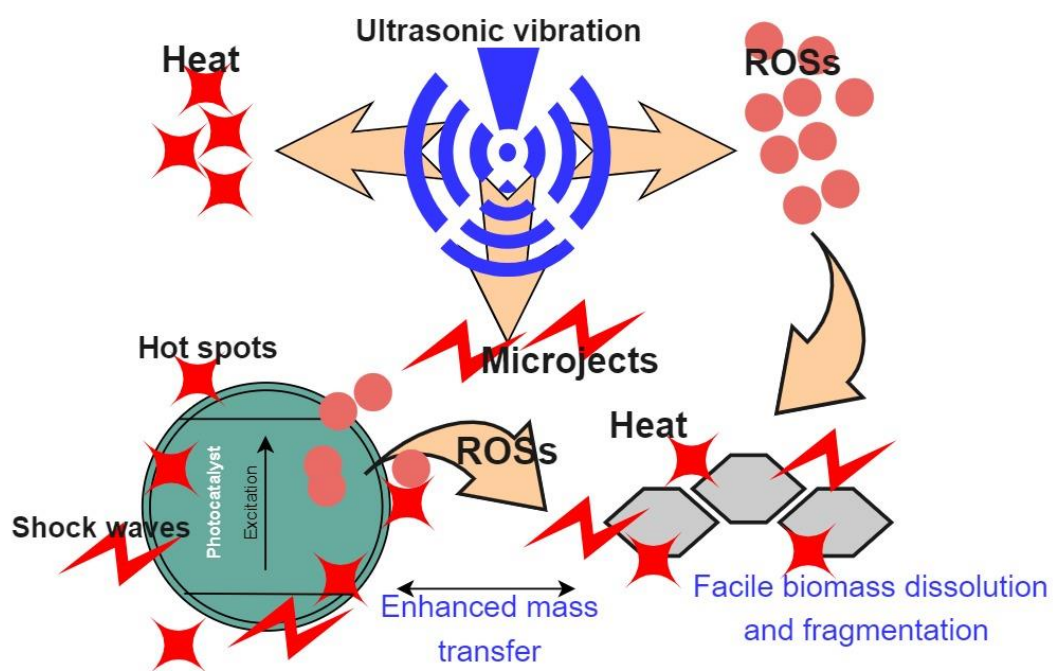


# Bioresource Technology

## Combined conversion of lignocellulosic biomass into high-value products with ultrasonic cavitation and photocatalytic produced reactive oxygen species - A review --Manuscript Draft--

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<b>Abstract:</b>	<p>The production of high-value products from lignocellulosic biomass is carried out through the selective scission of crosslinked C-C/C-O bonds. Photocatalytic technology has been proven to be a valuable tool for valorizing biomass at mild conditions. The photoproducted reactive oxygen species (ROS) can initiate the scission of crosslinked bonds and form radical intermediates. However, the low mass transfer of the photocatalytic process could limit the production of a high yield of products. The incorporation of ultrasonic cavitation in the photocatalytic system provides an exceptional condition to boost the fragmentation and transformation of biomass into the desired products within a lesser reaction time. This review critically discusses the main factors governing the application of photocatalysis for biomass valorization and tricks to boost the selectivity for enhancing the yield of desired products.</p>

### Graphical abstract



## Highlights

- Mechanisms of photoproduced ROSs to cleave crosslinked C–C/C–O in biomass
- Photocatalytic materials design and operating factors for biomass conversion
- Impact of ultrasonic vibration on the mass transfer and biomass valorization
- Synergistic effects of sonophotocatalysis to boost the yield of high value products
- Future directions for the optimization of sonophotocatalytic biomass conversion

1 **Combined conversion of lignocellulosic biomass into high-value products**  
2 **with ultrasonic cavitation and photocatalytic produced reactive oxygen**  
3 **species - A review**

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## 27 **Abstract**

28 The production of high-value products from lignocellulosic biomass is carried out through the  
29 selective scission of crosslinked C–C/C–O bonds. Several techniques are applied nowadays  
30 to optimize biomass conversion into desired products with high yields. Photocatalytic  
31 technology has been proven to be a valuable tool for valorizing biomass at mild conditions.  
32 The photoproducted reactive oxygen species (ROSs) can initiate the scission of crosslinked  
33 bonds and form radical intermediates. However, the low mass transfer of the photocatalytic  
34 process could limit the production of a high yield of products. The incorporation of ultrasonic  
35 cavitation in the photocatalytic system provides an exceptional condition to boost the  
36 fragmentation and transformation of biomass into the desired products within a lesser  
37 reaction time. This review critically discusses the main factors governing the application of  
38 photocatalysis for biomass valorization and tricks to boost the selectivity for enhancing the  
39 yield of desired products. Synergistic effects obtained through the combination of sonolysis  
40 and photocatalysis were discussed in depth. Under ultrasonic vibration, hot spots could be  
41 produced on the surface of the photocatalysts, improving the mass transfer through the jet  
42 phenomenon. In addition, shock waves can assist the dissolution and mixing of biomass  
43 particles.

44 **Keywords:** Biomass valorization; Selective scission of C–C/C–O; Photocatalysis; ultrasonic  
45 vibration; High value products; Circular bioeconomy.

## 46 **1. Introduction**

47 The large-scale conversion of biomass materials/wastes started during the mid of 19<sup>th</sup> century  
48 towards the generation of several chemicals, including cellulose esters and oils. However,  
49 since that time, the industrial conversion of biomass materials into high-value products has  
50 been ignored because of the low competition with less economical routes, such as the

51 catalytic conversion of hydrocarbons into different chemicals, which took over a decade.  
52 Nowadays, due to the dramatic increase in the worldwide population and industrial activities,  
53 as well as the decrease in natural resources making them more costly, i.e., hydrocarbons, the  
54 scientific and industrial communities started seriously investigating the valorization of  
55 biomass materials again into high-value products as an alternative sustainable route (Gallezot  
56 2012; Alonso, Bond, and Dumesic 2010). In academia, the scientific community has made a  
57 lot of effort within the last two decades to find the best ways to convert biomass materials  
58 effectively into specific chemicals. For that, several technologies are applied, such as  
59 combustion (Khodaei et al. 2015), pyrolysis (Kan, Strezov, and Evans 2016), gasification  
60 (Sikarwar et al. 2016; Molino, Chianese, and Musmarra 2016), direct liquefaction (Ali and  
61 Zhao 2020), and recently several advanced oxidation processes. i.e., Fenton (Kato et al. 2014;  
62 Wu et al. 2020), electro-Fenton (Chen et al. 2021), ozonolysis (Travaini et al. 2016) and  
63 photocatalysis (Granone et al. 2018; Li et al. 2021).

64 Combustion is one of the most widely used technologies for biomass conversion, wherein  
65 more than 90% of bioenergy production is obtained. It is considered a traditional people's  
66 daily route to generate heat (Demirbas 2007; Koppejan and Van Loo 2012). However, the  
67 large-scale combustion of biomass is still facing some technical challenges related to fuel  
68 characteristics, combustor types, and co-firing issues. Pyrolysis focuses on the thermal  
69 decomposition of biomass in an oxygen-free environment to produce different products,  
70 including solid charcoal, oils, chemicals, or even gas at higher temperatures (Vamvuka 2011;  
71 Chhiti and Kemiha 2013). This process could be applied largely because of its efficiency and  
72 sustainability (Demirbas et al. 2016; Yang et al. 2016). Gasification is the process that  
73 involves drying biomass waste, pyrolysis, and combustion of by-products, followed by  
74 gasification to generate multiple high-value products in different air environments, which  
75 could be oxygen, water steam, or carbon dioxide (Sikarwar et al. 2016; Heidenreich and

76 Foscolo 2015). Direct liquefaction is based on breaking down biomass macromolecules into  
77 fragments of small molecules in water or appreciative organic solvents. Then, these  
78 fragments could be combined through polymerization to produce high-value products such as  
79 oily compounds (Demirbaş 2000). Direct liquefaction is done at low temperatures and high  
80 pressure.

81 Advanced oxidation processes, such as photocatalysis, are based on generating reactive  
82 oxygen species (ROSs) to break down lignocellulosic biomass into high-value products.  
83 Photocatalysis can be initiated in the presence of a photocatalyst and light irradiation with  
84 energy equal to or higher than the band gap of the photocatalyst. In this sense, the electrons  
85 move from the valence band to the conduction band, leaving positive holes.  $\cdot\text{OH}$  radicals can  
86 be generated by oxidation water molecules by positive holes at the valence band, while  $\text{O}_2^{\cdot-}$   
87 species can be produced by reducing  $\text{O}_2$  on the conduction band. Photocatalytic biomass  
88 conversion is a new alternative technique with many hopes and technical challenges (Li et al.  
89 2021; Liu et al. 2019). One of the common issues in photocatalytic technology towards  
90 biomass conversion is mass transfer limitations because of the solid nature of biomass;  
91 therefore, ROSs cannot easily access biomass macromolecules resulting in low efficiency. On  
92 the other hand, since biomass materials are not dissolved in water, several organic solvents  
93 are used to dissolve the biomass. However, organic solvents would be less sustainable in  
94 large-scale applications, and extracting wanted products could be more difficult. In addition,  
95 the reaction of solvents with generated products might affect the purity of the final products.  
96 Organic solvents can also be ROSs scavengers, inhibiting biomass conversion. Recently,  
97 combining photocatalysis and sonolysis for biomass conversion has attracted much attention  
98 (Giannakoudakis, Łomot, and Colmenares 2020; Chatel et al. 2017). Sonolysis, or ultrasonic  
99 technology, is based on generating a cavitation field via ultrasonic vibration (Meroni et al.  
100 2021). Sonophotocatalysis has been widely applied to the oxidation of organic pollutants in

101 water (Joseph et al. 2009; Panda and Manickam 2017; Preeyanghaa, Vinesh, and Neppolian  
102 2022); however, it is still under investigation for biomass conversion.

