

Process intensification strategies for lignin valorization

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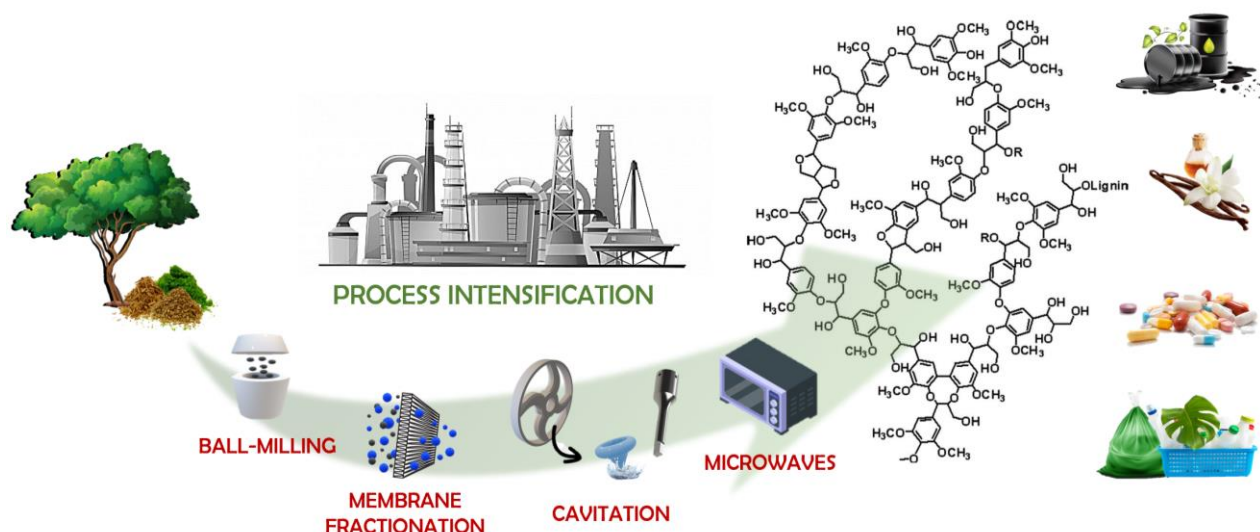
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1 Process intensification strategies for lignin valorization



2

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

4 Abstract

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

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

14 Recently, process intensification has gained considerable attention in the design of sustainable procedures for
15 lignin valorization. In particular, non-conventional technologies such as Ball milling, Ultrasounds (US) and
16 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 CO₂ 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.

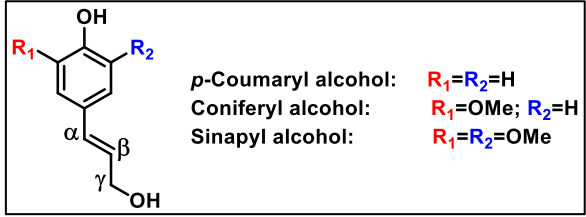


Figure 1: Building block monolignols of lignin.

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.

