy and the environmental concerns have prompted the development of sustainable technologies to produce renewable energy and chemicals. In this context, the exploitation of lignocellulosic biomass as a renewable resource has gained increasing interest: lignocellulose, in fact, is the primary component of plants, and, thus, it is the most abundant renewable resource on Earth. [1,2] It is mainly composed of cellulose (40-50%), hemicellulose (15-20%) and lignin (15-25%), with a small part of other extractable components such as water, proteins and minor compounds.[3] The composition of various lignocellulosic feedstocks is illustrated in Table 1

Feedstock	**Composition (% dry wt)**			**References**
	Cellulose	Hemicellulose	Lignin	
Bamboo	36-43	18-20	23	[4]
Corn stover	35.1-39.5	20.7-24.6	11.0-19.1	[5]
Cotton	85-95	5-15	0	[6]
Cotton stalk	31	11	30	[7]
Eucalyptus	45-51	11-18	29	[4,8]
Rice straw	29.2-34.7	23-25.9	17-19	[9]
Wheat straw	35-39	22-30	12-16	[9]
Grasses	25-40	25-50	10-30	[10]
Sugarcane bagasse	25-45	28-32	15-25	[4,8]
Pine	42-29	13-25	23-29	[8]

Poplar wood	45-51	25-28	10-21	[11]
Olive tree	25.2	15.8	19.1	[12]
Oat straw	31-35	20-26	10-15	[13]
Nut shell	25-30	22-28	30-40	[14]

Table 1: Composition of representative lignocellulosic feedstocks.

In last decades, significant technological advancements have been made for processing lignocellulosic biomass since the valorization of its principal components could offer a cheaper way to produce biofuels and chemicals. Indeed, cellulose and hemicellulose fractions are a potential source of fermentable sugars and value-added products, while lignin is a source of aromatic compounds. However, due to lignocellulose complex and highly resistant structure, its treatments usually require harsh condition, which is the reason why the design of cost-effective processes is necessary. Furthermore, the understanding of the complex structure of lignocellulose is fundamental for a suitable valorization. Moreover, for a sustainable global development, the exploitation of biomasses for the large-scale production of chemicals is very attractive. In fact, biomass plays an important role in reducing greenhouse gas emissions, since CO_2 derived from its wastes would originally have been absorbed during plant growth.[15]

For these reasons, recently, process intensification (PI) has received considerable attention as a strategy to enhance process efficiency and sustainability by reducing energy consumption, volumes handled and waste, while increasing productivity and safety in a simplified cost-effective process.[16] In this context, enabling technologies based on microwaves (MW), ultrasound (US) and mechanochemical activation play a central role in PI. In particular, US and ball mills, thanks to the generation of high-energy microenvironments, can strongly affect biomass structure enhancing mass transfer, while MW can promote biomass conversion efficiently, by prompting heat transfer. As a consequence, US and ball mills are typically applied in biomass pretreatment rather than conversion reaction, where MW reactor can find wide applications. Therefore, the design of sustainable and efficient processes for the valorization of lignin fraction could be addressed by enabling technologies. Despite the potential of mechanochemical and ultrasound activation in biomass conversion, these processes, as well as hydrodynamic cavitation, have been mostly applied to biomass pre-treatment, with the aim of separating its components and enhance the lignin extraction yields. Furthermore, the intrinsic efficiency for downstream separations of membrane technology, makes it a good candidate for intensifying the

fractionation of extracted lignin, in order to recover more uniform fractions for further valorization. Microwave technology, on the other hand, when used for biomass pretreatment and lignin recovery, afforded chemical modified and deconstructed lignin; for this reason, it could be more suitably exploited as an efficient tool for lignin depolymerization.

The aim of this review is to provide an overview of the most recent applications of non-conventional technologies for the PI of lignin extraction and conversion into high added value products, in order to highlight the advantages and the potential scalability of these technologies, compared to conventional procedures.

1.1 Lignin structure

Lignin is one of the main constituents of lignocellulosic biomass (15–30 % by weight) and the most abundant source of aromatic molecules in nature. [17] It consists of a highly complex structure interconnected with cellulose and hemicellulose through covalent and non-covalent bonds. [18] Despite its abundance, lignin conversion has received less attention compared to cellulose and hemicellulose in the biorefinery processes due to the challenges of converting it into high value-added products. The reason lies in the high resistance to biological and enzymatic degradation due to complex chemical linkages, that prevents plants from insects and microbial attack. In fact, lignin from bioethanol and paper pulp industry is traditionally seen as a by-product and mainly recycled as fuel for energy production. [19] However, the valorization of lignin has recently gained significant interest because it provides opportunities for different value-added applications. Furthermore, lignin can be converted into several profitable commodities, such as fuel and phenolic compounds. [17]

Lignin is a cross-linked amorphous hydrophobic polymer with a very complex structure which significantly varies depending on the plant species and the isolation process. Indeed, unlike cellulose and hemicellulose, lignin presents diverse monomer units and linkages (more than 400 bonding patterns are known) making it highly recalcitrant to depolymerization. Additionally, lignin weight can vary between 5 and 100 KDa within an isolated lignin. The main units are phenylpropene monomers (monolignols): trans-p-coumaryl alcohol (H-unit), trans-coniferyl alcohol (G-unit) and trans-sinapyl alcohol (S-unit) (Figure 1),[20] containing zero, one, and two methoxy groups, respectively. The ratio between these primary monomer units varies among different plants and species: coniferyl alcohol is abundant in softwood lignin (90-95%) while hardwood lignin contains both coniferyl and sinapyl alcohols and all the three monolignols are present in grass lignin.[21] Moreover,

lignin content in biomass decreases with the following order: softwood > hardwood > grass. Lignin monolignols are inter-linked through ether and C-C bonds, such as β-O-4, α-O-4, and 4-O-5, as well as C-C bonds such as β-1, β-5, 5-5', and β–β (Figure 2).[17] In lignin polymeric structure different functional groups are present including methoxyl, hydroxyl, benzyl alcohol, benzyl ether and carbonyl groups, which outcome in different reactivity. The proportion of these linkages and specific functional groups are highly dependent on the lignin sources and isolation methods.

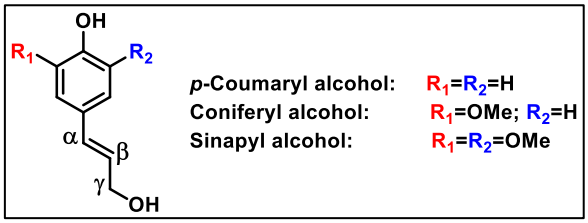


Figure 1: Building block monolignols of lignin.

The β-O-4-aryl ether bond is the most abundant, representing approximately 50% of all the linkages in native lignin.[22] Consequently, the effective cleavage of this specific bonds is crucial for lignin decomposition.[23,24] However, due to the presence of various functional groups, the proportions of these linkages are different and related to the vegetal species of origin. For instance, β-O-4 linkages are more abundant in hardwood lignin compared to softwood, making the valorization of this type of lignin highly challenging.[25] Furthermore, technical lignins, which are isolated from biomass after several treatments, highly differ from native lignin. Their structures are related to the isolation method and usually present higher C-C linkages, a broad molecular weight distribution and some contaminations such as ashes and sulfur, which make technical lignins difficult to depolymerize.[26] The most common technical lignins (Lignosulphonates, Kraft lignin, Soda lignin and Organosolv) derive from wood pulping and have been extensively studied for lignin valorization. Hence, the variety in both monomer content and chemical bonds makes the determination of the exact chemical structure of isolated lignin extremely difficult. Additionally, for an industrial general protocol of lignin conversion into fuels and chemicals, lignin structural variability should be carefully addressed within different issues such as depolymerization, re-condensation reactions and product separations.

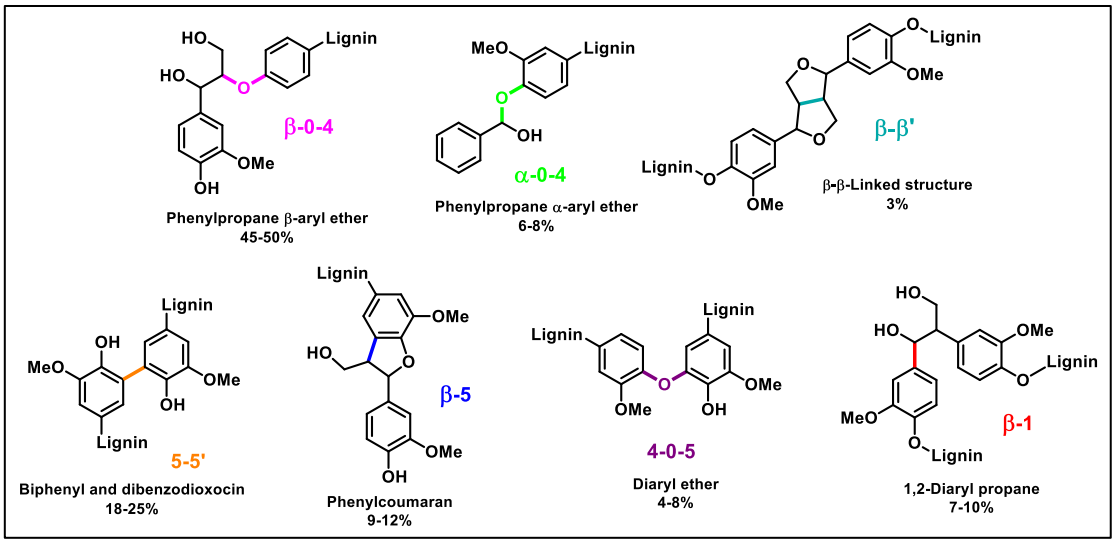


Figure 2: Typical lignin interunit linkages

2. Lignocellulose Pretreatment

Pretreatment is a crucial process step for the biomass conversion into high added value products. It involves the alteration and solubilization of lignocellulosic biomass aiming to achieve cellulose, hemicellulose and lignin conversion rapidly and easily, with greater yields. [27,28] Hence, an efficient separation of the main components from lignocellulosic biomass is a desirable condition in lignin valorization. Although several methods have been developed, the effective fractionation of biomass into its three main constituents is still challenging. In fact, it is required to deconstruct cell walls and isolate its components, without drastically modifying their native structure, thus aiming to simplify the subsequent conversion into valuable products (Figure 3). [29] Furthermore, the choice of the optimal pretreatment protocol and conditions highly depends on the feedstocks and the economic and environmental impact. The main issue still remains the removal of lignin, which is highly resistant to solubilization, and which inhibits the subsequent hydrolysis of cellulose and hemicellulose. Besides the necessity of its removal, delignification is a key step, as lignin can be recovered for further applications with potential high added value.

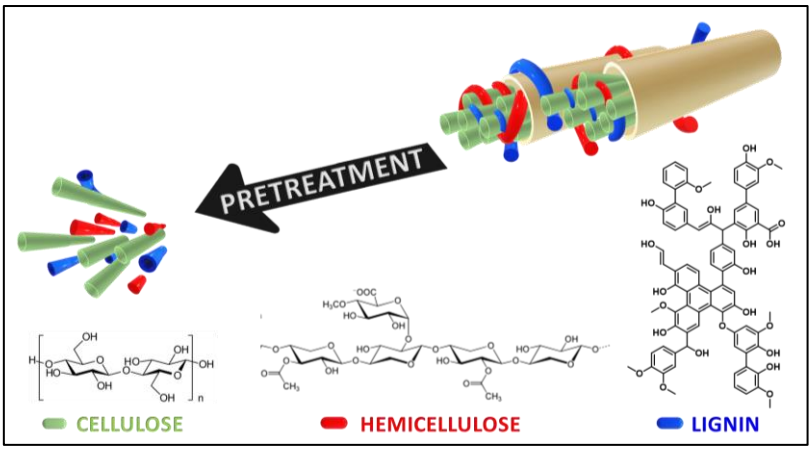


Figure 3: Pretreatment effect on lignocellulosic biomass

Other factors such as lignin content, cellulose crystallinity and size of the biomass particles are also crucial factors to consider in order to overcome lignocellulose recalcitrance. Thereby, pretreatment processes should maximize biomass delignification and depolymerize hemicellulose by enhancing solvent diffusion; moreover, it should reduce cellulose crystallinity and isolate uncondensed lignin, avoiding the formation of degradation products.

Pretreatment methods include physical, chemical and biological processes, or a combination of them (Figure 4).

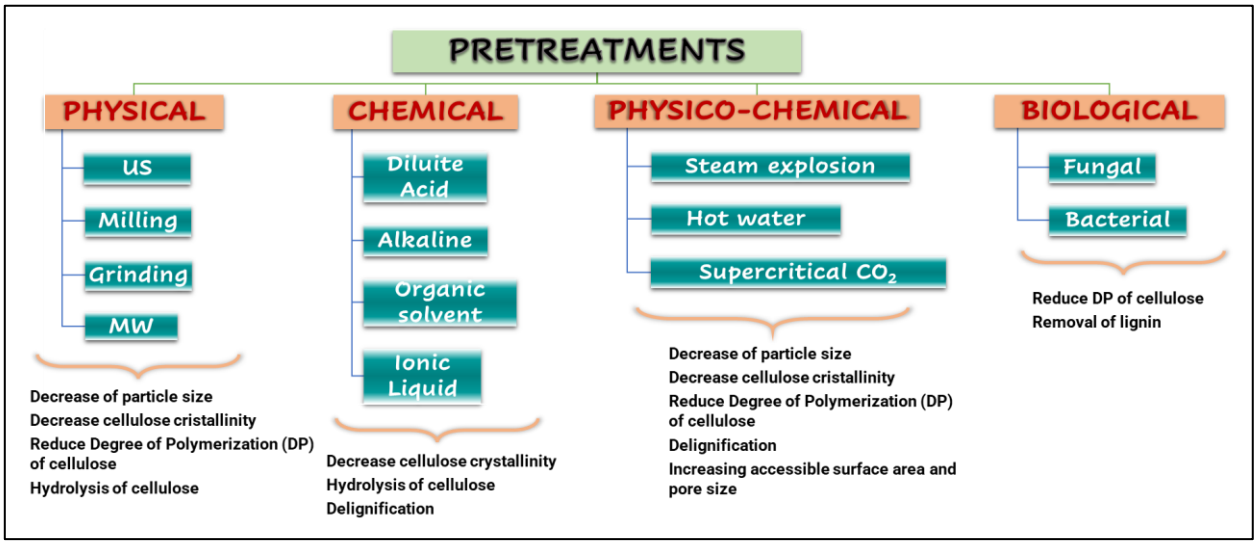


Figure 4: Various pretreatment processes of lignocellulosic biomass.