103 This work critically discusses the lignocellulosic biomass valorization into high-value  
104 products by photocatalytic and sonophotocatalytic means from a mechanistic and  
105 technological perspective. Several aspects that cover this field were discussed in different  
106 sub-sections. The first section discusses the composition and characterization of  
107 lignocellulosic biomass and the importance of valorization as an emerging circular  
108 bioeconomy approach. This sub-section discusses comparatively the existing pretreatment  
109 techniques of biomass by stressing their pros and cons. Afterwards, the photocatalytic  
110 conversion of lignocellulosic biomass, including the role of ROSs to initiate the  
111 fragmentation of aromatic rings and formation of intermediate radicals, the role of the  
112 photocatalytic design material towards the selective conversion, the effect of operating  
113 parameters and technical issues of photocatalytic process. Then, the ultrasonic technique was  
114 discussed, from the principle to its application for biomass pretreatment. The synergistic  
115 effects of combined ultrasonic vibration and photocatalytic towards biomass valorisation  
116 were discussed in depth. Finally, prospects and future directions were provided to help the  
117 reader further research the field. This review would effectively push forward the progress of  
118 biomass valorization and understanding the mechanism of photocatalytic and  
119 sonophotocatalytic towards producing a high yield of high-value products from biomass  
120 materials.

## 121 **2. Lignocellulosic biomass conversion**

### 122 **2.1. Characterization of biomass**

123 Lignocellulosic biomass is the dried waste of plants or food, which mostly consists of three  
124 main elements cellulose, lignin, and hemicellulose (Cai et al. 2017). Lignocellulosic biomass  
125 is the most available resource on the planet, which could be used to produce alternatively

126 different high-value products and energy (Ambaye et al. 2021; Ambaye et al. 2022). It can be  
127 primarily obtained from different sectors, including forest, agriculture, industrial companies,  
128 etc. The worldwide industrial and environmental communities highly recommend  
129 valorisation into high-value products because of their high carbon richness and worldwide  
130 availability. The production of chemicals and energy from biomass could significantly reduce  
131 gas emissions via substituting fossil energies (Binder and Raines 2009). The quantitative and  
132 qualitative physicochemical characterization of lignocellulosic biomass is crucial to optimize  
133 the conversion into wanted products flexibly. Different parameters are needed to be known.  
134 The primary biomass analysis could be divided into four types, as shown (Dahlquist 2013;  
135 Cai et al. 2017), which include (i): as received basis to estimate the total weight of biomass as  
136 it arrives without any type of pretreatment, (ii): air dried basis evaluates the biomass sample  
137 that is in an equilibrium of humidity, and it excludes moisture except the inherent, (iii): dry  
138 basis is the analytical result of free-moistures biomass; it leaves both external and intrinsic  
139 moisture, (iv): dry ash-free basis estimates the biomass, excluding all moistures and ash. This  
140 analysis is mainly used to present the accurate yield of compounds in the biomass sample.

## 141 **2.2. Emerging circular bioeconomy concept**

142 The circular economy has recently been a hot topic in academic and industrial research,  
143 notably global (Brandão, Goncalves, and Santos 2021). According to the European  
144 Commission strategies and related action plans, the circular economy is the closed-loop  
145 approach. Many literature reports have been published on the circular economy alone and  
146 how the circular economy and bioeconomy are co-related; the authors emphasized the most  
147 important differences and overlaps and how we can use them in the current business  
148 (D'Adamo et al. 2021). It is worth noting that there may not have been a single definition of  
149 the circular bioeconomy (Befort 2020). According to Muscat et al. (Muscat et al. 2021),  
150 circular bioeconomy is an emerging concept that helps to mitigate the rapid depletion of

151 fossil resources, promotes regenerative practices, prevents the degradation of natural  
152 resources such as water, carbon, and nutrients, and boosts the holistic approach of recycling  
153 and reuse of waste as feedstock to produce many bio-based products that have potential to  
154 replace fossil-based products in various industrial applications. Furthermore, biorefinery has  
155 attracted increasing attention as it converts different waste feedstocks such as lignocellulosic  
156 biomass, algal biomass, urban waste, and microbial-treated waste into high-value-added  
157 products such as biofuels, biopolymers, and biochemicals in sustainable and cost-effective  
158 manners (Muscat et al. 2021). Therefore, the biorefinery is a strategic mechanism to achieve  
159 the circular bioeconomy concept (Awasthi et al. 2022). Due to advancements in biomass  
160 conversion and biocatalyst technologies, it has become possible to construct an integrated  
161 biorefinery approach to produce multifaceted products. This approach improves resource  
162 efficiency and product yield, reduces reaction time, and paves the path toward the bio-based  
163 circular economy via a closed-loop method (Velvizhi et al. 2022). Thus, by closing the loop  
164 under the circular bioeconomy premises, sustainability and economic feasibility for bio-based  
165 products can be achieved (Carus and Dammer 2018).

166 In recent years, the use of lignocellulosic biomass as a renewable source for producing high-  
167 value-added products has gained more attention, constituting "green technology" in the  
168 biorefinery (Clark 2019). Currently, the primary use of lignocellulosic biomass in the  
169 industry is combustion. Its use as feedstock in the biorefinery for the production of green  
170 products has vast potential to replace fossil-based feedstocks in the chemical and polymer  
171 industries, so it combats the global environmental challenges and helps to improve  
172 sustainability in the production process (Yang et al. 2019). The compositions can vary from  
173 one biomass to another, as shown in **Table 1**, ranging from (32-50%) cellulose, (14-26%)  
174 hemicellulose and (13-50%) lignin. The utilization of each biomass component, i.e.,  
175 cellulose, hemicellulose, and lignin, is crucial to realize the circular bioeconomy in

176 biorefinery (Liu et al. 2021). However, the recalcitrant structure of biomass is a significant  
177 barrier to its utilization in the biorefinery plant to produce value-added products (Bhatia et al.  
178 2020). Pretreatment is the critical step for converting lignocellulosic biomass into  
179 fermentable sugars and improves the accessibility of cellulose to enzymatic or chemical  
180 hydrolysis by depolymerizing recalcitrant lignin structures and hemicelluloses or decreasing  
181 the crystallinity of the cellulose (Baral et al. 2019). According to the recent consensus,  
182 simple, green, and economically feasible pretreatments are needed to enable sustainability in  
183 biorefinery. In addition, pretreatment should not produce any toxic by-products or loss of  
184 fermentable sugars and should isolate the lignin. Until now, no standardized pretreatment  
185 method has been available for converting all biomasses. Hence, combining one or more  
186 pretreatment strategies will be highly beneficial to improve the efficiency of the biomass  
187 conversion process (Carrasquillo-Flores et al. 2013).

### 188 **2.3. Conventional pretreatment approaches**

189 Pretreatment methods are classified into physical, chemical, and biological. Among these  
190 three methods, chemical methods have been widely used for biomass depolymerisation (Baral  
191 et al. 2019). The most common chemical methods for biomass depolymerization involve the  
192 addition of acids, bases, organic acids, organosolv, ammonia, supercritical fluids, or ionic  
193 liquids (Bhatia et al. 2020). The pros and cons of these methods are shown in **Table 2**. For  
194 many years, these conventional methods have been used for the depolymerization of a variety  
195 of biomass. These methods' significant limitations have cost, high-energy demand, time  
196 consumption, low yield of fermentable sugars, produced toxic by-products, and lack of the  
197 recycling of solvents. These conventional methods are not suitable for the sustainable future  
198 of lignocellulosic biomass-based products (Sidana and Yadav 2021). To overcome these  
199 challenges, the advancement in pretreatment technologies is needed to efficiently convert  
200 carbohydrates to fermentable sugars and provide a route for valorising lignin.