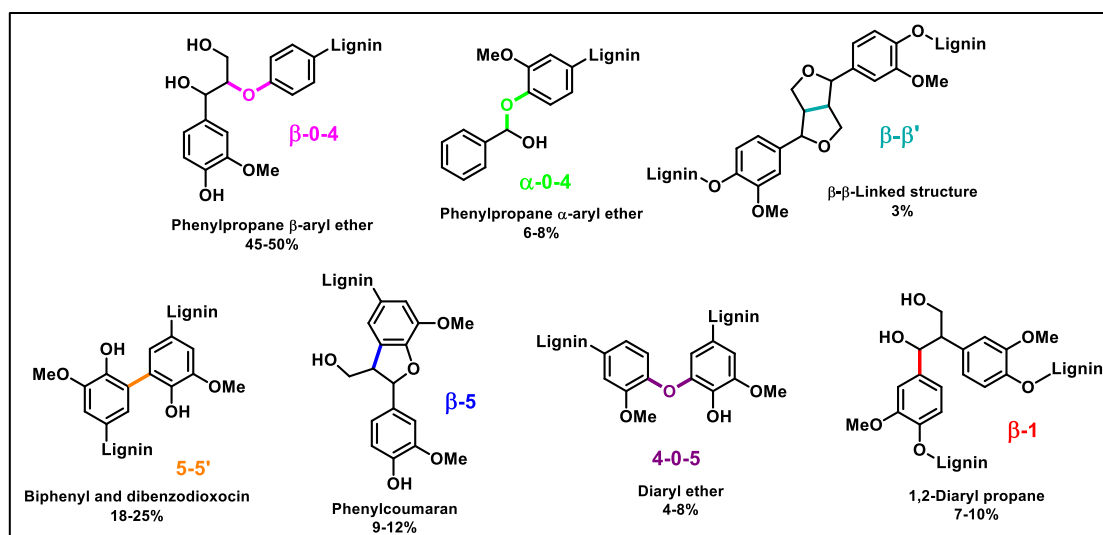


Figure 2: Typical lignin interunit linkages

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.

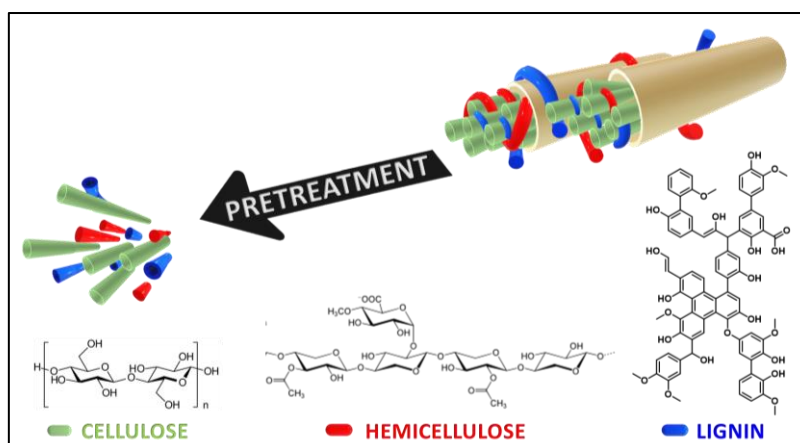


Figure 3: Pretreatment effect on lignocellulosic biomass

123 Other factors such as lignin content, cellulose crystallinity and size of the biomass particles are also crucial

124 factors to consider in order to overcome lignocellulose recalcitrance. Thereby, pretreatment processes should

125 maximize biomass delignification and depolymerize hemicellulose by enhancing solvent diffusion; moreover,

126 it should reduce cellulose crystallinity and isolate uncondensed lignin, avoiding the formation of degradation

127 products.

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

129 4).