Biological pre-treatments are based on the use of lignin-degrading enzymes and microorganisms such as fungi and bacteria for partial delignification of lignocellulosic materials. However, the biological approach is often

criticized because of the slowness of the process and the significant costs of enzymes. In chemical pre-treatments, the use of alkali, acids or, more recently, ionic liquids is required for the alteration of lignocellulosic biomass structure, thus, these methods may not be advantageous from a sustainability perspective. Physical pretreatments are used to enhance biomass deconstruction and solubilization; the major drawback is the high energy input required. Since each pre-treatment procedure reports some limitations such as the use of toxic chemicals, prolonged treatment times, elevated temperatures and pressures and high energy input, it is crucial to develop efficient and cost-effective procedures for the intensification of biomass pretreatment. [29,30]

In the last decades, enabling technologies such as milling, MW irradiation and US have been intensively exploited as more efficient alternatives to the traditional biomass pretreatment methods. Milling reduces biomass particle size and is typically applied prior to other pretreatment methods to improve feedstock handling. Moreover, it allows the separation of biomass constituents into different fractions by the rupture of the cell wall, reduces cellulose crystallinity and decreases particles size. Cavitation, generated by US or in the form of hydrodynamic cavitation (HC), also offers a promising intensification of biomass pretreatment; it enhances solvent penetration into lignocellulose walls, improving the mass transfer of the following extraction processes. [31] Though these processes usually require high energy input, they can provide milder conditions and a reduced amount of solvents compared to conventional fractionation methods. In fact, the energy required for pretreatment highly depends on the final particle size and the crystallinity reduction of the feedstock. However, usually the pretreatment step requires more energy than the energy content available in the biomass, thus making these methods still expensive for a full-scale process.[32]Therefore, the choice of a specific pretreatment method should consider all these aspects in order to guarantee an efficient and cost-effective process in biomass valorization.

2.1 Ball milling pretreatment of lignocellulosic biomass

Size reduction is a key point for the valorization of biomass into energy and chemicals. In fact, the surface/volume ratio increases within the accessible area of constituents and, therefore, enhances the consequent conversion rate. Moreover, it reduces the mass and heat transfer, limiting the required energy, and facilitates the storage. [27,33]

Due to the heterogeneous structure of lignocellulosic biomass, usually several steps are required in order to reduce the particles size. First, it is necessary to reduce the volume of lignocellulosic material, usually by cutting biomass from meters to centimeters. Then, an intermediate milling reduces particle size from cm to mm and lastly, fine and ultra-fine milling reduce the size from mm to 20-500 μm. Smaller sizes requires wet grinding with a consequent higher energy consumption.

Several types of mills have been used to fragment lignocellulosic biomass: knife mill, hammer mill, planetary and vibrant ball mill, which consist of a rotor driving different tools.[34] The most common mills in laboratory are vibrant and planetary ball mills. The motion of these instruments lead biomass to the collision with balls and walls of the vessel. This generates high localized energy able to crush materials into smaller dimensions. In vibrant ball mills, a rapid sideward movement leads balls inside the vessel to impact against the walls and its content. On the other side, planetary mills describe a circular movement while the vessels simultaneously and rapidly rotate in a counter direction, mimicking planets movement. As described before, this motion causes friction and impact at the wall surfaces.

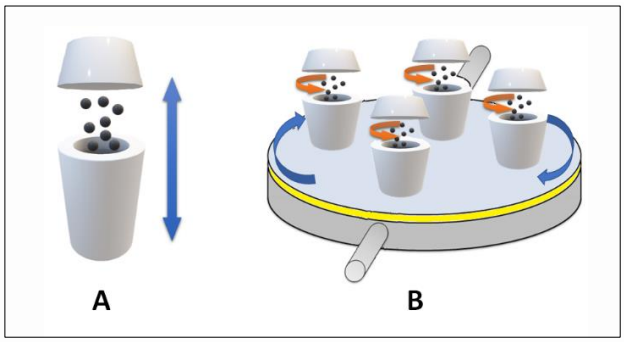


Figure 5: Vibrant mill (A) and planetary mill (B)

High milling speed generally led to faster grinding, which may also increase the temperatures, causing formation of undesirable byproducts. However, mechanical comminution is considered one of the most expensive processing steps in converting biomass, since high energy is required.

However, the use of milling is not limited exclusively to reduce particle size in order to enhance biomass fractionation for further applications. Björkman[35] developed a method which consist in the use of ball-mill to isolate lignin from wood. The biomass is first ball-milled and then extracted in aqueous dioxane (milled wood lignin, MWL). However, the recovery of MWL is rather low since it highly depends on the nature of the

biomass and milling time. When milling time increases from one day to one week, yield rises from 16% to 60%, highlighting that this method is time and energy consuming, since it mainly focuses on the recovery of lignin. [36] In most cases, the advantage of using MWL lies in the fact that it is considered the most representative of lignin in its native state, since it is isolated at room temperature in the absence of any strong acids or bases. [37,38]Milling pretreatment has been proven to be an efficient method to reduce crystallinity and particle size, enhancing solvent accessibility to lignocellulose and, thus, improving also alcoholysis reactions. In this regard, recently, a ball mill pretreatment has been applied to camphorwood sawdust, aiming to obtain elevated bio-oil yield in supercritical ethanol. The reduced crystallinity and particle size increased biomass surface area (from 1.88 to 4.77 m^2g^{-1}) enhancing the solubility in ethanol. The yield of aromatic rich bio-oil increased to 59.2% compared to the 39.6% obtained without pretreatment. [39]

Shi et al. [40] pretreated with ball mill Softwood Unbleached Kraft Pulp (UKP) to promote its dissolution in a NaOH/urea solvent. After 60 min of milling the particle size of UKP decreased to an average diameter of 5 μm, showing good distribution, and the crystal peaks of cellulose completely disappeared, indicating that the milling process could easily destroy the crystal structure of lignocellulose. Furthermore, the degree of polymerization (DP) was reduced from 1300 to 330. This promoted the subsequent solubilization of the pulp in NaOH/urea solvent. In fact, dissolved proportion of UKP increased from 25.6% to 96.0% after 60 min of milling pretreatment. However, biomass with an elevated lignin content could not dissolve in the NaOH/urea solvent due to the presence of lignin-carbohydrate complex. Ball milling treatment has been applied to investigate the effect of cellulose crystallinity, hemicellulose and lignin content on further enzymatic hydrolysis. Four fractions with different sizes (250-355 μm, 150-250 μm, 63-150 μm, and < 63 μm) were collected and then hydrolyzed. It was confirmed that monosaccharides yield increased within the decreasing of cellulose crystallinity [41] and that lignin removal greatly enhances enzymatic hydrolysis of biomass, since after delignification, even with higher cellulose crystallinity degree, high yields of glucose and pentoses were achieved, compared to the untreated samples. The energy requirement of mechanical comminution is extremely variable, as it is related to the type of instrument, initial and final particle sizes, and biomass characteristics (i.e., bulk density, processing amount, moisture content, and composition)[34].

2.2 Processes assisted by cavitation

Ultrasound (US) is a mechanical acoustic wave with the frequency range from roughly 10 kHz to 20 MHz generated by piezoelectric transducers which respond to an alternating current with mechanical vibrations to produce US of a certain frequency. [42,43] When the transducer is connected to a vessel filled with a solution, the mechanical vibrations of the piezoelectric material create a pressure wave through the solution (Figure 6).

In a typical US-assisted process, the pressure wave through the liquid medium creates alternating regions of high pressure (compression) and low pressure (rarefaction). The rarefaction of the cycle can stretch the liquid molecules apart creating cavities also known as cavitational microbubbles. [44] These microbubbles grow to a maximum of about 4-300 μm in diameter [44] and under the effect of ultrasonic field repetitively expand and contract. When acoustic energy has gained sufficient intensity, some microbubbles become unstable and violently collapse in several nanoseconds, generating shockwaves. [45] The microbubbles collapse is an adiabatic process, resulting in a huge amount of energy released. Therefore, local hotspots are formed that present extreme local conditions of high temperatures (ca. 5000 °C) and high pressures (ca. 50 MPa).[46]

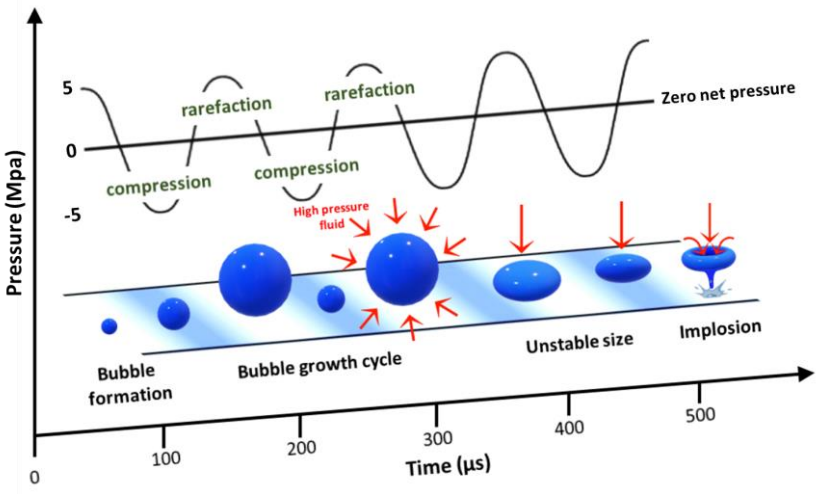


Figure 6: The acoustic generation of cavitational microbubbles

In liquid media cavitation facilitates the disintegration of solid particles, acting superficially and providing thermo-mechanical energy to the process. For instance, the instantaneous collapse of bubbles at the solid/solvent interface produces strong shockwaves and microjets at high speed (>100 m/s) toward solid surfaces.[42,46] This movement of the solvent is defined as micro-convection, which intensifies the transport of fluids and solid particles compared to conventional mechanical methods. Moreover, the high-energy

environment generated by shockwaves is able to break chemical bonds. Cavitation can be divided into acoustic (AC) or hydrodynamic (HC), depending on its generation method. In the first case, microbubbles are generated by the pressure variation of ultrasonic waves passing through a fluid, whereas in hydrodynamic cavitation the growth and collapse of the bubbles are induced by a rapid variation in the streamlines of the fluid, which is forced through a Venturi tube or by the relative movement of a rotor/stator system.[47]

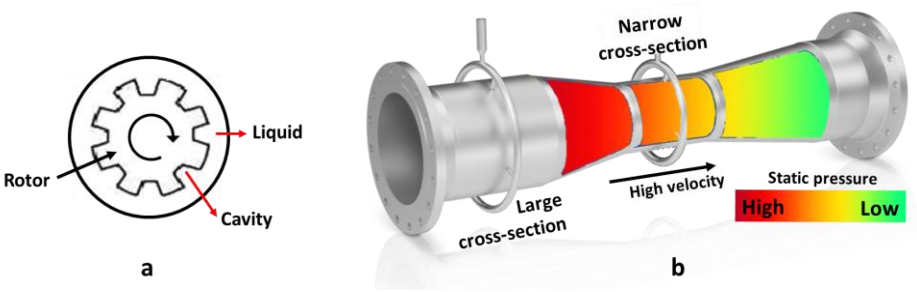


Figure 7: Rotor stator reactor (a) and venturi (b)

2.2.1 Reactors design

There are several types of reactor designed for cavitation (Figure 8). [48] Ultrasonic horns are the most used reactors and typically consist of an immersion transducer which generates high-intensity region in the liquid nearby the horn. The scaling-up process of this type of US systems is not very effective since it is not possible to transmit the acoustic energy in a large volume. Furthermore, ultrasonic horns suffer from erosion at the surface, thus, they are generally used for laboratory scale investigations. In ultrasonic bath, the reactor bottom is irradiated with a single or multiple transducers. In this case, the maximum of cavitation intensity occurs just above the surface of the transducer. Thus, the area of irradiating surface can be increased in order to improve energy distribution in the reactor.

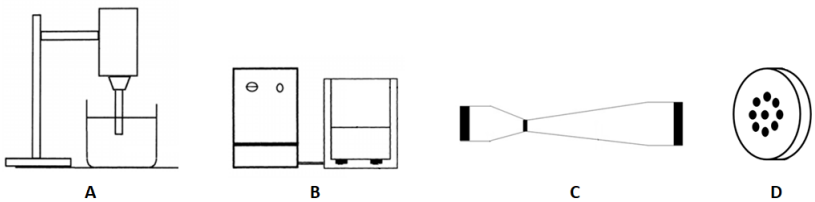


Figure 8: US immersion horn (A), US bath (B), venturi (C) and orifice plate (D)

HC can be generated by the flow of the liquid through an orifice plate or a valve: orifice plates can present single or multiple holes, with different diameters to ensure different cavitation intensities; furthermore, they offer more flexibility of controlling parameters such as inlet pressure, flow rate, cavitation intensity, making this system more suitable for specific applications. [49–51] The cavitation phenomena occur just after the orifice plate: when the liquid passes through the holes, due to the restricted area, the velocity increases resulting in a decreasing pressure. When the pressure goes below the medium vapor pressure, cavitation occurs. In the case of a Venturi tube, a higher velocity at the throat is generated, compared to an orifice. The Venturi configuration can be used for milder processes (typically pressure requirement between 15 and 20 bar) and physical transformations, while an orifice flow configuration is generally used for chemical reactions. In the rotor-stator system, the main energy consuming part is the spin of the rotor. Thus, the operating cost is associated to the electricity consumption by the motor, which is relatively low. Moreover, HC devices are easy to scale up compared to US reactors and several parameters, such as speed rotation, percentage of biomass and the time of treatment can be easily optimized.