**Table 1.** Overview of bio compositions of different lignocellulosic biomass from literature

Lignocellulosic biomass	Types	Cellulose content (%)	Hemicellulose content (%)	Lignin content (%)	Reference
<b>Agricultural Wastes</b>	Rice-husks	34.15	14.36	25.5	(Heng et al. 2017)
	Tequila Agave Bagasse	50.0	21.1	13.1	(González-García et al. 2019)
	Wheat bran	32.43	26.34	20.15	(Annamalai and Sivakumar 2016)
	Wheat straw	43.44	26.22	21.2	(Wang et al. 2021)
	Corn stover	37.15	14.03	27.69	(Wang et al. 2016)
	Wall-nutshell	26.7	23.4	49.8	(Ahorsu et al. 2019)
	Sugarcane bagasse	41	15	20	(Carrasquillo-Flores et al. 2013)
<b>Forest residues</b>	Beechwood	41	24	24	(Carrasquillo-Flores et al. 2013)
	Birch saw dust	37	32	23	(Lempiäinen et al. 2022)
	Pine saw dust	44	26	26	(Rusanen et al. 2019)
<b>Energy crops</b>	Switch grasses	39.42	20.25	21.22	(Wang et al. 2020)
	<i>Miscanthus sp</i>	41.7	25.3	22.2	(Gismatulina and Budaeva 2017)

**Table 2. Critical comparison of conventional pretreatment methods with their merits and demerits**

Name of method	Impact on the biomass	Merits	Demerits	Reference
Ball Milling	<ul style="list-style-type: none"><li>• Reduce crystallinity of cellulose</li></ul>	<ul style="list-style-type: none"><li>• Solvent-free</li><li>• Easy to operate</li></ul>	<ul style="list-style-type: none"><li>• High energy consumption</li><li>• Do not provide a route for lignin valorisation</li></ul>	(Lan et al. 2022)
Acid pretreatment	<ul style="list-style-type: none"><li>• Break recalcitrant lignin and hemicellulose</li></ul>	<ul style="list-style-type: none"><li>• Simple and low-cost</li><li>• Expensive enzymatic hydrolysis is not needed since acid has the potential to hydrolyse biomass into fermentable sugars</li></ul>	<ul style="list-style-type: none"><li>• Loss of fermentable sugar</li><li>• Generate toxic inhibitors for the fermentation process</li><li>• Sustainable issues</li></ul>	(Solarte-Toro et al. 2019)
Alkaline pretreatment	<ul style="list-style-type: none"><li>• Remove hemicellulose and lignin fractions</li></ul>	<ul style="list-style-type: none"><li>• Partially remove the lignin</li><li>• Compared to acid pretreatment less degradation of fermentable sugars</li></ul>	<ul style="list-style-type: none"><li>• Harsh condition needed</li><li>• Generate toxic by-products</li><li>• Sustainable issues</li></ul>	(Donkor et al. 2022)
Organosolv	<ul style="list-style-type: none"><li>• Extract the lignin and hemicellulose</li></ul>	<ul style="list-style-type: none"><li>• Efficiently gives a recovery of lignin</li><li>• Improve enzymatic digestibility of cellulose</li></ul>	<ul style="list-style-type: none"><li>• Expensive</li><li>• Recycling of solvents is needed</li></ul>	(Sun et al. 2022)
Ionic liquid	<ul style="list-style-type: none"><li>• Reduce crystallinity of cellulose</li><li>• Extract lignin</li></ul>	<ul style="list-style-type: none"><li>• Operate in mild conditions</li><li>• Efficiently dissolution of cellulose</li><li>• Selective, less toxic inhibitors produced during pretreatment</li></ul>	<ul style="list-style-type: none"><li>• Expensive</li><li>• Recycling issue</li><li>• Toxicity and poor biodegradability</li></ul>	(Roy and Chundawat 2022)
Liquid hot water	<ul style="list-style-type: none"><li>• Extract lignin and hemicellulose</li></ul>	<ul style="list-style-type: none"><li>• No catalyst is needed</li><li>• Simple operational setup</li><li>• High lignin conversion</li></ul>	<ul style="list-style-type: none"><li>• Time-consuming</li><li>• High energy demand</li><li>• High water consumption</li></ul>	(Chen et al. 2022)

### 1 3. Photocatalytic biomass conversion: mechanisms and challenges

#### 2 3.1. Generalities and mechanisms

3 Lignin, the main element of lignocellulosic biomass, is considered the most complex  
4 polymer among the other components. It is more interesting than cellulose and  
5 hemicellulose because of its carbon-rich monomers and high reduced O<sub>2</sub> yield  
6 (Colmenares 2019). It consists of methoxylated phenylpropanoid units (Li et al. 2015).  
7 The appropriate scission of crosslinked C–C/C–O can produce high-value products,  
8 including phenolic compounds and benzaldehydes (Huang et al. 2022). In addition, the  
9 deoxygenation of lipid-derived fatty forms long-chain alkane fuels, i.e., jet fuel and  
10 diesel. The most critical parameter in these reactions is the selectivity of bonds' scission  
11 or deoxygenation reaction. Photocatalysis can generate reactive oxygen species (ROSs)  
12 under light irradiation, which can undergo different complex transformations (Zhang  
13 and Wang 2020). ROSs can participate in breaking down specific bonds under mild  
14 conditions. At the same time, such scission transformations require a higher temperature  
15 of up to 150°C and the presence of stoichiometric reducing or oxidizing agents (Zhang  
16 and Wang 2020). **Figure 1** shows examples of high-value chemicals from biomass  
17 through the photocatalytic pathway. Under light irradiation, the photocatalyst is  
18 subjected to the excitation of electrons followed by e<sup>-</sup>/h<sup>+</sup> pairs generation. Oxidation  
19 and reduction reactions can occur on the photocatalytic materials' surface.  
20 Lignocellulosic biomass can act as an electron acceptor or donor, depending on  
21 conditions, properties of the photocatalyst, and potential of biomass compound as  
22 compared to energetic levels of conduction or/and valence band. In general, the transfer  
23 of ROSs to biomass is very slow because of the solid nature of biomass; however, many  
24 efforts have been reported to optimize the mass transfer between the generated ROSs  
25 and the biomass compound.

26 Specifically, photogenerated ROSs activate the biomass elements into a given radical  
27 intermediate, facilitating other reaction processes, such as the scission of bonds or  
28 intermediates combination to produce the desired product (Capaldo and Ravelli 2019).  
29 In terms of lignin, the main factor is the breaking down of interunit linkage, which  
30 produces several high-value aromatic monomers (Tsui, Wang, and Knowles 2020).  
31 ROSs attack the lignin structure and leads to activate the O–H bond, which undergoes  
32 the formation of the alkoxy radical. Alkoxy radicals provoke the weakness of adjacent  
33 C–C bonds, enabling its scission to open aromatic rings (Yayla et al. 2016; Ota et al.  
34 2019). In this case, the issue is that C $\alpha$ –H could be activated instead of C–O, which  
35 partially limits the fragmentation process of C–C bonds. The oxidation potential of the  
36 C $\alpha$ –H bond compared to the O–H bond in the lignin structure is a determining factor for  
37 selective O–H activation to boost the fragmentation of C–C bonds. In some lignin  
38 structures, O–H activation is spontaneous and thermodynamically favourable; however,  
39 C $\alpha$ –H activation would be more plausible in other cases, requiring different catalytic  
40 reactions to reverse it (Nguyen, Murray, and Knowles 2019). One of the common  
41 strategies to boost the activation of the O–H bond is the addition of an appropriate base  
42 to undergo a proton-coupled electron transfer (Zhou et al. 2018), as O–H exhibits a high  
43 polarity. Pretreatment of biomass with the chemical could boost the activation of O–H.

44 The photocatalytic activation of C $\beta$ –H can lead to the oxidative cleavage of C $\alpha$ –C $\beta$   
45 bonds of lignin structure ( $\beta$ -O-4 and C $\beta$ –H models). The photogenerated superoxide  
46 radicals ( $\cdot\text{O}_2$ ) react with the C $\beta$  radicals released from C $\beta$ –H bond to form an active  
47 peroxide intermediate, followed by dehydration which in turn boosts the C $\alpha$ –C $\beta$  bond  
48 cleavage in lignin. ROSs participate in the cleavage of C–C bonds of biomass, and  
49 photogenerated holes and electrons can play essential roles. It was reported that positive

50 holes could activate C $\alpha$  radical for the boosted weakness of C $\beta$ -O bond, followed by  
51 bond cleavage via the photogenerated electrons (Wu et al. 2018).

52 The advantages of photocatalysis over conventional techniques can be summarized as  
53 follows

- 54 - Photocatalysis can be operated for biomass conversion at mid conditions in  
55 terms of temperature. The scission of many bonds requires heating up to 150°C.
- 56 - The non-use of stoichiometric reducing or oxidizing agents to initiate the  
57 fragmentation of biomass.
- 58 - The heterogeneous nature of the process allows the easy separation of produced  
59 products. In many systems, extraction and column separation would be  
60 necessary to separate the generated products. In addition, recycling the  
61 photocatalyst is possible, which might reduce the cost of the valorization at a  
62 large scale.
- 63 - The quality and yield of products obtained by photocatalysis could be different  
64 than those obtained by other techniques. Therefore, photocatalysis could be  
65 competitive with existing methods to produce a specific product.
- 66 - The selectivity of biomass valorization can be controlled by the design of  
67 photocatalytic materials.
- 68 - ROSs can activate selectively some specific bonds, which could be difficult  
69 through techniques. E.g.,  $\cdot\text{O}_2$  reacts with C $\beta$  radicals to form an active peroxide  
70 intermediate.