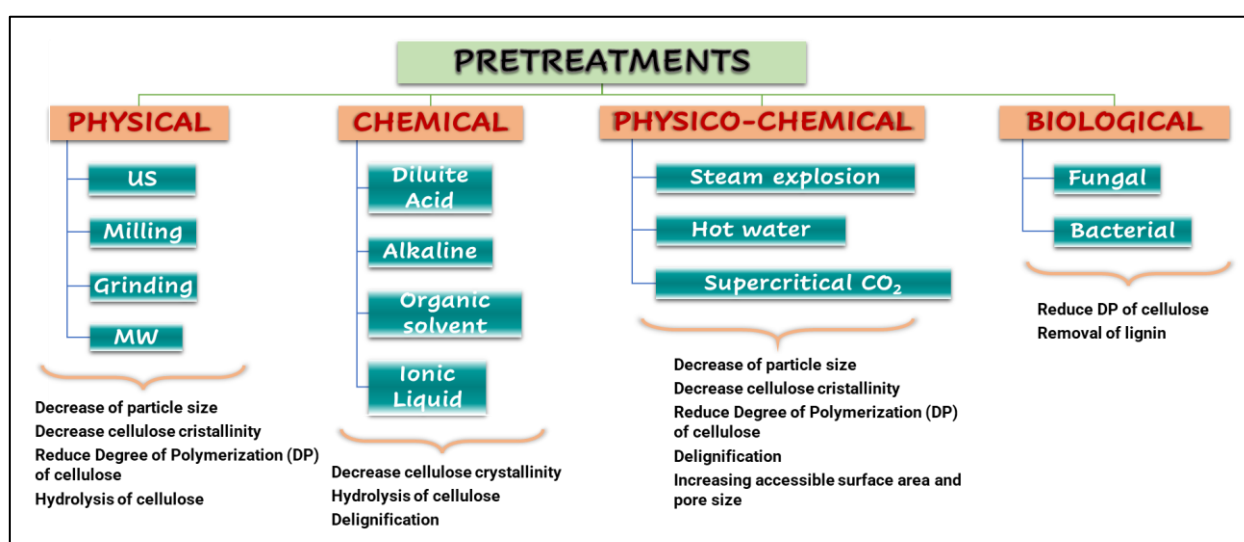


Figure 4: Various pretreatment processes of lignocellulosic biomass.

132 Biological pre-treatments are based on the use of lignin-degrading enzymes and microorganisms such as fungi

133 and bacteria for partial delignification of lignocellulosic materials. However, the biological approach is often

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

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

155 2.1 Ball milling pretreatment of lignocellulosic biomass

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

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

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

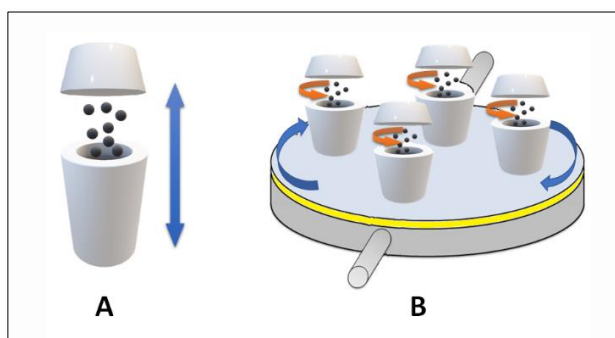


Figure 5: Vibrant mill (A) and planetary mill (B)

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

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

182 biomass and milling time. When milling time increases from one day to one week, yield rises from 16% to
183 60%, highlighting that this method is time and energy consuming, since it mainly focuses on the recovery of
184 lignin. [36] In most cases, the advantage of using MWL lies in the fact that it is considered the most
185 representative of lignin in its native state, since it is isolated at room temperature in the absence of any strong
186 acids or bases. [37,38] Milling pretreatment has been proven to be an efficient method to reduce crystallinity
187 and particle size, enhancing solvent accessibility to lignocellulose and, thus, improving also alcoholysis
188 reactions. In this regard, recently, a ball mill pretreatment has been applied to camphorwood sawdust, aiming
189 to obtain elevated bio-oil yield in supercritical ethanol. The reduced crystallinity and particle size increased
190 biomass surface area (from 1.88 to 4.77 m²g⁻¹) enhancing the solubility in ethanol. The yield of aromatic rich
191 bio-oil increased to 59.2% compared to the 39.6% obtained without pretreatment. [39]