2.2.2 Cavitation for biomass delignification

Cavitation technology has been recently applied to face the technological challenges related to the pretreatment step, necessary for the conversion of lignocellulosic biomass.[52] Indeed, current pretreatment options are expensive and require the addition of chemicals, which could be counterproductive in biofuel production, resulting in wasteful processes. For this reason, new technologies must consider processes with low environmental and economic impacts within high efficiency. US-assisted processes are influenced by frequency, duration of treatment, reactor configuration, type of biomass and solvent used. In particular, bubble cavitation is strictly connected to frequency: high frequencies (>150 kHz) do not promote active cavitation because of the insufficient duration of the ultrasonic cycle. Indeed, longer cycles are required for the growth, radial motion and collapse of the bubbles. However, short-lived bubbles can boost free-radical concentrations, leading to chemical effects, while mechano-physical effects are observed at low frequencies (20–80 kHz). The combination of these effects can modify the chemical and physical composition of lignocellulose. Indeed, the mechanoacoustic effects can alter the surface structure of the biomass, and the sonochemical production of oxidizing radicals can lead to a chemical attack of the components of lignocellulose.[52] In this frame, the

effect of hydrodynamic and ultrasonic cavitation on lignocellulosic biomass was reviewed according to wheat straw pretreatment.[53] The review highlighted the prevalence of physical effects of US in the delignification enhancement with low-frequency ultrasound.

The crucial point for a biorefinery approach relies in the enhancement of the efficiency of lignocellulose pretreatment and the following separation of the components at mild conditions. In addition, the production of undesired by-products along with lignin modification should be avoided, in view of further valorization steps. For this reason, the use of ultrasounds for biomass fractionation could be a promising technology that could be easily implemented in biorefinery processes.[54] US are mainly used for biomass pre-treatment, as an efficient tool for delignification, especially for sugar fermentation to biofuels. However, the so-extracted lignin could find higher added value applications than simple heat generation by burning or pelletizing, as the structure of lignin remains quite unchanged after US treatment.

In this context, US-assisted technology has been used for the pre-treatment of wheat straw (0.5M NaOH in 60% aqueous methanol) and compared with conventional fractionation. [55] US were applied for a time range of 5 to 35 minutes, obtaining the solubilization of 67.4% to 78.5% of the original lignin, whereas 61.0% of lignin solubilization was obtained at 60°C for 2.5 h without sonication. Moreover, US-isolated lignin showed slightly lower molecular weights and no significant differences with respect to the native lignin of wheat straw, confirming the efficiency of the US-assisted lignin extraction procedures.

The same research group performed a similar experiment using 0.5M KOH to extract lignin, comparing conventional and US-assisted procedures. [56] Even in this case, higher lignin yield in shorter times was obtained under US (from 43.9% to 49.1% when US were applied for 5 and 30 minutes respectively) compared to conventional extraction at 35°C for 2.5 h (43.9% of yield). In this case, the purity of lignin fraction was higher after US treatment and no significant changes from native lignin were observed.

More recently, Garcia et. al [54] evaluated the effect of US (420 W, 50/60 Hz) in the fractionation process of olive tree pruning residues. Different times (30, 60 and 120 minutes) and different solvent (water, NaOH 7.5% w/w and acetic acid at 60% v/v) were applied, using a US bath (420 W, 50/60 Hz) and a solid to liquid ratio of 1:10 (w/w). It was demonstrated that under US, lignin yield and selectivity in liquid fractions increased, compared to the reference sample conventionally treated. Additionally, a lower degree of cellulose degradation

and higher content of hemicellulose was found in US-treated samples. Moreover, the US-assisted process did not significantly affect lignin structure and thermal behavior, suggesting the suitability of the US technology for industrial applications. [54]

The effect of different frequencies (40 kHz, 376 kHz and 995 kHz) in US-assisted pretreatment of wheat straw was investigated by Bussemaker et al. [57] At each frequency, three different solid to liquid ratios (1/50, 1/20 and 1/15 g/ml) were tested and, in addition, different particle sizes (0–0.5, 0.5–1, and 1–2 mm) were evaluated at 1/20 g/ml. In order to preserve the energy efficiency of the process, time extraction of 25 minutes was chosen. In fact, protracted times have been demonstrated to increase lignin re-condensation. Authors showed that delignification was enhanced at low frequency of 40 kHz up to 7.2% compared to the reference sample, as a result of mechano-acoustic effects, whereas high frequencies (995 kHz) favored carbohydrate solubilization.

Recently, a comparison among three different US reactor configurations (longitudinal horn, vertical immersion horn and ultrasonic bath) on the efficacy of sawdust delignification was described. [58] The effect of different operating parameters such as Na2CO3 concentration (0.1, 0.15, 0.2, 0.25 M), H2O2 concentration (0.2, 0.4, 0.6, 0.8, 1 M) and biomass loading (2, 4, 6, 8, 10 wt%) has also been investigated. The optimized reaction conditions were found at 150 W for 70 minutes, with 0.2 M concentration of Na2CO3, H2O2 1 M and biomass loading of 10 wt%. Higher lignin yield was obtained with the longitudinal horn (87.4%), followed by ultrasonic horn (lignin yield of 85.1%) and ultrasonic bath (lignin yield of 82%), while only 42.4% of lignin yield was obtained with conventional method, confirming the process intensification benefits of US treatment. Additionally, the energy requirement for the delignification of sawdust was evaluated, finding that ultrasonic horn configuration presented lower power consumption (6.72 × 106 kJ/m3), followed by both longitudinal horn and ultrasonic bath (12.6 × 106 kJ/m3). However, authors declared that the higher energy consumption of longitudinal horn, compared to the immersion one, was due to the necessity of two additional stirrers on the extreme ends of the reactor to obtain a homogeneous mixing. Therefore, the efficacy of longitudinal horn is greater, since this configuration is able to process larger volumes with higher yields.

A US-assisted pretreatment of Vietnam's rice straw in NaOH 2M at 90°C was performed using an immersion horn (20 kHz 500 W) for a sonication time of 10, 20, 30, and 40 minutes.[59] The extraction was then carried

on in silent conditions at the same temperature for a total period of 1.5 h. Lignin yield with US irradiation was enhanced; in particular, when US radiation was performed for 30 minutes, 84.7% of lignin was extracted. A much longer time (2.5 h) was necessary to obtain the same yield with conventional treatment. Lignin obtained by US-assisted treatment showed high purity and no substantial differences in the structure from the native one, although it was found that US increased thermal stability and molecular weight of the recovered lignin.

Earlier research showed that ionic liquids (ILs) could catalyze the destruction of the intricate linkages of lignocellulose to remove lignin. [60] In this context, Zhang et al [61] studied a series of acidic imidazolium based ILs with various anions for corn stover fractionation under US irradiation (400 W) at 70°C for 3h. A yield of 60.48% of isolated lignin was achieved when [HMIM]Cl was used as IL.

In general, it could be noted that US-assisted lignocellulose delignification is more efficient than conventional treatments, exhibiting in many cases higher yields and selectivity of products in shorter times, meanwhile saving energy (Table 2).

Type of Biomass (% w/w)	***US-assisted pretreatment***	***Chemicals***	***Advantages***	***References***
Wheat straw *38.9% cellulose* *38.2% hemicellulose* *17.2% lignin* *2.1% ash* *2.3% wax*	20 kHz, 100 W Immersion horn	Methanol, 0.5M NaOH	US applied for 5 to 35 minutes lead to higher lignin yield (78.5% of the theoretical)	[55]
Wheat straw *38.8% cellulose* *39.5% hemicelluloses* *17.1% lignin* *1.8% ash* *2.2% wax*	20 kHz, 100 W Immersion horn	KOH	Higher lignin yield (49.1% compared to 43% without US)	[56]
Olive tree pruning *32.31% cellulose* *28.52% hemicellulose* *27.60% lignin* *2.80% ash* *3.86% extracts* *4.91% others*	50/60 Hz, 420 W	Acetic acid, NaOH	Higher lignin yield and selectivity. Lower degree of cellulose degradation and higher content of hemicellulose	[54]
Sawdust	50 W longitudinal horn ultrasonic horn ultrasonic bath	Na_2CO_3	Higher lignin yield was obtained with US reactors (87.4%, 85.1% and 82% respectively), compared to conventional method (42.4%)	[58]
Vietnam's rice straw	20 kHz, 500 W	NaOH	US applied for 10 to 40 min led to higher lignin yield (84.7%)	[57]
Corn stover	400W	Imidazolium-based ILs	[HMIM]Cl combined with US catalyzed lignocellulose fractionation under mild reaction conditions (70°C). 60.48% of isolated lignin was obtained after 3 h of reaction.	[61]

Table 2: US advantages in biomass pretreatment

Biomass pretreatments assisted by HC are more advantageous compared to the traditional methods since shorter time, lower energy consumption, and less chemical catalysts are usually required. Moreover, cavitation systems are highly attractive for scaling up and continuous processes thanks to their simple configuration. Recently, HC was used for the pretreatment of different lignocellulosic biomass with promising results; in particular, HC can lead to a higher lignin removal and an increased porosity of the remaining solid, enhancing the enzymatic hydrolysis for sugars production.[62,63] The efficiency of the HC process is strongly related to several key parameters, such as the viscosity of the fluid, the process temperature, particle size, and configuration of the system. In a recent study, sugarcane bagasse was treated by HC at 70 °C for 20 min in a low NaOH concentration (0.3 M) to improve the efficiency of alkaline pretreatment. [63] To perform the experiment, an orifice plate with 27 holes of 1 mm diameter was used. A lignin yield of 60.4% was obtained after 45 min of cavitation (0.48M of NaOH, 4.27% of S/L ratio), while conventional alkaline pretreatment led to 50.3% of lignin removal and US assisted to 59.6%. Moreover almost 93% yield of enzymatic digestibility was obtained under cavitation condition.

In another work, Kim et al. performed a HC-assisted alkaline (3% NaOH) pretreatment of reeds reaching 53.4% of lignin removal and high glucose release (326.5 g/kg of biomass) after enzymatic hydrolysis.[64] A combined process of HC and enzymatic hydrolysis was recently performed as intensification of corncob pretreatment. The optimized reaction conditions (5% of biomass loading, 6.5 U g−1 of enzyme loading) using an orifice plate led to 47,4% of delignification in 60 min, increasing the cellulose recovery from corncob (25.3%). [65] Recently, wheat straw was treated in alkali (KOH) and then subjected to HC using a rotor-stator cavitator to intensify the delignification step of paper manufacturing. [66] Researchers observed that the HC treating for 10–15 min improved the tensile index of the paper sheets up to 50% compared to conventional pretreatment.

Continuous processes are time and energy saving and the operational costs needed are lower compared to batch processes. However, currently, only a few continuous pretreatment methods with potential large-scale applications were reported. In this context, Terán Hilares et al. described a continuous method for the fractionation of sugarcane bagasse (SCB). [67]A suspension of 1% of SCB in alkaline solution (0.3 mol/L of

NaOH, 0.78% of H2O2) was fed into the cavitation reactor at 200 mL/min flow rate (7.5 min as residence time). The released glucose and xylose in the subsequent enzymatic hydrolysis process were, in average, higher (41.7 g/100 and 19.1 g/100 g, respectively), than the ones from SCB pretreated in batch for 90 min (26.88 g/100 g and = 11.97 g/100 g, respectively) and the ones from non-treated SCB (9.32 g/100 g and 2.71 g/100 g respectively).

HC-assisted processes have therefore proven an attractive method for the intensification of pretreatment processes and an advantageous alternative when compared to conventional pretreatment processes as alkaline, steam explosion and organosolv, due to the shorter reaction time, higher efficiency and less amounts of chemicals. In addition, the lower energy requirement makes the scalability of this process easier and economically feasible in a lignocellulosic biorefinery.

3. Lignin Fractionation

Due to its highly complex structure and molecular weight dispersity, an efficient valorization of technical lignin has been found challenging. [68] Thus, preparation of lignin with a more uniform structure is desirable to obtain value-added products. To this end, membrane fractionation has been proposed as one of the best ways to achieve specific molecular weights and distribution.

3.1 Membrane Lignin fractionation

Membrane filtration is a promising technology for the recovery and fractionation of lignin, since it presents a unique combination of economy, scalability, and flexibility in various industrial processes. [69]

Over the last decades, several membrane-based processes for the recovery and concentration of lignin solutions have been carried out, aiming to investigate the ability of membranes to isolate lignin. Due to the widely established process of Kraft pulping, most of the developed methods use black liquor as the raw material for lignin recovery while only a small part use spent sulfite liquor. Membrane processes were initially introduced to treat wastewater and therefore reduce water consumption by recycling clean water. However, last few decades tendency examined the implementation of membrane filtration in lignin separation and fractionation processes to enable its further valorization into phenolic compounds.[70] Membrane fractionation basically

consists in a separation process that employs a semipermeable membrane, which acts as a selective barrier for molecules. In comparison with other traditional processes of separation (evaporation or precipitation), it offers several advantages, such as continuous operation, the avoid of additional agents, lower energy consumption and the possibility of being combined with other techniques. However, some drawbacks could emerge, concerning the permeate flux decline, the lifetime of the membranes, and the low selectivity.[71,72]

Flux decline is one of the greatest challenges during filtration and is difficult to prevent because of the wide molecular weight distribution of the lignin molecules[69,73] The separation by molecular size depends on the material of the membrane (polymeric or ceramic). In particular, ceramic membranes are ideal for lignin recovery and fractionation because of their capability to tolerate extreme pH range and temperature along with their mechanical stability, though their selectivity is lower. [70] Different membrane geometries (flat disc, tubular) and different molecular weight cut-offs (MWCO) have been investigated. Moreover, membrane cleaning strategies have been developed to prevent fouling and re-establish membrane flux after lignin fractionation. A combination of rinsing and regular backflushing was shown to prevent fouling while increasing the average flux.[74] However, it is necessary to consider some aspects before performing a membrane separation process, such as lignin source, the pulping method used to obtain it, and the purpose of the process (e.g., lignin fractionation, carbohydrates separation, lignin concentration, etc.).[75] Moreover, the separation by molecular size also depends on membrane material. Lignin molecular weight is typically within the range of ultrafiltration (UF) technology (1-100 kDa); therefore, the dimensions are different from the other components of liquor enough to perform lignin separation and fractionation by UF membranes, leading to a more uniform lignin structure.[70]

Recently, Eucalyptus Kraft lignin fractionation using ceramic membranes with different MWCO (5, 15, and 50 kDa) was reported. [76] Results showed that ultrafiltration is an efficient process for the treatment of this type of lignin. The obtained fractions were studied, showing that the lignin isolated with a 50 kDa membrane presented the highest molecular weight with higher content of carbohydrates and inorganics. In contrast, from the 5 kDa membrane low Mw lignin with low dispersity value was obtained; this type of lignin represents an important source of phenolic monomers after oxidative depolymerization.