### 71 **3.2. Photocatalytic materials for biomass conversion**

72 Studies on the conversion of different biomass substrates have been undertaken using  
73 the genealogy of different photocatalysts such as semiconductors, carbon-based, metal

74 sulfides, and organometallic, among several others. However, using TiO<sub>2</sub>-based  
75 semiconductors as photocatalysts remains the most studied for biomass conversion,  
76 primarily due to their low cost, stability, and toxicity. Substrate choice plays a  
77 significant role in determining the type of products likely to be obtained during the  
78 application of biomass. **Table 3** summarizes the application of different photocatalysts  
79 to various biomass substrate fractions (lignin and carbohydrates).

80 Photo-conversion of TiO<sub>2</sub>-based for model, industrial and native lignin conversion to  
81 various aromatic building blocks have been reported. **Table 3** shows the conversion of  
82 different biomass substrates, such as lignin/model biomass, via TiO<sub>2</sub>-based  
83 photocatalysts. Except for a few scenarios, the use of TiO<sub>2</sub> as a standalone homogenous  
84 catalyst has led principally to the depolymerization of model compounds. TiO<sub>2</sub> shows  
85 the possibility of overoxidation (selectiveness) due to its excessive generation of ROSs.  
86 Hence various strategies have been reported to improve the performance of TiO<sub>2</sub>-based  
87 photocatalysts. Kobayakawa wrote the first report on the application of TiO<sub>2</sub> for lignin  
88 degradation in 1989 (Kobayakawa et al. 1989). However, lignin was degraded entirely  
89 to CO<sub>2</sub> and H<sub>2</sub>O. Consequently, numerous studies have been conducted to increase the  
90 photocatalytic effectiveness of TiO<sub>2</sub> utilizing various methods. Enhancing contact  
91 between the catalyst and lignin substrate is reported to be one strategy to improve the  
92 yield of monomers using TiO<sub>2</sub> (Nair, Dhar, and Vinu 2016; Srisasiwimon et al. 2018).  
93 Under UVA conditions, Srisasiwimon et al. (Srisasiwimon et al. 2018) recorded about  
94 40% conversion of kraft lignin and vanillin yield of 1%, with other aromatic-based  
95 monomers in low concentrations when a composite of TiO<sub>2</sub>/lignin was prepared using a  
96 microwave sol-gel method. The mechanistic study revealed effective co-radical ( $\cdot\text{O}_2^-$   
97 and  $\cdot\text{OH}$ ) production through enhanced contact. Tsapekos et al. (Tsapekos et al. 2018)  
98 utilized an AgCl-modified TiO<sub>2</sub> for rice husk depolymerization. Mechanistic studies

99 showed that electrons from the Fermi level of Ag migrated to the TiO<sub>2</sub> under  
100 equilibrium occurring at the interface of the two materials, forming a new energy level  
101 with additional free electrons. This type of substitution is also reported to enhance the  
102 selective oxidation of cyclohexane to cyclohexanone (Vinu and Madras 2009). Other  
103 support-based catalytic systems have been reported. Bi and Pt as co-catalyst were  
104 supported onto TiO<sub>2</sub> (1% Bi/Pt1%-TiO<sub>2</sub>) for photo-depolymerization of lignosulfonate  
105 lignin (Gong, Imbault, and Farnood 2017). The co-modified system successfully  
106 depolymerized lignin to vanillin, 4-phenyl-1-buten-4-ol, and vanillic acid, with yields  
107 higher than Bi-TiO<sub>2</sub> and Pt-TiO<sub>2</sub>. Bi and Pt loaded on TiO<sub>2</sub> would result in the  
108 production of O<sub>2</sub><sup>•-</sup> instead of highly oxidative radicals' success <sup>•</sup>OH. Preferably, O<sub>2</sub><sup>•-</sup>  
109 (0.89 V, vs SHE) is less oxidative than <sup>•</sup>OH; hence O<sub>2</sub><sup>•-</sup> is likely to be more selective  
110 towards aromatic monomers than radicals <sup>•</sup>OH. Overall, the 1% Bi/Pt1%-TiO<sub>2</sub> system  
111 produced the highest conversion and yield of guaiacol of 84.5%, with 22.7%,  
112 respectively. Metal sulfides have also been used to achieve key platform chemicals,  
113 which were extensively reviewed. The described sulfide photocatalysts encompass  
114 binary sulfides (CdS and ZnS) and multinary sulfides (like Zn<sub>1-x</sub>Cd<sub>x</sub>S and Zn<sub>m</sub>In<sub>2</sub>S<sub>m+3</sub>).  
115 The most extensively studied metal sulfide photocatalyst for biomass valorisation is  
116 undoubtedly CdS, which has a bandgap of 2.4 eV and is responsive to visible light  
117 (>520 nm). But during the photocatalytic process, sulfide photocatalysts experience  
118 photo-corrosion, which needs greater attention in future studies. Liu and colleagues (Liu  
119 et al. 2012) observed an improvement in performance towards the conversion of  
120 different model lignin compounds using 1D CdS@TiO<sub>2</sub> over CdS nanowires as  
121 compared to using CdS catalyst only. The 1D CdS@TiO<sub>2</sub> composite semiconductor  
122 nanoparticle system converted 34% benzyl alcohol, 39% 4-methoxyl benzyl alcohol,  
123 and 41% 4-methyl benzyl alcohol, compared to 13%, 21%, and 7% for CdS nanowires,

124 respectively. The plausible performance in the 1D CdS@TiO<sub>2</sub> compared to the 1D CdS  
125 NWs is ascribed to the extended prevalence of O<sub>2</sub><sup>•-</sup> and photoinduced electrons in the  
126 1D CdS@TiO<sub>2</sub> than the 1D CdS NWs. Notwithstanding this progress, the application of  
127 photocatalysis alone systems for lignin depolymerization have not been realized for  
128 large scale production. Carbohydrates have, over the years, been desirable substrates  
129 for producing high-value chemicals and fuels (H<sub>2</sub>). The initial stage in hydrogen  
130 production on metal (such as Pt) loaded TiO<sub>2</sub> is the photocatalysis-driven conversion of  
131 cellulose to glucose (Caravaca et al. 2016). The challenge of photoreforming biomass in  
132 water is difficult due to the strict pH demand. Hence, to achieve photo-reforming of  
133 cellulose, a simple one-pot strategy was reported by Zou et al. (Zou, Zhang, and Xu  
134 2018). Their study used 0.6M sulphuric acids to hydrolyse cellulose at 130°C under UV  
135 photocatalysis with platinized TiO<sub>2</sub>. The in-situ production of electron donors stimulates  
136 direct conversion since the converted products are acceptors, and donors, with low  
137 oxidative power. A novel plasmonic nanostructure made of TiO<sub>2</sub> nanofibers (NFs)  
138 supported H-form Y- zeolites (HY) embellished with Au-NPs (Au-HYT) was employed  
139 (Wang et al. 2015). At 130 °C for 24 hours under mild conditions, the yield of glucose  
140 and 5 hydroxymethylfurfural (HMF) was greater than 60%. The cellulose conversion  
141 process is greatly aided by the localized surface plasmon resonance (LSPR) action of  
142 Au-NPs and the HY's potent acidity. Significant studies have also been done to study  
143 other carbohydrates products as explicitly detailed in **Table 1**. While cellulose has  
144 received significant attention to produce H<sub>2</sub>, lignin has received little attention using  
145 TiO<sub>2</sub>-based photocatalyst. However, the transformation of lignin to H<sub>2</sub> has been reported  
146 to work well using metallic sulfides as photocatalysts. Li et al. (Li et al. 2018) reported  
147 the activity of NiS (20% loading)/CdS is 5041 times higher with apparent quantum

148 efficiency (AQE) of 44.9% than pristine CdS when the lignin and lactic acid acting as a  
149 hole scavenger.

**Table 3:** Application of TiO<sub>2</sub>-based catalysts on photocatalytic biomass conversion

Substrate	Catalyst	Solvent	Light source	Reaction conditions	Product	Yield	Sel. (%)	Reference
Cellulose	TiO <sub>2</sub> -S-Ni	H <sub>2</sub> O	Xe lamp 500 W	80°C, N <sub>2</sub> , 3h	H <sub>2</sub>	ND	181.2 µmol	(Hao et al. 2018)
Cellulose	TiO <sub>2</sub> (Pt)	H <sub>2</sub> SO <sub>4</sub>	Iron doped halide lamp 250 W	130°C, Ar, 10h	H <sub>2</sub>	ND	123 µmol	(Zou, Zhang, and Xu 2018)
Cellulose	Pt/TiO <sub>2</sub>	H <sub>2</sub> O	UV-A irradiation (4*15 W)	ND, N <sub>2</sub> , 4h	H <sub>2</sub>	ND	54 µmol	(Speltini et al. 2014)
Lignosulfonate	TiO <sub>2</sub>	H <sub>2</sub> O	Xe lamp 300 W	r.t., ND, 1h	Guaiacol	ND	8.7	(Gong, Imbault, and Farnood 2017)
Lignin (1g/L)	TiO <sub>2</sub> Laccase H <sub>2</sub> O <sub>2</sub> (5.55g/L)	Sodium acetate buffer solution (pH 5.0)	UV (315–400 nm)	rt, ND, 24h	Organic acids Fatty acids carbohydrates	ND	ND	(Kamwilaisak and Wright 2012)
Lignosulfonate (100mg/L)	Bi1%/Pt1%-TiO <sub>2</sub>	H <sub>2</sub> O	Xe lamp 300 W	rt, ND, 1hr	Guaiacol	22.7%	ND	(Kamwilaisak and Wright 2012)
Organosolv black liquour (50mL)	TiO <sub>2</sub>	60% (v/v) ethanol Solution, H <sub>2</sub> SO <sub>4</sub> added (pH 2)	300W UV	rt, ND, 0.5h	Syringaldehyde Vanillin Syringol Pirocatechol Sinapylaldehyde Oil	20% oil	ND	(Prado, Erdocia, and Labidi 2013)
1:1 w/w lignin TiO <sub>2</sub> ball milled mixtures (0.4 g)	0.4 g of 1:1 w/w ligninTiO <sub>2</sub> ball milled mixtures	H <sub>2</sub> O	125 W High pressure mercury light	rt, ND, 6h	Ethyl benzene acetovanillone, acetosyringone, syringaldehyde, vanillin,	ND	ND	(Nair, Dhar, and Vinu 2016)