192 Shi et al. [40] pretreated with ball mill Softwood Unbleached Kraft Pulp (UKP) to promote its dissolution in a
193 NaOH/urea solvent. After 60 min of milling the particle size of UKP decreased to an average diameter of 5
194 µm, showing good distribution, and the crystal peaks of cellulose completely disappeared, indicating that the
195 milling process could easily destroy the crystal structure of lignocellulose. Furthermore, the degree of
196 polymerization (DP) was reduced from 1300 to 330. This promoted the subsequent solubilization of the pulp
197 in NaOH/urea solvent. In fact, dissolved proportion of UKP increased from 25.6% to 96.0% after 60 min of
198 milling pretreatment. However, biomass with an elevated lignin content could not dissolve in the NaOH/urea
199 solvent due to the presence of lignin-carbohydrate complex. Ball milling treatment has been applied to
200 investigate the effect of cellulose crystallinity, hemicellulose and lignin content on further enzymatic
201 hydrolysis. Four fractions with different sizes (250-355 µm, 150-250 µm, 63-150 µm, and < 63 µm) were
202 collected and then hydrolyzed. It was confirmed that monosaccharides yield increased within the decreasing
203 of cellulose crystallinity [41] and that lignin removal greatly enhances enzymatic hydrolysis of biomass, since
204 after delignification, even with higher cellulose crystallinity degree, high yields of glucose and pentoses were
205 achieved, compared to the untreated samples. The energy requirement of mechanical comminution is
206 extremely variable, as it is related to the type of instrument, initial and final particle sizes, and biomass
207 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 cavitation 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 $^{\circ}\text{C}$) and high pressures (ca. 50 MPa).[46]

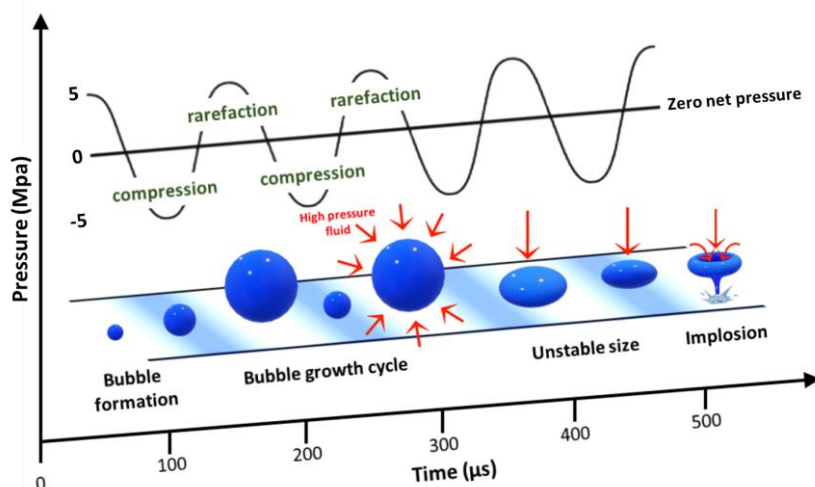


Figure 6: The acoustic generation of cavitation microbubbles

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]

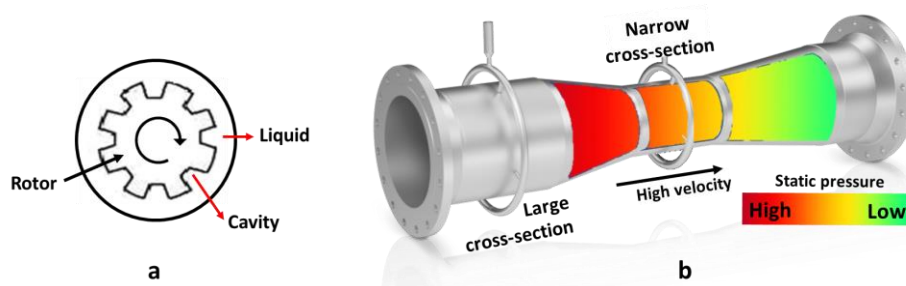


Figure 7: Rotor stator reactor (a) and venturi (b)

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.