A Bamboo Kraft lignin fractionation was performed by firstly dissolving the material in acetic acid to obtain a low viscosity solution and then fractionating it by UF into specific molecular weight fractions by sequential UF using membranes with different MWCO. [77] The three fractions presented different molecular weights with lower polydispersity compared to the non-treated Kraft lignin. The fraction obtained with a 5 kDa cut-off membrane showed the lowest molecular weight and higher amount of phenolic hydroxyl groups. Authors found that the addition of this low molecular weight lignin fraction into polyethylene provided a positive effect on the mechanical properties of the polymer.

D'Arrigo et al. [78] reported a multistep fractionation process of wheat straw grass lignin, using a mixture of water/ethanol as the solvent, followed by a microfiltration step through a 0.7 μm membrane, aiming to remove insoluble particles. Afterward, two UF operations were performed with a polyether sulfone (PES) membrane with a MWCO of 3 and 1 kDa. The molecular weight of recovered fractions after permeation decreased progressively. In particular, the filtration through a 3 kDa cut-off membrane leads to the recovery of a high molecular weight fraction that could be employed as macromonomer of lignin-based polymer. Furthermore, it allowed the retrieval of a low molecular weight fraction consisted in high value-added chemicals. The same research group performed a two-step organic solvent extraction of wheat straw lignin, followed by two UF steps using cellulose-based membranes (MWCO of 2 and 5 kDa).[79] Lignin stream was obtained by Soxhlet extraction using 2-butanone as the solvent. This step allows the transfer of lignin soluble components to the liquid phase, while separates solid residues. Afterwards, two sequential UFs generated two different lignin fractions with narrow molecular mass distribution.

A recent study compared acid precipitation and solvent fractionation with UF fractionation of Kraft softwood, organosolv hardwood, and grass lignin into low, medium and high molecular weight fractions. [80] Mass yield, structural (molecular weight distribution, elemental composition) and functional (OH-group number) of the obtained fractions were examined. Ceramic tubular membranes with MWCO of 1, 15, 50 and 150 kDa were used in the UF step. In general, authors reported that solvent extraction and acid precipitation provided better separation with better mass distribution, polydispersity, and functional OH-groups distribution.

Among lignin biorefining processes performed under H2-pressure (e.g., reductive catalytic fractionation, RCF), catalytic upstream biorefining (CUB) process employs H-donor as solvent in conjunction with Ni Raney

catalyst aiming to depolymerize lignin. Recently, a two-step membrane fractionation of lignin liquor from CUB process was exploited. [81] Isopropanol (2-PrOH) was employed both as a component of the lignin extracting liquor (2-PrOH/H2O 7:3, v/v) and as the H-donor for the selective hydrodeoxygenation process. The membrane cascade assisted both the concentration of the monophenol-rich fraction and the separation from the liquor. Membrane fractionation offers a suitable technology for lignin components separation from the liquor. Moreover, further chemicals addition in these processes is avoided, making their further utilization highly attractive.

4. Depolymerization of Isolated Lignin

The pretreatment processes aiming to extract lignin often produce lignin polymers which has undergone multiple chemical modifications, resulting in a heterogeneous mixture difficult to analyze. Thus, the key to lignin valorization passes through the selective depolymerization and the recovery of the end-products as individual lignols. In fact, the depolymerization of lignocellulose generates a variety of compounds that can be used as building blocks for valuable chemicals, fuels, polymers, or pharmaceuticals. [3,19] Lignin phenolic units have found, until now, only limited market application: they can be converted into BTX (benzene, toluene and xylene) or oxygenated compounds (e.g., phenols, aromatic alcohols, aldehydes, quinones, etc.) however, they are still overpriced compared to the petrol-derived analogues and the direct production of aromatics from lignin is typically low.[82] As above mentioned, one reason regards repolymerization of the reactive intermediates that is the cause of low aromatic yields.

The development of effective catalyst and new technologies are the keys to the successful conversion of lignin into high-quality products: moreover, bio-oil yield depends on various factors such as particle size, temperature, and reaction catalyst. Among them, heating rate is one of the most critical factors that can affect the composition of bio-oil. [83,84]In fact, higher heating rate (> 100 °C/s) favors the production of bio-oil compounds whereas a low heating rate leads to char formation: with higher heating rate, the rupture of various chemical bonds can occur simultaneously, reducing the production of stable oligomers, which can pave the way to undesirable solid products.

In addition, several processes such as pyrolysis or acid/base hydrolysis are used for the depolymerization of lignin: although the obtained products are prone to chemical instability due to their high oxygen content.

Therefore, oxygen content in aromatic products must be reduced before utilization: in this context reductive conversion of lignin, could be an effective strategy for lignin valorization, since it combines lignin depolymerization and deoxygenation in one process, resulting in more stable aromatics with higher heating value.

Thus, the development of new processes coupled with effective catalytic systems could not only reduce the difficulty in the lignin depolymerization, but also increase product yields improving the economy of the process. Existing technologies for biomass deconstruction and lignin depolymerization have, in fact, limitations related to efficiency and energy consumption. Therefore, process intensification through microwave (MW) technology could represent and advantageous strategy for time and, consequently, energy saving, including fast heating that can reduce undesired side-reactions.

4.1 MW technology

The use of MW has gained increasing interest in the field of biomass valorization in recent years. The interaction of microwaves with the matter results in dielectric heating, as an alternative to the traditional convective heating methods. In fact, the latter are based on superficial heat transfer, which is a rather slow and inefficient way for transferring energy into a reaction mixture. Nevertheless, microwaves exploit the direct interaction between the object and the applied electromagnetic radiation. This generates a homogeneous volumetric (non-superficial) heating.

The first use of MW in organic synthesis leads back to Gedye e Giguère, who noted that MW heating significantly enhanced the reaction rate. [85][86]MW heating also exhibits a positive influence on chemical reactions, enhancing yields and selectivity.[87] [88] Microwaves are electromagnetic radiations with frequencies between 0.3 and 300 GHz. The frequency used in MW reactors is fixed at 2.45 GHz; consequently, the associated energy is too low to break a chemical bond. Therefore, the effects of MW are due to the efficient heating of molecules by two mechanisms: dipole rotation and ionic conduction. [89] The first one describes the tendency of dipoles to constantly align themselves with the MW electric field by rotation, causing friction that generates heat. In ionic conduction mechanism, ionic particles oscillate under the influence of MW electric field, leading to the formation of a current. This current is subjected to internal resistance due to collisions between particles, which generate heat.

There are several types of MW reactors which differ in terms of MW source, cavity design, scale and automation. However, mono-mode and multi-mode are the two categories in which they are classified. Mono-modal reactors are designed in order to create a standing wave, which is directly focused on a single vessel (Figure 9A). Among many advantages, the most important is the high heating rate even though only one vessel can be irradiated, which makes mono-modal reactors ideal for reaction optimization and small-scale applications. In multi-mode reactors, the sample is placed inside a cavity where the waves are reflected, generating a disordered dispersion of radiation, which increases the area of effective heating (Figure 9B). Thus, a multi-mode MW reactor can accommodate a higher number of samples simultaneously, making these tools perfect for the screening of reaction conditions. Moreover, multi-mode MW are usually designed for scaling up reactions, unlike single-mode apparatus. However, heating control of samples is a major limitation of multi-mode apparatus because of temperature uniformity due to the chaos of the waves.

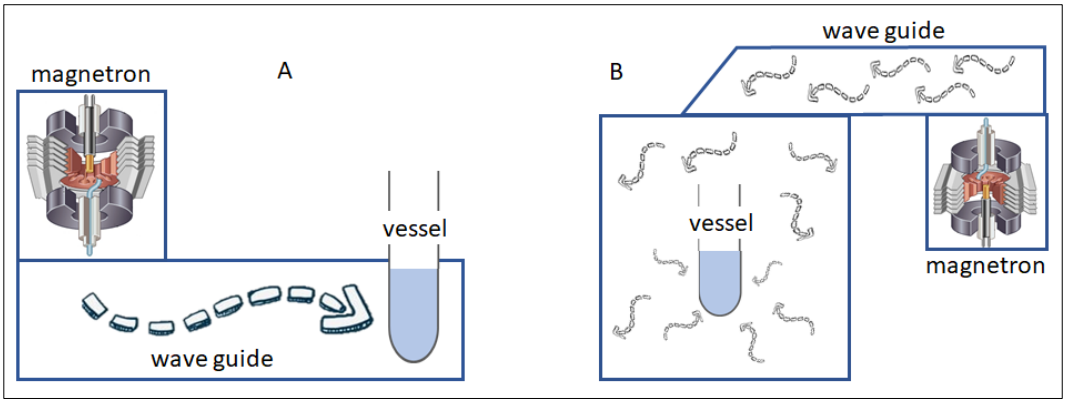


Figure 9: Monomodal (A) and multimodal (B) microwave reactors

Azuma et al.[90] introduced MW for biomass pretreatment before enzymatic hydrolysis for the first time in late 1980s. It was found that MW treatment in the presence of water initiates hemicellulose and lignin degradation, leading to a higher saccharification rate, compared to conventional processes such as steam explosion. A few studies reported the use of MW heating for lignin depolymerization[91,92], documenting a significant decrease in time required for biomass deconstruction. Furthermore, MW promote selective bond cleavage during lignin depolymerization, leading to a narrow molecular weight distribution compared to conventional heating techniques. Probably, this is due to the stretching of certain lignin bonds under the electric field imparted during MW irradiation, that could increase the probability of their breaking.

4.2 MW specific effects

The main advantage of using MW as heating technology relies in the reduction of time reaction. However, the rate-acceleration typically observed in microwave-assisted reactions may in some instances also lead to higher selectivity compared to the conventional heating processes. This is the reason why dielectric heating is claimed to have two different effects: thermal and non-thermal.[88] Thermal effects are those derived from microwave dielectric heating, which may cause different temperature regimes. Non-thermal effects, also called "specific microwave effects", are claimed when a reaction performed under microwave conditions behaves differently from the same reaction performed at the same temperature under conventional heating. For example, changes in reactivity and selectivity could be explained by the direct interaction between microwave radiation and the reaction system.[93,94] However, the existence of non-thermal effects is still a controversial question.[87,93] One of the reasons lies in the fact that the energy emitted from a microwave photon is too low to have any effect in breaking a chemical bond (0.0016 eV). Moreover, the commercially available microwave reactors are not suited to perform reliably study of bulk thermal phenomena associated with rapid heating. Other explanations refer to the experimental errors in temperature measurement. However, many researchers claimed that a direct interaction of the electromagnetic field with specific molecules could explain unexpected results which cannot be a consequence of thermal gradients.[95] Anyway, the rate acceleration can be attributed to thermal effects. In fact, microwave heating profiles are not easily reproducible by conventional techniques. Moreover, it has been demonstrated that heating profile can affect the product formation. [96] In addition, in multi-modal microwave reactors the presence of hot spots could occur, giving rise to local temperatures which are higher than the one measured in the bulk. These local hot spots, which are not accurately measurable, could explain unexpected results in microwave reactions. As a matter of fact, the existence of microwave specific effects appears to be a continuing debating area.

4.3 MW-assisted lignin depolymerization

Over the past few decades, the depolymerization of isolated lignin to aromatics became an attractive approach for lignin valorization into value-added chemicals. However, depolymerization strategies lack in selectivity towards aromatics compounds. Moreover, the cleavage of lignin linkages is still a difficult issue, since most of C-C bonds persist after depolymerization processes.[21] Lignin depolymerization approaches include acid

546 and base hydrolysis, oxidation and hydrogenation. Among these, lignin hydrogenation could selectively cleave
547 ether linkages into phenols partially avoiding repolymerization and self-condensation, leading to higher
548 monomer yield. [97] In recent years, several strategies have been developed that employ molecular hydrogen
549 in heterogeneous catalyzed processes. In particular, hydrogenolysis and hydrocracking provide lignin linkages
550 cleavage by the addition of hydrogen to the reaction mixture.[98] Microwave-assisted technology has been
551 recently proved a successful tool biomass conversion thanks to its fast and highly efficient heating compared
552 to conventional systems.[99]

553 Microwave-assisted lignin depolymerization in several organic solvents, acids and bases has been known to
554 efficiently afford aromatic monomers and oligomers at relatively mild conditions (<200 °C).[100,101]
555 Furthermore, microwaves accelerate lignin model compounds conversion into phenols, simultaneously
556 increasing product selectivity. [99] An important aspect to consider for heterogeneously catalyzed lignin
557 hydrogenation consist in the mass transfer to the catalyst surface of insolubilized lignin and molecular
558 hydrogen. Hydrogen pressure is also a key parameter, as it can lead to undesired products, when it is too high.
559 Nevertheless, for a sustainable approach it is necessary to reduce the consumption of fossil-derived hydrogen
560 which negatively affects the carbon footprint of chemical processes.[102]

561 For these reasons, recent strategies consist in the use of hydrogen-donor systems (e.g., alcohols, formic acid)
562 as the solvent. Formic acid (FA), which is a bulk industrial chemical, is cheaper than any H-donor solvent and
563 safer than molecular hydrogen. At elevated temperature it decomposes into CO2 and H2, even though in some
564 cases it could also go to CO[103]. Besides, it can be derived from renewable resources. Hydrogen donor
565 solvents are not only suitable to transfer hydrogen in the lignin depolymerization process, but they also enhance
566 lignin solubility. For instance, the use of alcohols as H-donor solvents have gained increasing attention in
567 lignin hydrogenation due to the higher lignin solubility, which enhances the contact with the catalyst, and the
568 capability of suppressing repolymerization reactions, which can lead to the undesired bio-char.[104] Therefore,
569 hydrogen donor solvents, coupled with heterogeneous catalysts, could promote the selective cleavage of C-C
570 and ether bonds in lignin.