ND-no data

### 1 **3.3. Operating factors for biomass conversion**

2 Photocatalytic conversion of lignin depends on factors such as pH, temperature, type of  
3 solvent, treatment time, and type of photocatalyst, among other factors. Fundamentally,  
4 these tuneable factors can broadly be studied through the (i) identification of solvents  
5 capable of reducing complex interlinkages, (ii) identification of novel and highly  
6 selective photocatalytic systems adapted to biomass chemical structure (iii)  
7 identification of biomass activation strategies (Chatel, De Oliveira Vigier, and Jérôme  
8 2014). These factors affect product yield, selectivity, and biomass conversion to value-  
9 added products (Colmenares, Varma, and Nair 2017; Nair, Dhar, and Vinu 2016). The  
10 appropriate design of parameters affecting photocatalysis could open doors for  
11 developing new and efficient/eco-friendly strategies for high-value chemicals from both  
12 carbohydrate and lignin biomass fractions.

13 The optimal selection of solvents plays a significant role in the photocatalytic  
14 conversion of biomass. An ideal solvent in the best-case scenario must possess  
15 characteristics such as (a) does not act as a photocatalysis quencher or a strong light  
16 absorber; (b) easily dissolves biomass (c) is recyclable, reusable, and non-toxic, and (d)  
17 inert to prevent wearing (Raikwar, Majumdar, and Shee 2021; Xiang et al. 2020).  
18 Unlike liginosulfonates made by the sulfite process, kraft lignin, for example, is difficult  
19 to dissolve in water but is easily soluble in highly alkaline conditions (Colmenares,  
20 Varma, and Nair 2017; Nair, Dhar, and Vinu 2016). Han et al. (Han et al. 2019), in a  
21 similar study, recorded almost a 100% yield and selectivity of 2-phenoxy-1-  
22 phenylethanone (PP-one) from 2-phenoxy-1-phenylethanol (PP-ol) under visible  
23 conditions (440–460 nm) and Ni/CdS as the catalyst. Mechanistically, it was clear that  
24 the outstanding performance in this system is linked to the excellent solubility of PP-  
25 one in pure Acetonitrile (MeCN) permitting enhanced dissociation on the surface of

26 Ni/CdS catalyst. Interestingly, by carefully changing the solvent mixture, MeCN/H<sub>2</sub>O  
27 (v/v = 2:8), PP-one (yield=47%) with other products such as phenol (yield=52%) and  
28 acetophenone (yield=51%) were formed. This clearly shows that pH also plays an  
29 advanced role during depolymerization reactions. According to Kitano et al. (Kitano et  
30 al. 2014), increasing pH in the presence of -OH anions produces highly oxidative •OH  
31 species by scavenging photogenerated rhodium ion-modified TiO<sub>2</sub>.

32 Aside lignin related studies, Colmenares et al. (Colmenares, Magdziarz, and  
33 Bielejewska 2011) reported the conversion of glucose to arabitol, glucaric acid, and  
34 gluconic acid using TiO<sub>2</sub> as a photocatalyst under UV light irradiation. The  
35 photocatalyst type, reaction time, and solvent all impacted the selectivity and  
36 conversion of glucose. For instance, when the ratio of acetonitrile and water was  
37 changed (1:9 and 1:1), selectivity of organic compounds of 39.3% and 71.3% were  
38 achieved, respectively.

### 39 **3.4. Technical challenges**

40 Though some progress have been made so far (especially using model lignin), the sole  
41 application of photocatalysis for biomass conversion still poses some significant  
42 challenges, especially the application of photocatalysis for the depolymerisation of  
43 lignin. TiO<sub>2</sub>'s broad use as a photocatalyst has two key limits that confine its  
44 photocatalytic proficiency: (1) photogenerated electron-hole pairs recombine very fast,  
45 (2) a large bandgap of TiO<sub>2</sub> causes only 3 to 5 % of the available solar spectrum to be  
46 used for photocatalysis (Du et al. 2016; Hussain et al. 2017). Therefore, further research  
47 should be targeted at developing mild or innovatively coupling green strategies to  
48 produce lignin-derived platform chemicals from lignin (Questell-Santiago et al. 2020;  
49 Shivhare et al. 2021; Wan and Lee 2021). Therefore, exploring a novel synergetic

50 approach or highly selective catalyst to enhance both the pretreatment and cracking  
51 steps is critical for the large-scale application of photocatalysis. New strategies are  
52 needed to improve the intimate contact between the solid catalyst and solid native lignin  
53 or lignocellulosic biomass (Renders et al. 2019). Regarding lignin, firstly, selective  
54 cleavage of certain bonds has been predominantly studied using lignin model  
55 compounds, which may not fully represent the structure of technical and native lignin.  
56 The target of most depolymerization studies has been limited to the cleavage of C-O  
57 ether bonds due to their higher amount and low energy requirements relative to C-C  
58 (Wan and Lee 2021). Currently, problems such as robust reaction conditions,  
59 unselective, poor bond cleavage, and numerous reaction steps are problems facing C-C  
60 bond cleavage (Questell-Santiago et al. 2020). However, one-step/one-pot  
61 depolymerization of both C-O and C-C bond appear fascinating, which could enhance  
62 selective cleavage and full utilization of lignin (Nguyen, Murray, and Knowles 2019).

#### 63 **4. Sonophotocatalysis for biomass conversion**

##### 64 **4.1. Principle of ultrasonic cavitation**

65 Ultrasound is an emerging technology for chemical and processing applications referred  
66 to as sound waves described by frequencies exceeding 20 kHz working in specific  
67 media (Meroni et al. 2021; Harifi and Montazer 2015). It can be described by low- (20-  
68 100 KHz, i.e., wavelengths in water in the 7.4-1.5 cm interval), intermediate- (100 KHz  
69 – 1 MHz, corresponding to 15-1.5 mm wavelength window in water medium), and  
70 high- (1-10 MHz, i.e., wavelength lower than 150  $\mu\text{m}$  in water) frequencies. Ultrasound  
71 can break the cell wall, successfully inducing natural product component extraction  
72 processes (Ruiz-Jiménez, Priego-Capote, and de Castro 2004; Cravotto et al. 2008). In  
73 particular, ultrasound cavitation is a unique physical phenomenon induced by the

74 propagation of an ultrasound wave in liquid media. In this case, the ultrasound waves  
75 cause the growth of bubbles thanks to the nucleation of existing gas bubbles or gaseous  
76 sacs present at the surfaces of solid impurities; in turn, an oscillatory pressure field is  
77 applied to the resulting bubbles. This latter generates high-pressure cycles, compressing  
78 the gas within the bubble, and low pressure causes the forced expansion of the bubble.  
79 The ultrasound field induces the bubble growth according to the rectified diffusion of  
80 the dissolved gases and solvent to the bubble oscillation and coalescence (Wood, Lee,  
81 and Bussemaker 2017). Once a bubble achieves the resonance size, it grows to a  
82 maximum in the acoustic cycle due to its strong coupling to the acoustic field (Xu,  
83 Zeiger, and Suslick 2013). Then, the bubble implosion occurs together with the  
84 consequent fragmentation into smaller bubbles, which can dissolve or repeat the process  
85 (**Figure 2**). The above phenomenon of ultrasound-induced nucleation, growth, and  
86 collapse of bubbles is called acoustic cavitation (Mason et al. 2011).

87 In this context, each bubble can continue its growth-collapse cycle without fragmenting  
88 or giving only single bubble cavitation. The collapsing effect results in heat generation  
89 in the liquid medium, causing adiabatic heating of the bubble content (Schanz et al.  
90 2012). In this frame, high values of temperature and pressure are achieved, inducing the  
91 formation of radical species (e.g., hydroxyl radicals formed *via* decomposition of water  
92 molecules), giving rise to sonochemical reactions (Mahamuni and Adewuyi 2010), or  
93 light emission (sonoluminescence) (Gao et al. 2020). In addition, shock waves in the  
94 liquid medium can be created thanks to the bubble implosion: these can induce mass  
95 transfer by turbulent mixing or the sonofragmentation due to the acceleration of  
96 suspended solid particles (Kim and Suslick 2021).