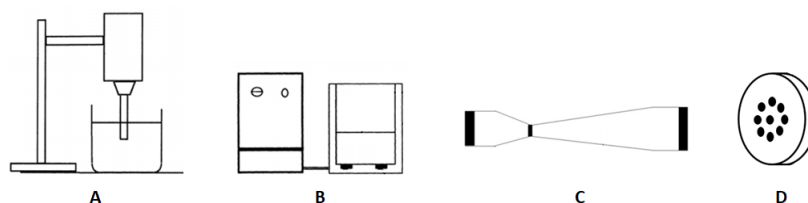


Figure 8: US immersion horn (A), US bath (B), venturi (C) and orifice plate (D)

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

259 2.2.2 Cavitation for biomass delignification

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

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

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

284 In this context, US-assisted technology has been used for the pre-treatment of wheat straw (0.5M NaOH in
285 60% aqueous methanol) and compared with conventional fractionation. [55] US were applied for a time range
286 of 5 to 35 minutes, obtaining the solubilization of 67.4% to 78.5% of the original lignin, whereas 61.0% of
287 lignin solubilization was obtained at 60°C for 2.5 h without sonication. Moreover, US-isolated lignin showed
288 slightly lower molecular weights and no significant differences with respect to the native lignin of wheat straw,
289 confirming the efficiency of the US-assisted lignin extraction procedures.

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

295 More recently, Garcia et. al [54] evaluated the effect of US (420 W, 50/60 Hz) in the fractionation process of
296 olive tree pruning residues. Different times (30, 60 and 120 minutes) and different solvent (water, NaOH 7.5%
297 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
298 of 1:10 (w/w). It was demonstrated that under US, lignin yield and selectivity in liquid fractions increased,
299 compared to the reference sample conventionally treated. Additionally, a lower degree of cellulose degradation

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

303 The effect of different frequencies (40 kHz, 376 kHz and 995 kHz) in US-assisted pretreatment of wheat straw
304 was investigated by Bussemaker et al. [57] At each frequency, three different solid to liquid ratios (1/50, 1/20
305 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
306 at 1/20 g/ml. In order to preserve the energy efficiency of the process, time extraction of 25 minutes was
307 chosen. In fact, protracted times have been demonstrated to increase lignin re-condensation. Authors showed
308 that delignification was enhanced at low frequency of 40 kHz up to 7.2% compared to the reference sample,
309 as a result of mechano-acoustic effects, whereas high frequencies (995 kHz) favored carbohydrate
310 solubilization.

311 Recently, a comparison among three different US reactor configurations (longitudinal horn, vertical immersion
312 horn and ultrasonic bath) on the efficacy of sawdust delignification was described. [58] The effect of different
313 operating parameters such as Na₂CO₃ concentration (0.1, 0.15, 0.2, 0.25 M), H₂O₂ concentration (0.2, 0.4,
314 0.6, 0.8, 1 M) and biomass loading (2, 4, 6, 8, 10 wt%) has also been investigated. The optimized reaction
315 conditions were found at 150 W for 70 minutes, with 0.2 M concentration of Na₂CO₃, H₂O₂ 1 M and biomass
316 loading of 10 wt%. Higher lignin yield was obtained with the longitudinal horn (87.4%), followed by ultrasonic
317 horn (lignin yield of 85.1%) and ultrasonic bath (lignin yield of 82%), while only 42.4% of lignin yield was
318 obtained with conventional method, confirming the process intensification benefits of US treatment.
319 Additionally, the energy requirement for the delignification of sawdust was evaluated, finding that ultrasonic
320 horn configuration presented lower power consumption (6.72×10^6 kJ/m³), followed by both longitudinal
321 horn and ultrasonic bath (12.6×10^6 kJ/m³). However, authors declared that the higher energy consumption
322 of longitudinal horn, compared to the immersion one, was due to the necessity of two additional stirrers on the
323 extreme ends of the reactor to obtain a homogeneous mixing. Therefore, the efficacy of longitudinal horn is
324 greater, since this configuration is able to process larger volumes with higher yields.

325 A US-assisted pretreatment of Vietnam's rice straw in NaOH 2M at 90°C was performed using an immersion
326 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).