571 In recent literature, hydrogen donor solvents combined with microwaves have been reported as an efficient
572 tool for the lignin liquefaction under mild reaction conditions, with or without the presence of catalysts [105–

108] Toledano et al. [106] studied the effects of the type of metal catalyst in a microwave-assisted hydrogen-free depolymerization of organosolv lignin. Catalyst screening included different metal nanoparticles: Ni (2, 5, and 10 wt.%), Pd (2 wt.%), Pt (2 wt.%), and Ru (2 wt.%) supported on Al-SBA-15. Depolymerization reactions were conducted in a multimode microwave reaction system with a 400W constant power. Experiments were performed for 30 min at average temperature of 140°C, using formic acid as H-donor. The highest bio-oil yield of 30 wt.% was obtained when Ni10%AlSBA was used as the catalyst, while 5 wt.% of bio-oil yield was obtained when Pd2%Al-SBA was used.

When formic acid was used, bio-char formation was lower as compared to other H-donors. This could be ascribed to the decomposition of formic acid into gases (e.g., CO, CO_2 and H_2) during the lignin depolymerization, whereas different H-donor solvents could react with lignin radical fragments leading to the formation of bio-char. Shen et al.[107] performed lignin depolymerization in formic acid at 130°C and 30 min, using HUSY zeolite as the catalysts. The yield in bio-oil was enhanced in the presence of the catalysts. Moreover, bio-oil yield increased to 88.28 wt% (15.36% of aromatic monomers and 67.52% of oligomer fractions), when HUSY modified by 0.2 mol/L oxalic acid was used.

Reaction time and temperature effects on the phenolic yield compounds from the microwave-assisted acidic solvolysis of black-liquor lignin were also investigated. [107] Depolymerization occurred in a microwave digestor at a reaction temperature of 110–180°C and a reaction time of 5–90 min. Results indicated that the yield of liquid products increased when the reaction temperature was below 160°C and decreased when the reaction time was superior to 30 min. Depolymerization and repolymerization reactions were both enhanced by increasing the temperature and prolonging the reaction time. Hence, the key to obtain high yield of mono-phenolic compounds is to avoid re-condensation reactions.

Vinu et al.[109] investigated the microwave-assisted degradation of lignin in the presence of different organic solvents including ethylene glycol (EG), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) under moderate conditions (100–140 °C, 20–80 min). Molecular weight (Mw) reduction of lignin was observed in all the solvents, and it was found to be highly dependent on the solvent polarity and temperature. Results showed a molecular weight (Mw) reduction at 120°C in polar protic solvents, whereas the reduction of Mw in aprotic polar solvents increased at higher temperatures, showing that the combination of microwave and polar

solvent greatly affected the decrease of Mw. Moreover, in EG, the cleavage of C-O bonds, leading to the formation of guaiacol, was preferred over C-C bond, while in DMSO anisole, guaiacol, syringaldehyde and acetosyringone were obtained by cleavage of both C-O and C-C bonds.

Microwave-assisted lignin hydrogenation using isopropanol was investigated, finding the highest yield of bio-oil (45.35 wt.%) at 120°C with the reaction time of 30 min, together with 38.65% of char as and 14.73% residual lignin.[110] Prolonged times increased the formation of biochar, whereas the bio-oil yield decreased, confirming that protracted reaction time leads to condensation of monomers to oligomers.

Shao et al. [111] proposed the depolymerization of alkaline lignin in methanol/formic acid media. Formic acid acted mainly through acid-catalyzed cleavage of the linkages in lignin. Oligomers in bio-oil were mainly composed of dimers and trimers, according to the MALDI-TOF MS analysis. Different FA/lignin mass ratio, reaction temperature and reaction time were applied, aiming to investigate their effects on product yield and distribution. The highest bio-oil yield of 72.0 wt.%, including 6.7 wt.% monomers, was achieved at 160 °C and a FA/lignin mass ratio of 4 after a reaction time of 30 min. Additionally, the bio-oil yield was compared with the one obtained at the same conditions under conventional heating: 41.1 wt.% yield of bio-oil including 0.89 wt.% of monomers was obtained, indicating that microwave significantly improved bio-oil yield.

Recently, a comparative study on various alcohols in microwave-assisted lignin depolymerization has been carried out. [112]Methanol and ethanol showed higher conversion rate of 84.86% and 84.22%, respectively and lower Mw of liquefied products, when compared with butanol, ethanediol and isopropanol. The reason lies in the fact that the Mw of methanol and ethanol is lower, providing higher permeability and fluidity. In addition, in lignin depolymerization processes, usually alcohols are incorporated into the lignin-derived products within acidic medium; consequently, repolymerization of lignin-degraded products is avoided and the conversion of lignin into low molecular weight liquid products is enhanced.[113] Lignin conversion when butanol was used counted only 49.34%; this could be explained by the increased lengthiness of the carbon chain, which provides more hydrophobic alcohols. Higher hydrophobicity is not beneficial for the conversion of biomass, especially when combined with microwave dielectric heating.

In summary, low molecular alcohols and acids demonstrate to be promising in the microwave-assisted lignin depolymerization processes, both as solvents able to promote solvolysis and as H-donors for reductive depolymerization. Thus, their versatility should be further investigated for effective liquefaction of lignin.

5. Scale-up

In the biorefinery concept the exploitation of biomass-derived feedstocks, such as lignocellulosic materials, is the key for the sustainable production of a plethora of useful compounds which are, until now, derived from petroleum. However, the estimated selling price of the products obtained from renewable sources would not compete with the prices of the ones produced by fossil fuel, since the cost of the feedstock is typically higher. Hence, lowering the price of bio-derived product is the bullet point of biorefinery. [114,115]

In this framework, green technologies such as MW, US and HC have recently showed promising results in the valorization of lignocellulose. However, these methods need to be deeply studied for their techno-economic feasibility at industrial scale. Notable advantages of the above-mentioned techniques lie in the higher selectivity, shorter reaction time and often higher yields, which make these processes highly attractive for industrial scale applications. However, it is also fundamental to consider the economies and profitability of the scaling-up.[28] Usually, the applicability of a new technology at industrial scale requires techno-economical assessments and energy consumption studies (Figure 9).

A necessary preliminary step to efficiently process and transform biomass at industrial scale, involves size reduction, through which biomass can be, first of all, stored and easily managed. Without providing a suitable grinding degree, biomass cannot be efficiently converted: in fact, particle size can affect biomass conversion, since the yield of volatiles decreased with the increasing of biomass dimension. [83]However, grinding is a highly energy consuming process; therefore, it is imperative to find the most suitable parameter conditions in order to increase the efficiency of the process.[115]

US and HC are consolidated technologies for PI, since the high-energy hot spots generated by cavitation strongly promote a faster and more efficient disruption of the lignocellulose matrix, increasing the accessibility for further processing steps with generally shorter reaction times, milder conditions and lower energy consumption. Generally, US systems are less energy efficient than HC reactors: the principal limitation

consists in the low pressure-wave penetration through reaction mixture. Consequently, cavitation only occurs near the transducer. HC reactors have been reported to be a realistic tool for large scale applications and an alternative to acoustic cavitation for the intensification of lignocellulosic processes, since the scaling up is comparatively easier and the only energy consuming device is the one related to the rotor-stator reactor[63,116]. In fact, these systems are simply equipped with a pump, a tank, pipes, valves and a cavitation device (orifice plate or venture tube), while the limitations of using US on large scale consist in a lower power efficiency, higher fabrication costs and lower irradiating surfaces.[116]

Moreover, in HC reactors speed rotation, percentage of biomass and the time of treatment can be easily optimized depending on the types of biomasses. In fact, the selection of an optimal design configuration of the reactor is necessary to improve cavitation and achieve cost-effective operation. Rotor-stator reactors are the most attractive ones to operate in continuous or semi-continuous processes, while orifice plate setup appears to be the most flexible device for higher scale operations, since the intensity of cavitation can be simply monitored, and the consuming energy can be reduced.[117]

The two major processes used in the pulp and paper industry to recover lignin from the spent liquor are the sulfite pulping process and the Kraft process[118]. Both these processes involve lignin solubilization, its separation from the insoluble cellulose and hemicellulose by filtration and the following recovery by precipitation. The major drawback for an improved valorization of lignin at industrial scale consists in the broad molecular weight distributions, which highly affects the reactivity of lignin, suggesting membrane fractionation as a necessary step aiming to obtain lignin with more uniform characteristics, which could lead to more reproducible processes. Furthermore, the separation of lignin from the black liquor in the pulp mill process is relatively easy: suitable membrane cut-offs allow an efficient control of the molecular mass distribution, with no need of pH modification or temperature variation, ensuring low energy requirements and higher product value. [119] Generally, membrane filtration is used in pulp mills to recover the spent pulping liquor in order to burn it and use it as external fuel. Thus, to overcome this strategy and valorize lignin at industrial scale, alternative methods are required. Spent liquor composition varies depending on the type of wood and process performed and usually consists of 60 % lignin, 30 % sugars and 10 % inorganic materials.[120]

Membrane filtration could be then used to separate the liquor into more purified lignin fractions, which are commercially more valuable and could be used in several applications: (as dispersing agent, precipitates, binders and adhesives). For example, vanillin synthesis from guaiacol accounts for 85% of the world stream, while only the 15% is produced from lignin recovered by membrane filtration from spent sulphite liquor at Borregaard Industries, in Norway.[118] Hence, low costs and high energy-efficiency of membrane separation process are fundamental requisites which can define whether concentration and fractionation could be economically feasible; for instance, a comparison between lignin precipitation and ultrafiltration showed that the first one is cheaper; however, the removal of high molecular-weight lignin by ultrafiltration was found to be feasible and economically attractive in a simulation study. [119]

An ongoing challenge is related to membrane fouling and the related flux decline caused by deposition of particles, macromolecules, salts, and others; therefore, it is highly difficult to prevent. Moreover, the necessity of frequently cleaning membrane plates is the principal cause of the increasing costs.

Recently, US-assisted filtration has shown to be an effective tool for fouling control by accelerating the permeate flux towards membranes, removing particles in the pores and on the surface thanks to the action of cavitation, increasing the overall filtration performance. [121–123] However, a critical issue concerns membrane damage due to the intense cavitation, thus US intensity should be chosen aiming to both minimize energy consumption and potential membrane damage. Moreover, the economic value and industrial application feasibility are challenges that must be still addressed: in fact, US energy requirements could be in contrast with the applicability at industrial scale. However, at present, there are no studies on the viability of US-assisted membrane cleaning and its effective application at large-scale membrane processes. In general, the fractionation capability with low chemicals loadings and low energy consumption, make membrane separation an excellent tool in the biorefinery process and an economically feasible process at industrial scale.[76]

Concerning MW technology, time saving, and product selectivity are the principal advantages, together with the relatively simple equipment and the easiness to control reaction parameters. Therefore, these aspects can significantly reduce the cost of final products making large-scale production feasible.[99,114] Furthermore, the fast-heating rate and the rapid cooling, by turning off MW, can reduce the formation of char in lignin

depolymerization. In addition, to achieve optimal lignin conversion, depolymerization strategies require low temperature aiming to avoid condensation of lignin intermediates. Thus, new generation of MW devices provide more reproducible experiments thanks to the possibility to better control reaction parameters.[124] Therefore, process intensification based on MW heating, together with the developing of pilot scale continuous apparatus, is gaining increasing interest.[125,126]

However, even if it is recognized that MW provide better quality of bio-products in shorter time, MW processes at industrial scale are not common. In fact, the implementation costs for MW apparatus are still elevated since this technology is in its early stages. Moreover, the energy efficiency of MW-assisted reactions should be considered case-by-case; it has been demonstrated that processes performed with laboratory scale MW reactors are typically energy inefficient. Nevertheless, when moving from lab scale to kilogram scale and from single mode to multimode reactors, MW heating processes become, in general, more energy efficient than the conventional ones.[127] Bermúdez et al. found that the energy consumed per gram of sample is dependent on the amount of sample used: consumption decreases when moving from few grams to 50-100 g. Moreover, when moving to kilograms scale, the energy consumption is almost constant, indicating that when a MW apparatus is not used at its maximum loading capacity, there will be a significant waste of energy. [127] In-depth studies on the techno-economic feasibility at industrial scale of enabling technologies have not been performed in detail yet. The reason lies in the fact that a limited number of scientific studies has been conducted at large scale up to date. Moreover, pilot scale processes are usually performed on modified laboratory apparatuses, thus, there is still a large gap between laboratory research and industrial applicability. However, enabling technologies have widely demonstrated to be highly attractive and potentially feasible for process intensification of biomass. Nevertheless, there is still the necessity for a multidisciplinary approach for the implementation of new technologies at industrial scale.