97 In the case of an asymmetric bubble collapse at either the boundaries or surfaces of  
98 solids, liquid jets of high speed (also named microjets) can be propagated from the

99 bubble to the surface, causing surface erosion, pitting, and deformation (**Figure 3**).

100 Besides that, microjets can also be exploited for metal surface activation and surface  
101 engineering. Eventually, the ultrasound irradiation, which occurs during the  
102 crystallization step, can result in the sonocrystallization, i.e., the crystal seeds generation  
103 that causes the decrease of the induction time together with the increase of the  
104 crystallization yield and promotion of the selectivity to the desired morphology of the  
105 crystals (Ruecroft et al. 2005; Sander, Zeiger, and Suslick 2014).

106 Considering all these premises, an evident complexity related to the cavitation  
107 phenomenon emerges. Indeed, different experimental parameters need to be  
108 appropriately optimized to develop a specific application with the lowest operating costs  
109 possible.

110 In this context, the frequency of the sound field is the first point to analyze: the higher  
111 the frequency, the higher the number of cavitation bubbles, and the smaller the average  
112 bubble size. In other words, the higher frequency entails a short phase of expansion  
113 during the oscillation growth. This leads to a lower vapor in the bubbles, so smaller  
114 bubbles are present (Yasui 2002). Then, the higher the frequency, the shorter the  
115 oscillating period: this directly impacts the collapse and fragmentation phases, which  
116 are quicker. These phenomena strongly affect cavitation activity. By way of example,  
117 the size of the collapsing bubbles influences the maximum temperature that can be  
118 achieved during the implosion step. Moreover, larger bubbles obtained at lower  
119 frequencies contain more vapor because of the longer acoustic period (Yasui 2001). In  
120 this way, the heat consumption by the endothermic chemical reactions causes the  
121 decrease of the collapse temperature at low frequencies (Ashokkumar 2011). Therefore,  
122 the composition of the vapor in the bubble and the collapse temperature have a  
123 fundamental role in determining the number of radicals formed during the bubble

124 collapse (Yasui et al. 2007). In this context, it thus emerges that the number of radicals  
125 formed *per* collapsed bubble is more significant at lower frequencies, even if the radical  
126 yield also depends on the whole number of bubbles, which is higher by increasing the  
127 frequencies.

128 Another point, which deserves to be considered, is the prevalence of physical or  
129 chemical effects. Indeed, when frequencies are in the 20-100 kHz range, cavitation  
130 bubbles are few, but they possess large sizes. Thus, cavitation mainly produces physical  
131 effects on liquid circulation and turbulence, and chemical effects are negligible. In  
132 particular, the decrease in the intensity of the cavitation collapse is observed with the  
133 increase in the ultrasound frequency (Mason and Lorimer 2002). In this case, larger  
134 intensities are needed to induce the cavitation phenomenon.

135 In the depicted scenario, it thus emerges that low frequency is preferred when intense  
136 physical effects are required (i.e., extraction, cell disruption, or polymer degradation).  
137 Then, when frequencies are higher than 500 kHz, the increasing bubble number  
138 promotes the overall radical yield, and the chemical effects prevail (Sancheti and  
139 Gogate 2017). Eventually, the frequency values between a few hundred kHz and 1 MHz  
140 are selected for chemical syntheses and pollutant degradation in wastewater  
141 degradation. In these cases, the optimal frequency is the result of the balance between  
142 chemical and physical effects (Sancheti and Gogate 2017).

#### 143 **4.2. Ultrasonic pretreatment of biomass**

144 The conversion of biomass into high-value products by ultrasonic treatment would face  
145 several problems and challenges, most of which are listed as follows:

146 - Crude biomass exhibits a very recalcitrant structure due to the reticular connection of  
147 lignin, which requires strong solvents and harsh and costly operating parameters (Yu,  
148 Lou, and Wu 2008; Huber, Iborra, and Corma 2006).

149 - Raw biomass from different regions and resources exhibit different chemical  
150 compositions or uncertain ratios of lignin, cellulose, hemicellulose, sugars, proteins, and  
151 other traces of organic/inorganic constituents (Chemical, Biofuels, and Huber 2008).  
152 This matter makes biomass conversion at a large scale more challenging/complicated,  
153 and several in situ analysis and modifications in the conversion processing are required.

154 - The selectivity of catalytic processes to produce the desired chemicals and fuels is  
155 very challenging because of the complicity and sensitivity of catalytic processes  
156 themselves and the heterogeneity of raw biomass, as mentioned above (Friend and Xu  
157 2017; Bayu, Abudula, and Guan 2019). The catalytic materials type also could affect  
158 biomass conversion's selectivity (Dutta 2012; Dusselier et al. 2015).

159 - Low mass transfer between catalytic materials and biomass mass is a severe issue. In  
160 addition, biomass conversion has low thermal conductivity (Mettler, Vlachos, and  
161 Dauenhauer 2012; Lifka and Ondruschka 2004).

162 - The high cost of biomass treatment could be a critical problem for transferring this  
163 technology because of the use of a lot of energy and reagents/solvents to carry the  
164 biomass conversion.

165 - The extraction of the final products from the mixture is also challenging. The recovery  
166 of catalysts and the removal of solvents would affect the degree of the purification of  
167 final products.

168 In this section, the role of the ultrasonic process in assisting biomass conversion into  
169 high-value products or as a pretreatment approach will be addressed. Ultrasonic  
170 cavitation can assist biomass conversion as it can deliver to the medium an exceptional  
171 condition by providing chemical and physical effects (Ensminger and Bond 2011;  
172 Meroni et al. 2021). In the cavitation field, the lignocellulosic biomass undergoes facile

173 fragmentation and transformation into the desired products within a lesser reaction time.  
174 The ultrasonic vibration can boost the mass and heat transfer between the catalysts and  
175 the biomass constituents, allowing a faster conversion and use of less catalyst quantity  
176 and less solvent (Lu et al. 2016; Luo, Fang, and Smith Jr 2014). Ultrasonic vibration  
177 can boost the interaction of intermediates to form the final products.

178 The bubbles collapsing on the surface of solids in water can produce high temperatures  
179 and high pressure, which ensures different physicochemical effects. In terms of  
180 chemical effects, free hydroxyl radicals can be generated due to the breaking down of  
181 H<sub>2</sub>O molecules. Such radicals can participate in the oxidative conversion of biomass. In  
182 contrast, the physical effect can be applied to promote biomass's dissolving and  
183 enhance mass transfer (Bussemaker and Zhang 2013; Ebringerová and Hromádková  
184 2010). Water or solvent circulation around the catalysts and biomass is significantly  
185 enhanced due to generated pressure from the cavitation. Several reports mentioned  
186 cavitation is a critical factor in boosting the delignification and relocalization of biomass  
187 (Iskalieva et al. 2012).

188 The ultrasonic process has been associated with different techniques for biomass  
189 conversion and mainly provides the same physicochemical environment, which boosts  
190 any catalytic process. Of these combinations, we might cite ultrasound-assisted  
191 biological biomass conversion (Bundhoo and Mohee 2018), ultrasound-assisted  
192 electrochemical biomass conversion (Neha et al. 2020), ultrasound-assisted Fenton  
193 biomass conversion (Zhang et al. 2016), ultrasound-assisted acid hydrolysis biomass  
194 conversion (Bizzi et al. 2019), ultrasound-assisted metal-based catalytic biomass  
195 conversion (Chai et al. 2021; Guldhe et al. 2014), and ultrasound-assisted photocatalytic  
196 biomass conversion (Guldhe et al. 2014).

### 197 **4.3. Effect of cavitation on the photocatalytic biomass conversion**

198 As mentioned above, biomass conversion by heterogeneous catalysts suffers from low  
199 mass transfer and the requirement to use organic solvents to enhance the contact and  
200 dissolution of biomass for effective conversion. However, these conditions result in  
201 different issues, including the difficult extraction of the final products, contamination of  
202 final products, possible interaction of solvents with intermediates (inhibition of  
203 conversion process) or scavenging of photogenerated reactive oxygen species (ROSs),  
204 and then, of course, the high cost of the valorisation. However, combining ultrasonic  
205 with photocatalysis for biomass conversion would solve many issues and boost the  
206 conversion in terms of the high yield of desired products, better quality, and low cost  
207 (Chatel et al. 2017). Because of the violent physical effect of the ultrasonic vibration,  
208 water can be used instead of organic solvents to dissolve the biomass.

209 Under ultrasonic vibration, biomass hydrolysis can be enhanced several times,  
210 facilitating its conversion into high-value products. This behaviour is essential in  
211 catalytic and photocatalytic processes toward biomass valorisation. In terms of  
212 catalysis, many reports concluded that the presence of ultrasonic vibration during the  
213 catalytic conversion of biomass is a significant factor that boosts biomass conversion. It  
214 was reported that the acid hydrolysis of palm oil to xylose was improved more than  
215 twice in the presence of ultrasonic cavitation (Yunus et al. 2010).