<i>Type of Biomass (% w/w)</i>	<i>US-assisted pretreatment</i>	<i>Chemicals</i>	<i>Advantages</i>	<i>References</i>
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 ₂ CO 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]

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 Hilaes 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

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

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

411 Recently, Eucalyptus Kraft lignin fractionation using ceramic membranes with different MWCO (5, 15, and
412 50 kDa) was reported. [76] Results showed that ultrafiltration is an efficient process for the treatment of this
413 type of lignin. The obtained fractions were studied, showing that the lignin isolated with a 50 kDa membrane
414 presented the highest molecular weight with higher content of carbohydrates and inorganics. In contrast, from
415 the 5 kDa membrane low Mw lignin with low dispersity value was obtained; this type of lignin represents an
416 important source of phenolic monomers after oxidative depolymerization.

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

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

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

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

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

451 4. Depolymerization of Isolated Lignin

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

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

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

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

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

481 4.1 MW technology

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

488 The first use of MW in organic synthesis leads back to Gedye e Giguère, who noted that MW heating
489 significantly enhanced the reaction rate. [85][86] MW heating also exhibits a positive influence on chemical
490 reactions, enhancing yields and selectivity.[87] [88] Microwaves are electromagnetic radiations with
491 frequencies between 0.3 and 300 GHz. The frequency used in MW reactors is fixed at 2.45 GHz; consequently,
492 the associated energy is too low to break a chemical bond. Therefore, the effects of MW are due to the efficient
493 heating of molecules by two mechanisms: dipole rotation and ionic conduction. [89] The first one describes
494 the tendency of dipoles to constantly align themselves with the MW electric field by rotation, causing friction
495 that generates heat. In ionic conduction mechanism, ionic particles oscillate under the influence of MW electric
496 field, leading to the formation of a current. This current is subjected to internal resistance due to collisions
497 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.

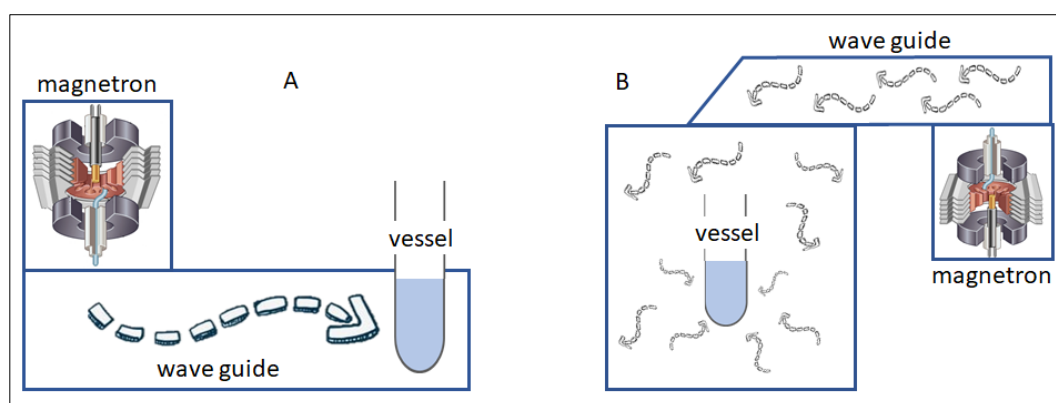


Figure 9: Monomodal (A) and multimodal (B) microwave reactors

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.

519 4.2 MW specific effects

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

541 4.3 MW-assisted lignin depolymerization

542 Over the past few decades, the depolymerization of isolated lignin to aromatics became an attractive approach
543 for lignin valorization into value-added chemicals. However, depolymerization strategies lack in selectivity
544 towards aromatics compounds. Moreover, the cleavage of lignin linkages is still a difficult issue, since most
545 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–

573 108] Toledano et al. [106] studied the effects of the type of metal catalyst in a microwave-assisted hydrogen-
574 free depolymerization of organosolv lignin. Catalyst screening included different metal nanoparticles: Ni (2,
575 5, and 10 wt.%), Pd (2 wt.%), Pt (2 wt.%), and Ru (2 wt.%) supported on Al-SBA-15. Depolymerization
576 reactions were conducted in a multimode microwave reaction system with a 400W constant power.
577 Experiments were performed for 30 min at average temperature of 140°C, using formic acid as H-donor. The
578 highest bio-oil yield of 30 wt.% was obtained when Ni10%AlSBA was used as the catalyst, while 5 wt.% of
579 bio-oil yield was obtained when Pd2%Al-SBA was used.