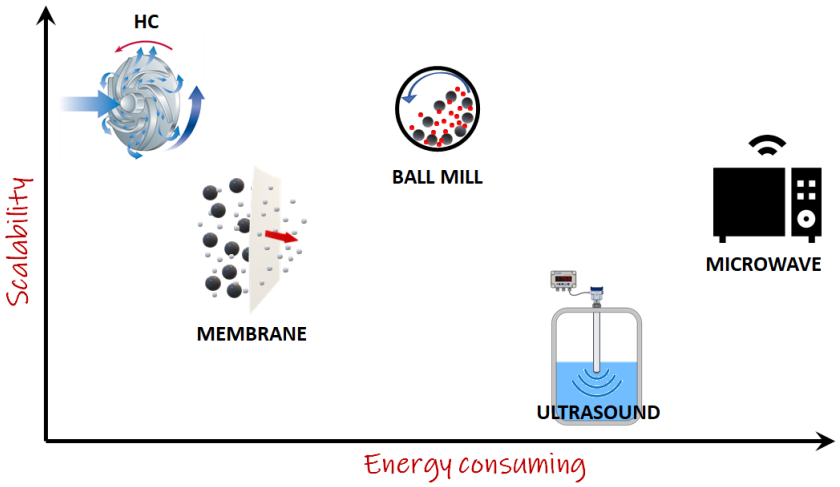


Figure 10: Comparison of enabling technologies in terms of scalability and energy consumption.

6. Future perspectives

The development of systems that can convert lignin into valuable products should be the goal of future research efforts for a sustainable lignin reductive process and its feasibility at industrial scale: efforts should include higher conversion with high product yield and selectivity, recyclability of solvent and catalysts and facile product isolation.

Therefore, the valorization of lignin into high-added value products requires the implementation of new enabling systems. A crucial step in the process concerns the study of dimeric model compounds: C-O-C linkages in fact constitute a significant fraction in lignin, thus, future studies should take into account the conversion of more suited model compounds and preferably real lignin substrates.[128] It is known that the major drawback in lignin depolymerization consist in C–C bonds formation during the reaction process, therefore, extensive research has been made on the cleavage of C–C linkage dimers to improve the effective depolymerization of condensed lignin such as Kraft lignin. [129]Hence, aside from studying the conversion of β-O-4 model compounds, future research should point fractionation strategies that prevent lignin re-condensation.

In this context, reductive catalytic fractionation (RFC) has gained increasing attention, since lignin isolation and depolymerization are simultaneous processes, resulting in less side reactions that can led to char formation as solid by-product.[130] Another strategy to avoid C-C bonds formation concerns the use of

stabilizing agent in the reaction media. It is known that, with respect to oxidative depolymerization, hydrogen plays an important role in stabilizing reactive intermediates, acting as radical scavenger. Recently, aldehydes were studied as protecting group to stabilize lignin's a,g-diol group during extraction process, in order to prevent condensation reactions, resulting in higher aromatics yields. In fact, in aldehyde-stabilized lignins, the β-O-4 bonds are almost completely preserved as acetal structures, thus the subsequent hydrogenolysis gives lignin monomers at near-theoretical yields.[131]

Hence, future attention must be paid to lignin extraction process aiming to obtain isolated lignins with low degrees of structure modifications. In this framework, enabling technologies coupled with recent strategies in depolymerization processes could be a winning approach for biomass valorization.

CONCLUSION

In order to improve the sustainability and efficiency of wood-based biorefineries, lignin valorization strategies should be considered and implemented, since the capital investment strongly depends on integrated processes of biomass fractions upgrading (cellulose, hemicellulose and lignin).

Several problems are related to valorization of lignin concerning mainly its recovery from product stream with high purity, the preserving of native structure, since structure modification can alter its reactivity. Although there are various methods to overcome these problems, they are usually only partial solutions since heterogeneous structure and unique reactivity limit their use at industrial level. Existing methods can only partially solve these problems. Though, promising approaches are emerging which could allow lignin valorization into molecules for specific applications.

In lignin valorization protocols, the most important aspect to consider should be the treatment cost. In fact, up to now, the knowledge about lignin structure has paved the way for new sustainable green routes to produce bioenergy and value-added chemicals, aiming to overcome the disadvantage of conventional reactors. Furthermore, the limitations in achieving high product selectivity are the major bottleneck in lignin valorization.

Over the last decades, enabling technologies such as US, HC, MW and milling have demonstrated to lead to better results both in biomass pretreatment and in lignin depolymerization, thanks to the optimal mass and heat

772 transfer, which allow the enhancement of biomass exploitation, reducing time reaction and energy
773 consumption. However, the efficiency of new technologies is prone to be opposed to energy cost requirements.
774 Therefore, a comprehensive understanding on the techno-economic aspects of unconventional technologies is
775 crucial to an optimal design of scaling up procedures, aiming to a full industrialization.

776 In conclusion, process intensification through the development of milder and greener processes for biomass
777 fractionation and lignin depolymerization should be rapidly implemented in biorefineries context, to make
778 them a promising alternative to traditional oil refineries.

779

780 [1] S.S. Hassan, G.A. Williams, A.K. Jaiswal, Moving towards the second generation of lignocellulosic
781 biorefineries in the EU: Drivers, challenges, and opportunities, Renewable and Sustainable Energy
782 Reviews. 101 (2019) 590–599. https://doi.org/10.1016/j.rser.2018.11.041.

783 [2] A. Kumar, J. Singh, C. Baskar, S. Ramakrishna, Bioenergy: Biofuels process technology, in: Advances
784 in Bioprocess Technology, Springer International Publishing, 2015: pp. 165–207.
785 https://doi.org/10.1007/978-3-319-17915-5_10.

786 [3] V. Menon, M. Rao, Trends in bioconversion of lignocellulose: Biofuels, platform chemicals &
787 biorefinery concept, Progress in Energy and Combustion Science. 38 (2012) 522–550.
788 https://doi.org/10.1016/j.pecs.2012.02.002.

789 [4] E.F. Alves, S.K. Bose, R.C. Francis, J.L. Colodette, M. Iakovlev, A. van Heiningen, Carbohydrate
790 composition of eucalyptus, bagasse and bamboo by a combination of methods, Carbohydrate
791 Polymers. 82 (2010) 1097–1101. https://doi.org/10.1016/j.carbpol.2010.06.038.

792 [5] N. MOSIER, Features of promising technologies for pretreatment of lignocellulosic biomass,
793 Bioresource Technology. 96 (2005) 673–686. https://doi.org/10.1016/j.biortech.2004.06.025.

794 [6] C.J. Huntley, K.D. Crews, M.L. Curry, Chemical functionalization and characterization of cellulose
795 extracted from wheat straw using acid hydrolysis methodologies, International Journal of Polymer
796 Science. 2015 (2015). https://doi.org/10.1155/2015/293981.

797 [7] S. Karthyani, A. Pandey, L.P. Devendra, Delignification of cotton stalks using sodium cumene
798 sulfonate for bioethanol production, Biofuels. 11 (2020) 431–440.
799 https://doi.org/10.1080/17597269.2017.1370884.

800 [8] H. Pereira, Variability in the chemical composition of plantation eucalyptus, Wood Fiber Sci. 20
801 (1988) 82–90.

[9] S. Prasad, A. Singh, H.C. Joshi, Ethanol as an alternative fuel from agricultural, industrial and urban residues, Resources, Conservation and Recycling. 50 (2007) 1–39. https://doi.org/10.1016/j.resconrec.2006.05.007.

[10] D. Stewarta, A. Azzinib, A.T. Hall, I.M. Morrisona, Sisal fibres and their constituent non-cellulosic polymers, 1997.

[11] R. Torget, T.-A. Hsu, Two-Temperature Dilute-Acid Prehydrolysis of Hardwood Xylan Using a Percolation Process, 1994.

[12] C. Cara, E. Ruiz, J.M. Oliva, F. Sáez, E. Castro, Conversion of olive tree biomass into fermentable sugars by dilute acid pretreatment and enzymatic saccharification, Bioresource Technology. 99 (2008) 1869–1876. https://doi.org/10.1016/j.biortech.2007.03.037.

[13] R.M. Rowell, T.P. Schultz, R. Narayan, Emerging Technologies for Materials and Chemicals from Biomass, n.d. https://pubs.acs.org/sharingguidelines.

[14] M. Sinner, J. Puls, H. Dietrichs, Carbohydrate Composition of nut shells and some other agricultural residues, Starch . 31 (1979) 276–279. https://doi.org/https://doi.org/10.1002/star.19790310807.

[15] L.R. Lynd, Overview and evaluation of fuel ethanol from cellulosic biomass: Technology, Economics, the Environment, and Policy, Annual Reviews LYNDDUN.TXT AR016-15 Annu. Rev. Energy Environ. 9 (1996) 403–65. www.annualreviews.org.

[16] J.P.M. Sanders, J.H. Clark, G.J. Harmsen, H.J. Heeres, J.J. Heijnen, S.R.A. Kersten, W.P.M. van Swaaij, J.A. Moulijn, Process intensification in the future production of base chemicals from biomass, Chemical Engineering and Processing: Process Intensification. 51 (2012) 117–136. https://doi.org/10.1016/j.cep.2011.08.007.

[17] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, Chemical Reviews. 110 (2010) 3552–3599. https://doi.org/10.1021/cr900354u.

826 [18] B.M. Upton, A.M. Kasko, Strategies for the conversion of lignin to high-value polymeric materials:
827 Review and perspective, Chemical Reviews. 116 (2016) 2275–2306.
828 https://doi.org/10.1021/acs.chemrev.5b00345.

829 [19] W. Schutyser, T. Renders, S. van den Bosch, S.F. Koelewijn, G.T. Beckham, B.F. Sels, Chemicals from
830 lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading, Chemical
831 Society Reviews. 47 (2018) 852–908. https://doi.org/10.1039/c7cs00566k.

832 [20] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, in:
833 Industrial Crops and Products, 2004: pp. 131–141. https://doi.org/10.1016/j.indcrop.2004.04.016.

834 [21] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Liquid fuels, hydrogen and chemicals from lignin: A
835 critical review, Renewable and Sustainable Energy Reviews. 21 (2013) 506–523.
836 https://doi.org/10.1016/j.rser.2012.12.022.

837 [22] S. Chu, A. v. Subrahmanyam, G.W. Huber, The pyrolysis chemistry of a β-O-4 type oligomeric lignin
838 model compound, Green Chemistry. 15 (2013) 125–136. https://doi.org/10.1039/c2gc36332a.

839 [23] J. Lu, M. Wang, X. Zhang, A. Heyden, F. Wang, β-O-4 Bond Cleavage Mechanism for Lignin Model
840 Compounds over Pd Catalysts Identified by Combination of First-Principles Calculations and
841 Experiments, ACS Catalysis. 6 (2016) 5589–5598. https://doi.org/10.1021/acscatal.6b00502.

842 [24] M. Zhou, J. Xu, J. Jiang, B.K. Sharma, A Review of Microwave Assisted Liquefaction of Lignin in
843 Hydrogen Donor Solvents: Effect of Solvents and Catalysts, Energies. 11 (2018).
844 https://doi.org/10.3390/en11112877.

845 [25] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Liquid fuels, hydrogen and chemicals from lignin: A
846 critical review, Renewable and Sustainable Energy Reviews. 21 (2013) 506–523.
847 https://doi.org/10.1016/j.rser.2012.12.022.

848 [26] T. Li, S. Takkellapati, The current and emerging sources of technical lignins and their applications,
849 Biofuels, Bioproducts and Biorefining. 12 (2018) 756–787. https://doi.org/10.1002/bbb.1913.

[27] A. Barakat, H. de Vries, X. Rouau, Dry fractionation process as an important step in current and future lignocellulose biorefineries: A review, Bioresource Technology. 134 (2013) 362–373. https://doi.org/10.1016/j.biortech.2013.01.169.

[28] H. Wang, Y. Pu, A. Ragauskas, B. Yang, From lignin to valuable products–strategies, challenges, and prospects, Bioresource Technology. 271 (2019) 449–461. https://doi.org/10.1016/j.biortech.2018.09.072.

[29] Y. Zheng, J. Zhao, F. Xu, Y. Li, Pretreatment of lignocellulosic biomass for enhanced biogas production, Progress in Energy and Combustion Science. 42 (2014) 35–53. https://doi.org/10.1016/j.pecs.2014.01.001.

[30] A.K. Kumar, S. Sharma, Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review, Bioresources and Bioprocessing. 4 (2017). https://doi.org/10.1186/s40643-017-0137-9.

[31] P.N. Patil, P.R. Gogate, L. Csoka, A. Dregelyi-Kiss, M. Horvath, Intensification of biogas production using pretreatment based on hydrodynamic cavitation, Ultrasonics Sonochemistry. 30 (2016) 79–86. https://doi.org/10.1016/j.ultsonch.2015.11.009.

[32] M. Jędrzejczyk, E. Soszka, M. Czapnik, A.M. Ruppert, J. Grams, Physical and chemical pretreatment of lignocellulosic biomass, in: Second and Third Generation of Feedstocks: The Evolution of Biofuels, Elsevier, 2019: pp. 143–196. https://doi.org/10.1016/B978-0-12-815162-4.00006-9.

[33] B.C. Vidal, B.S. Dien, K.C. Ting, V. Singh, Influence of feedstock particle size on lignocellulose conversion - A review, Applied Biochemistry and Biotechnology. 164 (2011) 1405–1421. https://doi.org/10.1007/s12010-011-9221-3.

[34] L. Kratky, T. Jirout, Biomass Size Reduction Machines for Enhancing Biogas Production, Chemical Engineering and Technology. 34 (2011) 391–399. https://doi.org/10.1002/ceat.201000357.

873 [35] A. Björkman, Isolation of Lignin from Finely Divided Wood with Neutral Solvents, Nature. 174 (1954)
874 1057–1058. https://doi.org/DOI https://doi.org/10.1038/1741057a0.

875 [36] H. Kim, J. Ralph, Solution-state 2D NMR of ball-milled plant cell wall gels in DMSO-d 6/pyridine-d5,
876 Organic and Biomolecular Chemistry. 8 (2010) 576–591. https://doi.org/10.1039/b916070a.