216 In photocatalysis, dissolved oxygen in the medium can have two roles in biomass  
217 conversion, positive and negative. The conversion of  $O_2$  by photogenerated electrons  
218 produces superoxide radicals ( $\cdot O_2^-$ ) which participate in the oxidation and fragmentation  
219 of biomass into desired products. On the other hand, too many ROSs, including  $\cdot O_2^-$   
220 species, can reduce the selectivity via unwanted oxidation of intermediates into fewer

221 value products or CO<sub>2</sub>. One of the roles of the ultrasonic process is to reduce the content  
222 of O<sub>2</sub> in water because of the cavitation effect.

223 Ultrasonic cavitation can enhance the surface area of the catalysts and allows better  
224 dispersion. Hot spots can be produced on the surface of the catalyst at a temperature of  
225 5000°C and 1000 bars, causing a jetting phenomenon that might generate a high  
226 velocity of up to 600 km/h (Giannakoudakis, Łomot, and Colmenares 2020), as shown  
227 in **Figure 3**. In general, water molecules can form a layer on the surface of the  
228 photocatalyst, which limits the surface reaction and mass transfer; therefore, organic  
229 solvents are primarily used to get fast reactions. However, in the presence of an  
230 ultrasonic field, this water molecules barrier can be broken due to hot spots and physical  
231 effects, allowing the use of water as a solvent (Giannakoudakis et al. 2019). Because of  
232 these synergistic effects, sonophotocatalysis offers enhanced biomass conversion as  
233 compared to single photocatalysis. Piyali et al. reported that lignin depolymerization by  
234 sonophotocatalysis was 2.7 times superior to photocatalysis (Dhar, Teja, and Vinu  
235 2020). As shown in Figure 6, both the yield and number of products can be improved  
236 because of synergistic effects. Four products were found in sonophotocatalysis with a  
237 total yield of 67 mgL<sup>-1</sup>, against only two products with a total yield of 40 mgL<sup>-1</sup>.

## 238 **5. Research needs and future directions**

239 To intensify the photocatalytic process, the involvement of ultrasonic vibration with the  
240 photocatalytic conversion of biomass brings several advantages. It would make the  
241 process more effective and sustainable on a large scale. From the kinetics point of view,  
242 the photocatalytic process can be enhanced by improving the mass transfer because of  
243 the effect of shock waves and jetting phenomena, promoting the mixing of the  
244 photocatalyst with biomass, as well as improving the transfer of ROSs to the biomass

245 matter. Ultrasonic ROSs production can participate directly in the oxidation process of  
246 biomass and radical intermediate formation. Ultrasonic fields can control the dissolved  
247 oxygen in the medium, which is very beneficial for photocatalytic biomass conversion.  
248 In general, biomass should be dissolved in organic solvents to allow its fragmentation  
249 and conversion by photocatalytic means; however, using solvents is not recommended  
250 from a sustainable and economic point of view. On top of that, the presence of solvents  
251 could play the role of ROSs scavenger; interaction with radical biomass intimidates,  
252 reducing the quality of the final products. Also, separating some products from solvents  
253 might be difficult at the end of the conversion. The presence of ultrasounds can allow  
254 the use of water as a solvent, as the produced heat and shock waves can lead to excellent  
255 biomass dissolution in water. The ultrasonic process makes shock waves, and heat can  
256 also clean the photocatalyst's surface. The photocatalytic conversion of biomass in the  
257 presence of ultrasonic vibration leads to an increase in yield and the variety of produced  
258 products since many transformation reactions are slow or difficult by single  
259 photocatalysis.

260 Several challenges are still facing the appropriate application of sonophotocatalysis for  
261 biomass conversion. The selectivity of the conversion is an essential factor that needs to  
262 be intensively investigated in future studies. The optimization parameters of the  
263 ultrasonic process to assist the photocatalytic biomass conversion is imperative, such as  
264 the intensity of ultrasound, the frequency, and the time. The geometry of  
265 sonophotocatalytic reactor is essential to obtain a homogenous reaction medium.  
266 Further studies on optimizing biomass dissolution in water by the ultrasonic process are  
267 highly recommended from the sustainable and large-scale application points of view.  
268 Even though many studies have been reported on sonophotocatalytic biomass  
269 conversion; however, a careful understanding of mechanisms is still required.

270 From a mechanistic perspective, understanding the conversion of biomass into the  
271 desired products is still under debate because of several factors. The biomass structure is  
272 not unique; therefore, the transformation and the obtained products would be different  
273 by changing the biomass support. Most reported studies have emphasized using model  
274 lignin which is easy to convert, and its mechanistic conversion would be understandable  
275 and unique in some cases. However, it is very challenging to understand the  
276 photocatalytic mechanistic pathways of native or/and industrial biomass conversion due  
277 to the complex structure and the formation of various radical intermediates. In this  
278 sense, it is expected that several side interactions among different radical intermediates  
279 would take place to form a variety of final products. Studying the selectivity of the  
280 photocatalytic and sonophotocatalytic processes towards the valorisation of native and  
281 industrial biomass should receive more attention. Even though sonophotocatalytic has  
282 proved to be an effective synergistic process to enhance biomass valorization, the  
283 negative side of ultrasonic vibration could be studied. Sonolysis, if not optimized, could  
284 probably lead to a considerable number of products because of the effective  
285 fragmentation of biomass. The effect of sonolysis on the plausible total mineralization  
286 of biomass to CO<sub>2</sub> could be checked during the photocatalytic experiments. A strong  
287 cavitation field could occur by ring-opening desired products into other ones. Finally,  
288 research studies regarding the commercialization/industrial aspects are highly  
289 recommended.

## 290 **6. Conclusions**

291 This review critically discusses the combining of ultrasonic and photocatalytic  
292 processes for biomass conversion into high-value products. Photocatalysis as a single  
293 process suffers from many issues, including low mass transfer, weak fragmentation and  
294 low yield of generated products. Several aspects that govern biomass transformation by

295 photocatalysis and sonophotocatalysis from the mechanistic and technical perspectives  
296 were discussed in this review. Based on the literature, further studies on the  
297 optimization of affecting factors and understanding the sonophotocatalytic biomass  
298 conversion mechanisms are still needed. Overall, sonophotocatalysis would be an  
299 attractive competitive option for biomass valorization into high products.

### 300 **CRedit authorship contribution statement**

301 **Ridha Djellabi:** Conceptualization, Writing – original draft, Writing – review &  
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303 **Dominic Aboagye, Melissa Greta Galloni, Vaibhav Vilas Andhalkar, Sana  
304 Nouacer:** co-writing and review.

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306 Contreras:** review & editing, Supervision, Validation, Visualization