580 When formic acid was used, bio-char formation was lower as compared to other H-donors. This could be
581 ascribed to the decomposition of formic acid into gases (e.g., CO, CO₂ and H₂) during the lignin
582 depolymerization, whereas different H-donor solvents could react with lignin radical fragments leading to the
583 formation of bio-char. Shen et al.[107] performed lignin depolymerization in formic acid at 130°C and 30 min,
584 using HUSY zeolite as the catalysts. The yield in bio-oil was enhanced in the presence of the catalysts.
585 Moreover, bio-oil yield increased to 88.28 wt% (15.36% of aromatic monomers and 67.52% of oligomer
586 fractions), when HUSY modified by 0.2 mol/L oxalic acid was used.

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

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

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

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

607 Shao et al. [111] proposed the depolymerization of alkaline lignin in methanol/formic acid media. Formic acid
608 acted mainly through acid-catalyzed cleavage of the linkages in lignin. Oligomers in bio-oil were mainly
609 composed of dimers and trimers, according to the MALDI-TOF MS analysis. Different FA/lignin mass ratio,
610 reaction temperature and reaction time were applied, aiming to investigate their effects on product yield and
611 distribution. The highest bio-oil yield of 72.0 wt.%, including 6.7 wt.% monomers, was achieved at 160 °C
612 and a FA/lignin mass ratio of 4 after a reaction time of 30 min. Additionally, the bio-oil yield was compared
613 with the one obtained at the same conditions under conventional heating: 41.1 wt.% yield of bio-oil including
614 0.89 wt.% of monomers was obtained, indicating that microwave significantly improved bio-oil yield.

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

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

628 5. Scale-up

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

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

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

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

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

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

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

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

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

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

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

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

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

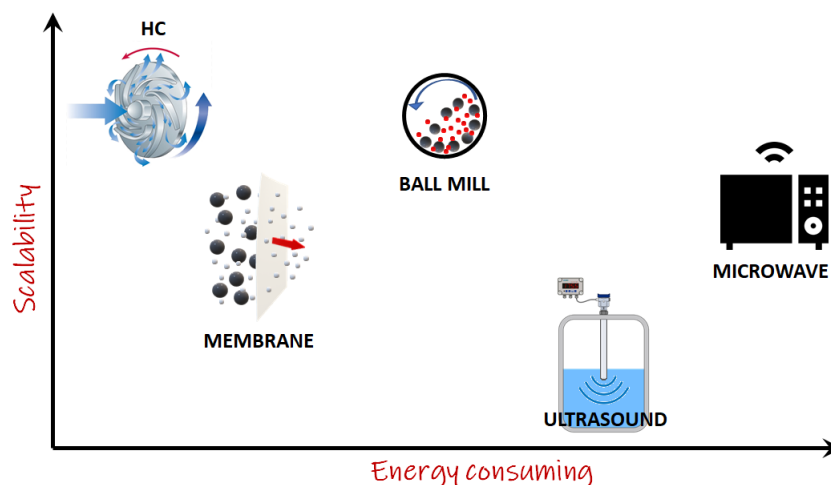


Figure 10: Comparison of enabling technologies in terms of scalability and energy consumption.

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

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

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

755 CONCLUSION

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

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

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

770 Over the last decades, enabling technologies such as US, HC, MW and milling have demonstrated to lead to
771 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

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