877 [37] A. Fujimoto, Y. Matsumoto, H.M. Chang, G. Meshitsuka, Quantitative evaluation of milling effects on
878 lignin structure during the isolation process of milled wood lignin, Journal of Wood Science. 51
879 (2005) 89–91. https://doi.org/10.1007/s10086-004-0682-7.

880 [38] T. Ikeda, K. Holtman, J.F. Kadla, H.M. Chang, H. Jameel, Studies on the effect of ball milling on lignin
881 structure using a modified DFRC method, Journal of Agricultural and Food Chemistry. 50 (2002) 129–
882 135. https://doi.org/10.1021/jf010870f.

883 [39] C. Yang, X. Yuan, X. Wang, K. Wu, Y. Liu, C. Liu, H. Lu, B. Liang, Ball milling promoted direct
884 liquefaction of lignocellulosic biomass in supercritical ethanol, Frontiers of Chemical Science and
885 Engineering. 14 (2020) 605–613. https://doi.org/10.1007/s11705-019-1841-0.

886 [40] Z. Shi, Y. Liu, H. Xu, Q. Yang, C. Xiong, S. Kuga, Y. Matsumoto, Facile dissolution of wood pulp in
887 aqueous NaOH/urea solution by ball milling pretreatment, Industrial Crops and Products. 118 (2018)
888 48–52. https://doi.org/10.1016/j.indcrop.2018.03.035.

889 [41] M. Yoshida, Y. Liu, S. Uchida, K. Kawarada, Y. Ukagami, H. Ichinose, S. Kaneko, K. Fukuda, Effects of
890 cellulose crystallinity, hemicellulose, and lignin on the enzymatic hydrolysis of Miscanthus sinensis
891 to monosaccharides, Bioscience, Biotechnology and Biochemistry. 72 (2008) 805–810.
892 https://doi.org/10.1271/bbb.70689.

893 [42] K.S. Suslick, The Chemical Effects of Ultrasound, 260 (1989) 80–87.
894 https://doi.org/10.2307/24987145.

895 [43] M. Ashokkumar, T. Mason, Sonochemistry, Kirk-Othmer Encylcopedia of Chemical Technology, John
896 Wiley and Sons,. (2007).

[44] M. Ashokkumar, The characterization of acoustic cavitation bubbles - An overview, in: Ultrasonics Sonochemistry, Elsevier B.V., 2011: pp. 864–872. https://doi.org/10.1016/j.ultsonch.2010.11.016.

[45] M. Ashokkumar, J. Lee, S. Kentish, F. Grieser, Bubbles in an acoustic field: An overview, Ultrasonics Sonochemistry. 14 (2007) 470–475. https://doi.org/10.1016/j.ultsonch.2006.09.016.

[46] K.S. Suslick, D.A. Hammerton, R.E.Jr. Cline, The Sonochemical Hot Spots, J. Am. Chem. Soc. 108 (1986) 5641–5642.

[47] M.J. Madison, G. Coward-Kelly, C. Liang, M.N. Karim, M. Falls, M.T. Holtzapple, Mechanical pretreatment of biomass – Part I: Acoustic and hydrodynamic cavitation, Biomass and Bioenergy. 98 (2017) 135–141. https://doi.org/10.1016/j.biombioe.2017.01.007.

[48] P.R. Gogate, Cavitational reactors for process intensification of chemical processing applications: A critical review, Chemical Engineering and Processing: Process Intensification. 47 (2008) 515–527. https://doi.org/10.1016/j.cep.2007.09.014.

[49] P.R. Gogate, A.B. Pandit, Hydrodynamic cavitation reactors: a state of the art review, Reviews in Chemical Engineering. 17 (2001). https://doi.org/https://doi.org/10.1515/REVCE.2001.17.1.1.

[50] P.R. Gogate, I.Z. Shirgaonkar, M. Sivakumar, P. Senthilkumar, N.P. Vichare, A.B. Pandit, Cavitation Reactors: Efficiency Assessment Using a Model Reaction, n.d.

[51] P. Thanekar, P. Gogate, Application of hydrodynamic cavitation reactors for treatment of wastewater containing organic pollutants: Intensification using hybrid approaches, Fluids. 3 (2018). https://doi.org/10.3390/fluids3040098.

[52] M.J. Bussemaker, D. Zhang, Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications, Industrial and Engineering Chemistry Research. 52 (2013) 3563–3580. https://doi.org/10.1021/ie3022785.

[53] A. Iskalieva, B.M. Yimmou, P.R. Gogate, M. Horvath, P.G. Horvath, L. Csoka, Cavitation assisted delignification of wheat straw: A review, Ultrasonics Sonochemistry. 19 (2012) 984–993. https://doi.org/10.1016/j.ultsonch.2012.02.007.

[54] A. García, M.G. Alriols, R. Llano-Ponte, J. Labidi, Ultrasound-assisted fractionation of the lignocellulosic material, Bioresource Technology. 102 (2011) 6326–6330. https://doi.org/10.1016/j.biortech.2011.02.045.

[55] R. Sun, X.F. Sun, X.P. Xu, Effect of ultrasound on the physicochemical properties of organosolv lignins from wheat straw, Journal of Applied Polymer Science. 84 (2002) 2512–2522. https://doi.org/10.1002/app.10670.

[56] R. Sun, J. Tomkinson, Comparative study of lignins isolated by alkali and ultrasound-assisted alkali extractions from wheat straw, n.d. www.elsevier.com/locate/ultsonch.

[57] M.J. Bussemaker, F. Xu, D. Zhang, Manipulation of ultrasonic effects on lignocellulose by varying the frequency, particle size, loading and stirring, Bioresource Technology. 148 (2013) 15–23. https://doi.org/10.1016/j.biortech.2013.08.106.

[58] S. Devadasu, S.M. Joshi, P.R. Gogate, S.H. Sonawane, S. Suranani, Intensification of delignification of Tectona grandis saw dust as sustainable biomass using acoustic cavitational devices, Ultrasonics Sonochemistry. 63 (2020). https://doi.org/10.1016/j.ultsonch.2019.104914.

[59] N. Dinh Vu, H. Thi Tran, N.D. Bui, C. Duc Vu, H. Viet Nguyen, Lignin and Cellulose Extraction from Vietnam's Rice Straw Using Ultrasound-Assisted Alkaline Treatment Method, International Journal of Polymer Science. 2017 (2017). https://doi.org/10.1155/2017/1063695.

[60] S.H. Lee, T. v. Doherty, R.J. Linhardt, J.S. Dordick, Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis, Biotechnology and Bioengineering. 102 (2009) 1368–1376. https://doi.org/10.1002/bit.22179.

[61] P. Zhang, S.J. Dong, H.H. Ma, B.X. Zhang, Y.F. Wang, X.M. Hu, Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids, Industrial Crops and Products. 76 (2015) 688–696. https://doi.org/10.1016/j.indcrop.2015.07.037.

[62] F.A.F. Antunes, A.K. Chandel, R. Terán-Hilares, A.P. Ingle, M. Rai, T.S. dos Santos Milessi, S.S. da Silva, J.C. dos Santos, Overcoming challenges in lignocellulosic biomass pretreatment for second-generation (2G) sugar production: emerging role of nano, biotechnological and promising approaches, 3 Biotech. 9 (2019). https://doi.org/10.1007/s13205-019-1761-1.

[63] R. Terán Hilares, L. Ramos, S.S. da Silva, G. Dragone, S.I. Mussatto, J.C. dos Santos, Hydrodynamic cavitation as a strategy to enhance the efficiency of lignocellulosic biomass pretreatment, Critical Reviews in Biotechnology. 38 (2018) 483–493. https://doi.org/10.1080/07388551.2017.1369932.

[64] I. Kim, I. Lee, S.H. Jeon, T. Hwang, J.I. Han, Hydrodynamic cavitation as a novel pretreatment approach for bioethanol production from reed, Bioresource Technology. 192 (2015) 335–339. https://doi.org/10.1016/j.biortech.2015.05.038.

[65] K. Thangavelu, R. Desikan, O.P. Taran, S. Uthandi, Delignification of corncob via combined hydrodynamic cavitation and enzymatic pretreatment: Process optimization by response surface methodology, Biotechnology for Biofuels. 11 (2018). https://doi.org/10.1186/s13068-018-1204-y.

[66] M.P. Badve, P.R. Gogate, A.B. Pandit, L. Csoka, Hydrodynamic cavitation as a novel approach for delignification of wheat straw for paper manufacturing, Ultrasonics Sonochemistry. 21 (2014) 162–168. https://doi.org/10.1016/j.ultsonch.2013.07.006.

[67] R. Terán Hilares, R.M. Dionízio, C.A. Prado, M.A. Ahmed, S.S. da Silva, J.C. Santos, Pretreatment of sugarcane bagasse using hydrodynamic cavitation technology: Semi-continuous and continuous process, Bioresource Technology. 290 (2019). https://doi.org/10.1016/j.biortech.2019.121777.

[68] H. Sadeghifar, A. Ragauskas, Perspective on Technical Lignin Fractionation, ACS Sustainable Chemistry & Engineering. (2020) acssuschemeng.0c01348. https://doi.org/10.1021/acssuschemeng.0c01348.

967 [69] D. Humpert, M. Ebrahimi, P. Czermak, Membrane technology for the recovery of lignin: A review,
968 Membranes. 6 (2016). https://doi.org/10.3390/membranes6030042.

969 [70] J. Fernández-Rodríguez, X. Erdocia, F. Hernández-Ramos, M.G. Alriols, J. Labid, Lignin separation and
970 fractionation by ultrafiltration, in: Separation of Functional Molecules in Food by Membrane
971 Technology, Elsevier, 2018: pp. 229–265. https://doi.org/10.1016/B978-0-12-815056-6.00007-3.

972 [71] A. Toledano, A. García, I. Mondragon, J. Labidi, Lignin separation and fractionation by ultrafiltration,
973 Separation and Purification Technology. 71 (2010) 38–43.
974 https://doi.org/10.1016/j.seppur.2009.10.024.

975 [72] A.S. Jönsson, A.K. Nordin, O. Wallberg, Concentration and purification of lignin in hardwood kraft
976 pulping liquor by ultrafiltration and nanofiltration, Chemical Engineering Research and Design. 86
977 (2008) 1271–1280. https://doi.org/10.1016/j.cherd.2008.06.003.

978 [73] H. Pakkanen, R. Alén, Molecular mass distribution of lignin from the alkaline pulping of hardwood,
979 softwood, and wheat straw, Journal of Wood Chemistry and Technology. 32 (2012) 279–293.
980 https://doi.org/10.1080/02773813.2012.659321.

981 [74] M. Ebrahimi, N. Busse, S. Kerker, O. Schmitz, M. Hilpert, P. Czermak, Treatment of the bleaching
982 effluent from sulfite pulp production by ceramic membrane filtration, Membranes. 6 (2015) 1–15.
983 https://doi.org/10.3390/membranes6010007.

984 [75] A.S. Jönsson, Membranes for lignin and hemicellulose recovery in pulp mills, in: Membrane
985 Technologies for Biorefining, Elsevier Inc., 2016: pp. 105–133. https://doi.org/10.1016/B978-0-08-
986 100451-7.00005-0.

987 [76] C.A.E. Costa, P.C.R. Pinto, A.E. Rodrigues, Lignin fractionation from E. Globulus kraft liquor by
988 ultrafiltration in a three stage membrane sequence, Separation and Purification Technology. 192
989 (2018) 140–151. https://doi.org/10.1016/j.seppur.2017.09.066.

990 [77] C. Huang, J. He, R. Narron, Y. Wang, Q. Yong, Characterization of Kraft Lignin Fractions Obtained by
991 Sequential Ultrafiltration and Their Potential Application as a Biobased Component in Blends with
992 Polyethylene, ACS Sustainable Chemistry and Engineering. 5 (2017) 11770–11779.
993 https://doi.org/10.1021/acssuschemeng.7b03415.

994 [78] C. Allegretti, S. Fontanay, Y. Krauke, M. Luebbert, A. Strini, J. Troquet, S. Turri, G. Griffini, P. D'Arrigo,
995 Fractionation of Soda Pulp Lignin in Aqueous Solvent through Membrane-Assisted Ultrafiltration,
996 ACS Sustainable Chemistry and Engineering. 6 (2018) 9056–9064.
997 https://doi.org/10.1021/acssuschemeng.8b01410.

998 [79] C. Allegretti, S. Fontanay, K. Rischka, A. Strini, J. Troquet, S. Turri, G. Griffini, P. D'Arrigo, Two-step
999 fractionation of a model technical lignin by combined organic solvent extraction and membrane
1000 ultrafiltration, ACS Omega. 4 (2019) 4615–4626. https://doi.org/10.1021/acsomega.8b02851.

1001 [80] V. Rohde, S. Böringer, B. Tübke, C. Adam, N. Dahmen, D. Schmiedl, Fractionation of three different
1002 lignins by thermal separation techniques—A comparative study, GCB Bioenergy. 11 (2019) 206–217.
1003 https://doi.org/10.1111/gcbb.12546.

1004 [81] Z. Sultan, I. Graça, Y. Li, S. Lima, L.G. Peeva, D. Kim, M.A. Ebrahim, R. Rinaldi, A.G. Livingston,
1005 Membrane Fractionation of Liquors from Lignin-First Biorefining, ChemSusChem. 12 (2019) 1203–
1006 1212. https://doi.org/10.1002/cssc.201802747.

1007 [82] S.S. Wong, R. Shu, J. Zhang, H. Liu, N. Yan, Downstream processing of lignin derived feedstock into
1008 end products, Chemical Society Reviews. 49 (2020) 5510–5560.
1009 https://doi.org/10.1039/d0cs00134a.

1010 [83] F.X. Collard, J. Blin, A review on pyrolysis of biomass constituents: Mechanisms and composition of
1011 the products obtained from the conversion of cellulose, hemicelluloses and lignin, Renewable and
1012 Sustainable Energy Reviews. 38 (2014) 594–608. https://doi.org/10.1016/j.rser.2014.06.013.