307

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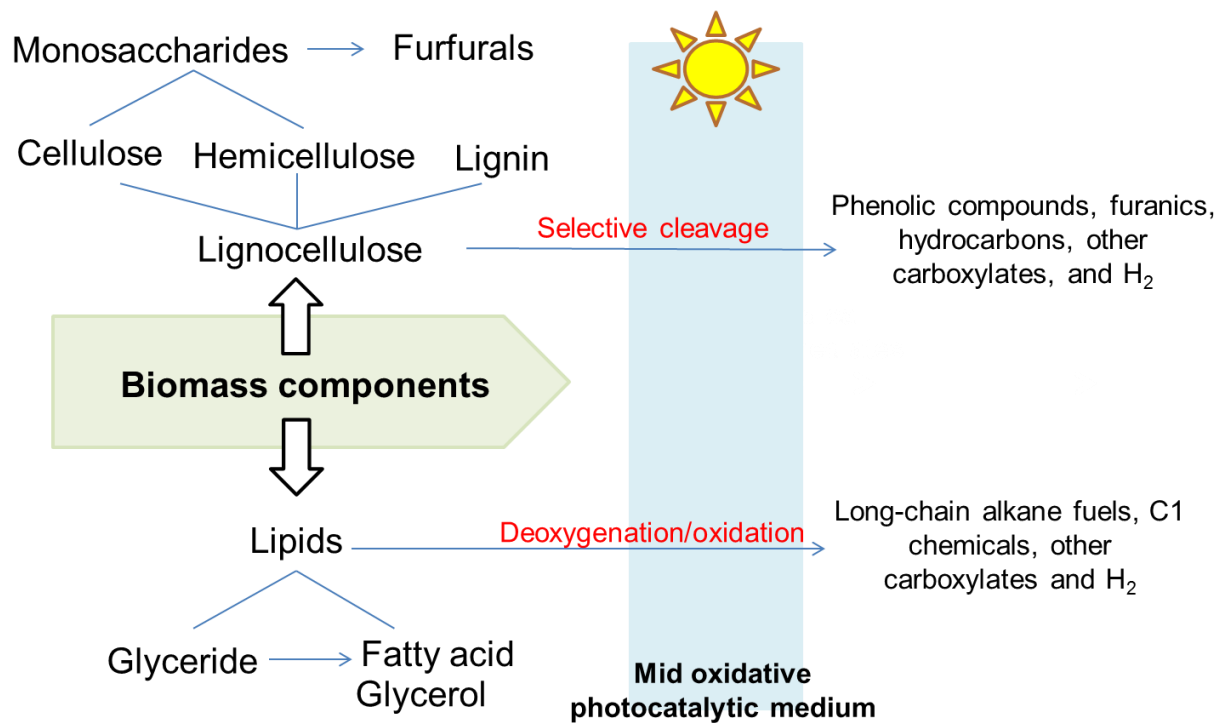
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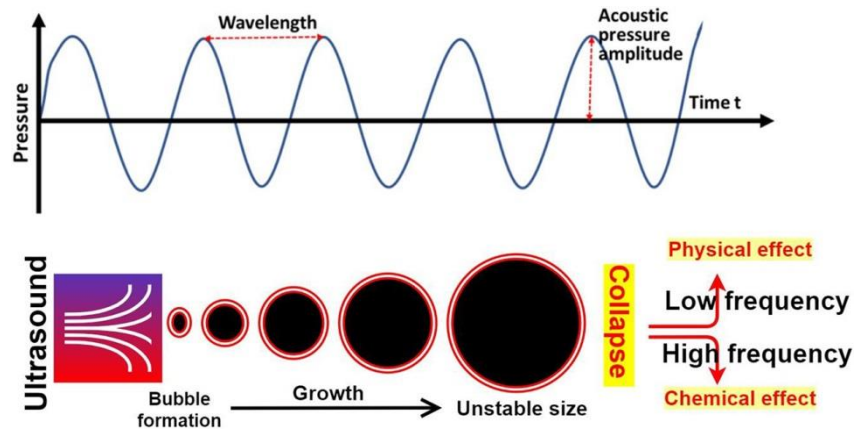
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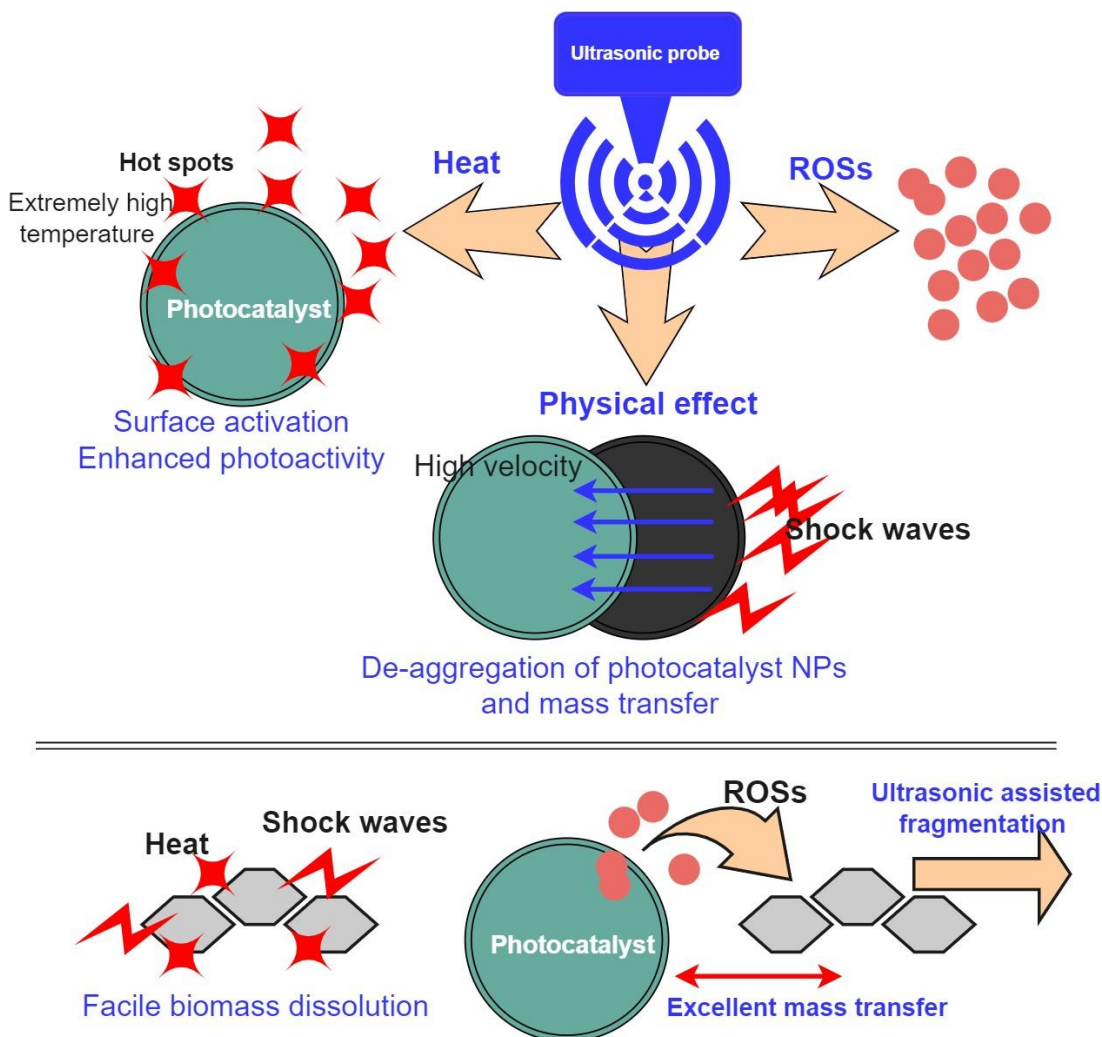
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**Figures**

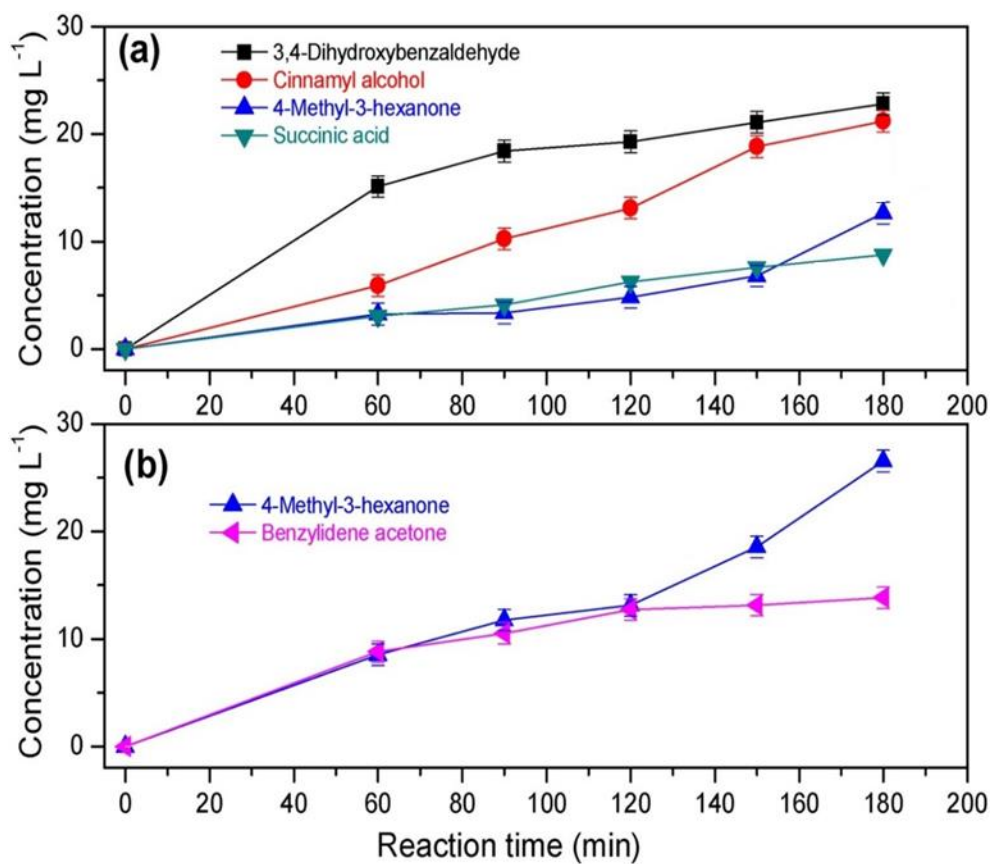
**Figure 1.** The scheme shows the photocatalytic production of various high-value products from biomass materials.



**Figure 2.** Scheme of the acoustic cavitation phenomenon, reproduced with permission from Ref (Meroni et al. 2021).



**Figure 3.** Main mechanisms of sonophotocatalytic biomass conversion: ultrasonic vibration could produce ROSs, physical vibration effect, and heat to boost the photocatalytic process; shock waves can promote the mass transfer through jet phenomenon, causing an effective de-aggregation of nanoparticles: shock waves can also assist the transfer of biomass molecules to the surface of photocatalyst for enhanced ROSs attack; the dissolution of biomass can be improved under ultrasonic vibration, and on top of that, water can be used instead of organic solvents by the force of cavitation and produced heat; ROSs produced from ultrasonic vibration can participate in the radical conversion of biomass; also, ultrasound can assist the interaction of radical intimidates and control the yield of dissolved oxygen.



**Figure 4.** Generated profiles obtained by sonophotocatalysis (a) and photocatalysis (b) in lignin depolymerisation, reproduced with permission from (Dhar, Teja, and Vinu 2020).

**Competing interests:** The author declares no competing interests.