1013 [84] L. Fan, Y. Zhang, S. Liu, N. Zhou, P. Chen, Y. Cheng, M. Addy, Q. Lu, M.M. Omar, Y. Liu, Y. Wang, L.
1014 Dai, E. Anderson, P. Peng, H. Lei, R. Ruan, Bio-oil from fast pyrolysis of lignin: Effects of process and

upgrading parameters, Bioresource Technology. 241 (2017) 1118–1126. https://doi.org/10.1016/j.biortech.2017.05.129.

[85] R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, The use of microwave ovens for rapid organic synthesis, Tetrahedron Letters. 27 (1986) 279–282.

[86] R.J. Giguere, T.L. Bray, S.M. Duncan, G. Majctich, Application of commercial microwave ovens to organic synthesis, Tetrahedron Letters. 27 (1986) 4945–4948. https://doi.org/https://doi.org/10.1016/S0040-4039(00)85103-5.

[87] C.O. Kappe, Controlled microwave heating in modern organic synthesis, Angewandte Chemie - International Edition. 43 (2004) 6250–6284. https://doi.org/10.1002/anie.200400655.

[88] A. de La Hoz, Á. Díaz-Ortiz, A. Moreno, Microwaves in organic synthesis. Thermal and non-thermal microwave effects, Chemical Society Reviews. 34 (2005) 164–178. https://doi.org/10.1039/b411438h.

[89] C. Gabriel, S. Gabriel, E.H. Grant, B.S.J. Halstead, D. Michael, P. Mingos, Dielectric parameters relevant to microwave dielectric heating, 1998.

[90] J. Azuma, F. Tanaka, T. Koshijima, Microwave irradiation of lignocellulosic materials I. Enzymatic susceptibility of microwave-irradiated woody plants, Mokuzai Gakkaishi. 30 (1984) 501–509.

[91] L. Shao, Q. Zhang, T. You, X. Zhang, F. Xu, Microwave-assisted efficient depolymerization of alkaline lignin in methanol/formic acid media, Bioresource Technology. 264 (2018) 238–243. https://doi.org/10.1016/j.biortech.2018.05.083.

[92] P.D. Muley, J.K. Mobley, X. Tong, B. Novak, J. Stevens, D. Moldovan, J. Shi, D. Boldor, Rapid microwave-assisted biomass delignification and lignin depolymerization in deep eutectic solvents, Energy Conversion and Management. 196 (2019) 1080–1088. https://doi.org/10.1016/j.enconman.2019.06.070.

[93] P. Lidström, J. Tierney, B. Wathey, J. Westman, Microwave assisted organic synthesis: a review, (n.d.).

[94] E.C. Gaudino, G. Cravotto, M. Manzoli, S. Tabasso, From waste biomass to chemicals and energy via microwave-assisted processes, (2019) 1202–1235. https://doi.org/10.1039/c8gc03908a.

[95] J. Asomaning, S. Haupt, M. Chae, D.C. Bressler, Recent developments in microwave-assisted thermal conversion of biomass for fuels and chemicals, Renewable and Sustainable Energy Reviews. 92 (2018) 642–657. https://doi.org/10.1016/j.rser.2018.04.084.

[96] D. Stuerga, K. Gonon, M. Lallemant, Microwave heating as a new way to induce selectivity between competitive reactions. Application to isomeric ratio control in sulfonation of naphthalene., Tetrahedron. 49 (1993) 6229–6234. https://doi.org/https://doi.org/10.1016/S0040-4020(01)87961-8.

[97] Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, Bright Side of Lignin Depolymerization: Toward New Platform Chemicals, Chemical Reviews. 118 (2018) 614–678. https://doi.org/10.1021/acs.chemrev.7b00588.

[98] A. Toledano, L. Serrano, J. Labidi, A. Pineda, A.M. Balu, R. Luque, Heterogeneously Catalysed Mild Hydrogenolytic Depolymerisation of Lignin Under Microwave Irradiation with Hydrogen-Donating Solvents, ChemCatChem. 5 (2013) 977–985. https://doi.org/10.1002/cctc.201200616.

[99] W. Yunpu, D. Leilei, F. Liangliang, S. Shaoqi, L. Yuhuan, R. Roger, Review of microwave-assisted lignin conversion for renewable fuels and chemicals, Journal of Analytical and Applied Pyrolysis. 119 (2016) 104–113. https://doi.org/10.1016/j.jaap.2016.03.011.

[100] A. Toledano, L. Serrano, J. Labidi, A. Pineda, A.M. Balu, R. Luque, Heterogeneously Catalysed Mild Hydrogenolytic Depolymerisation of Lignin Under Microwave Irradiation with Hydrogen-Donating Solvents, ChemCatChem. 5 (2013) 977–985. https://doi.org/10.1002/cctc.201200616.

[101] A. Toledano, L. Serrano, A. Pineda, A.A. Romero, R. Luque, J. Labidi, Microwave-assisted depolymerisation of organosolv lignin via mild hydrogen-free hydrogenolysis: Catalyst screening, Applied Catalysis B: Environmental. 145 (2014) 43–55. https://doi.org/10.1016/j.apcatb.2012.10.015.

[102] C. Xu, R.A.D. Arancon, J. Labidi, R. Luque, Lignin depolymerisation strategies: Towards valuable chemicals and fuels, Chemical Society Reviews. 43 (2014) 7485–7500. https://doi.org/10.1039/c4cs00235k.

[103] R. Zou, Y. Zhao, Y. Wang, D. Duan, L. Fan, L. Dai, Y. Liu, R. Ruan, Microwave-assisted Depolymerization of Lignin with Metal Chloride in a Hydrochloric Acid and Formic Acid System, BioResources. 13 (2018) 3704–3719. https://doi.org/DOI: 10.15376/biores.13.2.3704-3719.

[104] S. Zhu, J. Guo, X. Wang, J. Wang, W. Fan, Alcoholysis: A Promising Technology for Conversion of Lignocellulose and Platform Chemicals, ChemSusChem. 10 (2017) 2547–2559. https://doi.org/10.1002/cssc.201700597.

[105] D. Duan, Y. Wang, R. Ruan, M. Tayier, L. Dai, Y. Zhao, Y. Zhou, Y. Liu, Comparative study on various alcohols solvolysis of organosolv lignin using microwave energy: Physicochemical and morphological properties, Chemical Engineering and Processing: Process Intensification. 126 (2018) 38–44. https://doi.org/10.1016/j.cep.2017.10.023.

[106] A. Toledano, L. Serrano, A. Pineda, A.A. Romero, R. Luque, J. Labidi, Microwave-assisted depolymerisation of organosolv lignin via mild hydrogen-free hydrogenolysis: Catalyst screening, Applied Catalysis B: Environmental. 145 (2014) 43–55. https://doi.org/10.1016/j.apcatb.2012.10.015.

[107] D. Shen, N. Liu, C. Dong, R. Xiao, S. Gu, Catalytic solvolysis of lignin with the modified HUSYs in formic acid assisted by microwave heating, Chemical Engineering Journal. 270 (2015) 641–647. https://doi.org/10.1016/j.cej.2015.02.003.

[108] J. Milovanović, N. Rajić, A.A. Romero, H. Li, K. Shih, R. Tschentscher, R. Luque, Insights into the Microwave-Assisted Mild Deconstruction of Lignin Feedstocks Using NiO-Containing ZSM-5 Zeolites, ACS Sustainable Chemistry and Engineering. 4 (2016) 4305–4313. https://doi.org/10.1021/acssuschemeng.6b00825.

[109] P. Dhar, R. Vinu, Understanding lignin depolymerization to phenols via microwave-assisted solvolysis process, Journal of Environmental Chemical Engineering. 5 (2017) 4759–4768. https://doi.org/10.1016/j.jece.2017.08.031.

[110] Q. Liu, P. Li, N. Liu, D. Shen, Lignin depolymerization to aromatic monomers and oligomers in isopropanol assisted by microwave heating, Polymer Degradation and Stability. 135 (2017) 54–60. https://doi.org/10.1016/j.polymdegradstab.2016.11.016.

[111] L. Shao, Q. Zhang, T. You, X. Zhang, F. Xu, Microwave-assisted efficient depolymerization of alkaline lignin in methanol/formic acid media, Bioresource Technology. 264 (2018) 238–243. https://doi.org/10.1016/j.biortech.2018.05.083.

[112] D. Duan, Y. Wang, R. Ruan, M. Tayier, L. Dai, Y. Zhao, Y. Zhou, Y. Liu, Comparative study on various alcohols solvolysis of organosolv lignin using microwave energy: Physicochemical and morphological properties, Chemical Engineering and Processing: Process Intensification. 126 (2018) 38–44. https://doi.org/10.1016/j.cep.2017.10.023.

[113] J. Xu, J. Jiang, C. Hse, T.F. Shupe, Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy, Green Chemistry. 14 (2012) 2821–2830. https://doi.org/10.1039/c2gc35805k.

[114] S. Farag, J. Chaouki, Economics evaluation for on-site pyrolysis of kraft lignin to value-added chemicals, Bioresource Technology. 175 (2015) 254–261. https://doi.org/10.1016/j.biortech.2014.10.096.

[115] A. Vishtal, A. Kraslawski, CHALLENGES IN INDUSTRIAL APPLICATIONS OF TECHNICAL LIGNINS, 2011.

[116] J. Carpenter, M. Badve, S. Rajoriya, S. George, V.K. Saharan, A.B. Pandit, Hydrodynamic cavitation: An emerging technology for the intensification of various chemical and physical processes in a chemical process industry, Reviews in Chemical Engineering. 33 (2017) 433–468. https://doi.org/10.1515/revce-2016-0032.

[117] P.R. Gogate, Hydrodynamic Cavitation for Food and Water Processing, Food and Bioprocess Technology. 4 (2011) 996–1011. https://doi.org/10.1007/s11947-010-0418-1.

[118] E.A.B. da Silva, M. Zabkova, J.D. Araújo, C.A. Cateto, M.F. Barreiro, M.N. Belgacem, A.E. Rodrigues, An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin, Chemical Engineering Research and Design. 87 (2009) 1276–1292. https://doi.org/10.1016/j.cherd.2009.05.008.

[119] A.-S. Jönsson, O. Wallberg, Cost estimates of kraft lignin recovery by ultrafiltration, Desalination. 237 (2009) 254–267. https://doi.org/10.1016/j.desal.2007.

[120] O. Wallberg, A. Holmqvist, A.S. Jönsson, Ultrafiltration of kraft cooking liquors from a continuous cooking process, Desalination. 180 (2005) 109–118. https://doi.org/10.1016/j.desal.2004.12.032.

[121] K.K. Ng, C.J. Wu, H.L. Yang, S.C. Panchangam, Y.C. Lin, P.K.A. Hong, C.H. Wu, C.F. Lin, Effect of Ultrasound on Membrane Filtration and Cleaning Operations, Separation Science and Technology (Philadelphia). 48 (2012) 215–222. https://doi.org/10.1080/01496395.2012.682289.

[122] P. Pirkonen, A. Grönroos, J. Heikkinen, B. Ekberg, Ultrasound assisted cleaning of ceramic capillary filter, Ultrasonics Sonochemistry. 17 (2010) 1060–1065. https://doi.org/10.1016/j.ultsonch.2009.10.016.

[123] H.W.D. Camara, H. Doan, A. Lohi, In-situ ultrasound-assisted control of polymeric membrane fouling, Ultrasonics. 108 (2020). https://doi.org/10.1016/j.ultras.2020.106206.

[124] W. Yunpu, D. Leilei, F. Liangliang, S. Shaoqi, L. Yuhuan, R. Roger, Review of microwave-assisted lignin conversion for renewable fuels and chemicals, Journal of Analytical and Applied Pyrolysis. 119 (2016) 104–113. https://doi.org/10.1016/j.jaap.2016.03.011.

[125] Q. Lin, G. Chen, Y. Liu, Scale-up of microwave heating process for the production of bio-oil from sewage sludge, Journal of Analytical and Applied Pyrolysis. 94 (2012) 114–119. https://doi.org/10.1016/j.jaap.2011.11.014.

[126] D. Beneroso, T. Monti, E.T. Kostas, J. Robinson, Microwave pyrolysis of biomass for bio-oil production: Scalable processing concepts, Chemical Engineering Journal. 316 (2017) 481–498. https://doi.org/10.1016/j.cej.2017.01.130.

[127] J.M. Bermúdez, D. Beneroso, N. Rey-Raap, A. Arenillas, J.A. Menéndez, Energy consumption estimation in the scaling-up of microwave heating processes, Chemical Engineering and Processing: Process Intensification. 95 (2015) 1–8. https://doi.org/10.1016/j.cep.2015.05.001.

[128] C.W. Lahive, P.C.J. Kamer, C.S. Lancefield, P.J. Deuss, An Introduction to Model Compounds of Lignin Linking Motifs; Synthesis and Selection Considerations for Reactivity Studies, ChemSusChem. 13 (2020) 4238–4265. https://doi.org/10.1002/cssc.202000989.

[129] J. Zhang, Catalytic transfer hydrogenolysis as an efficient route in cleavage of lignin and model compounds, Green Energy and Environment. 3 (2018) 328–334. https://doi.org/10.1016/j.gee.2018.08.001.

[130] T. Renders, G. van den Bossche, T. Vangeel, K. van Aelst, B. Sels, Reductive catalytic fractionation: state of the art of the lignin-first biorefinery, Current Opinion in Biotechnology. 56 (2019) 193–201. https://doi.org/10.1016/j.copbio.2018.12.005.

[131] W. Lan, M.T. Amiri, C.M. Hunston, J.S. Luterbacher, Protection Group Effects During α,γ-Diol Lignin Stabilization Promote High-Selectivity Monomer Production, Angewandte Chemie. 130 (2018) 1370–1374. https://doi.org/10.1002/ange.201710838.