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Role of advanced oxidation processes in lignocellulose pretreatment towards biorefinery applications: a review on emerging trends and economic considerations

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Renewable energy sources have been recognized as a viable alternative to fossil fuels. Among them, lignocellulosic biomass has emerged as a promising option for producing valuable bio-products, especially employing residual or waste material due to its consistency, reliability, local availability, and carbon neutrality. However, its efficient utilization is limited by the recalcitrance of cell walls, mainly caused by two chemical compounds, hemicellulose and lignin, reducing the accessibility to cellulose. Consequently, the hemicellulose and/or lignin in the cell wall need to be removed or rearranged to increase the accessibility to cellulose through the pretreatment of lignocellulosic biomass. Among the different pretreatments, oxidative processes efficiently enhance the digestibility of cellulose in lignocellulosic biomass, breaking down the complex structure of lignocellulosic biomass and making it more accessible for subsequent enzymatic or microbial degradation. Moreover, oxidative processes improve the reaction kinetics, are versatile in treating a wide range of lignocellulosic feedstocks, and reduce the generation of waste products. Therefore, this review aims to provide a detailed overview of the properties and composition of lignocellulosic biomass, its potential, and a comprehensive analysis of oxidative pretreatments, their advancements and recently developed innovative technologies. Furthermore, the application and economic feasibility of utilizing lignocellulosic biomass and the key obstacles hindering its widespread adoption are highlighted in this review.

1. Introduction

Excessive utilization of fossil fuels, rapid development of industrialization and growing human population have significantly increased the energy demand over the years. In this case, the use of renewables plays a major role in addressing the global challenges of climate change and energy security. Among the various renewable options, lignocellulosic biomass (LCB) appears to be fundamental in the transition towards a sustainable and low-carbon future due to several advantages such as:[1]

- it is versatile and reliable;
- it is not intermittent like wind and solar power;
- it can be stored and converted into various forms of energy, including heat, electricity, and biofuels;
- it can be easily integrated with existing infrastructure.

Another important benefit of biomass is its carbon neutrality. Indeed, different from fossil fuels, the combustion of biomass releases carbon that was absorbed during plant growth, establishing a carbon-neutral or even carbon-negative energy system, where the carbon emitted is offset by the carbon absorbed during the growth of new biomass feedstocks.[2] Additionally, biomass contributes to improving rural economies by promoting sustainable agriculture and local job creation. The local production of bioenergy strengthens regional economies while diminishing the socio-economic disparities between urban and rural areas. Finally, when residual biomass such as agricultural residues, forest thinning, and other organic waste, is employed, the waste to be disposed of in landfills is reduced, improving the circular economy in waste management. By effectively recovering this organic waste, it reduces methane emissions from decomposition while also decreasing the need for landfill expansion.

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Table 1 Composition of various sources of LCB feedstock materials[11–16]

LCB source	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Bamboo	26–47	17–24	18–36
Barley straw	28–46	17–38	6–19
Bermuda grass	26–48	13–37	10–20
Corn stalk	35–50	17–39	7–59
Cotton stalk	39–67	12–23	13–19
Elephant grass	24–47	26–36	12–24
Hardwood (Poplar)	32–53	15–28	2–25
Oat straw	17–36	23–40	12–38
Rice husk	37–50	16–29	24–30
Rice straw	20–57	15–33	6–26
Rye straw	17–20	33–35	27–30
Softwood (Pine)	39–56	14–47	12–35
Sorghum straw	27–37	26–33	0.2–10
Sugarcane bagasse	20–43	12–45	11–30
Wheat straw	16–58	15–50	8–32

Typically, LCB is composed of 30–50% cellulose, 15–30% hemicelluloses and 10–30% lignin.[3] The typical composition of different LCB feedstock is reported in Table 1. To limit the recalcitrance of LCB due to the presence of hemicelluloses and lignin, it is usually pretreated to improve the digestibility of cellulose.[4] Physical and mechanical pretreatments, which aim to reduce the size, increase the surface area and reduce the degree of polymerization, enhance the effectiveness of bioconversion processes without producing toxic materials but have a high energy demand.[5] Physical methods can be combined with chemical processes, which use relatively high temperatures and pressures. Some physico-chemical pretreatments have the benefit of avoiding the use of chemicals or catalysts, such as liquid hot water pretreatment;[6] however, in general, they eventually generate inhibitory byproducts, require high investment and operating costs for high-pressure systems, and use chemical agents.[7] Alternatively, biological pretreatments, which employ lignocellulolytic microorganisms such as fungi and bacteria to break down the structure of biomass, are characterized by low energy demand and environmental impact, mild conditions, and no inhibitor generation during the process, but they are not still viable on a large scale due to their high cost.[8] Thus, in parallel with these pretreatments, the scientific community is also considering the possibility of lignin valorisation to produce chemicals or fuels by using ionic liquids and deep eutectic solvents.[9]

In this context, due to their relatively mild conditions, low-cost operation and reduced load of chemical reagents, oxidative pretreatments appear to be a promising solution to increase the digestibility of cellulose in LCB.[4] Initially, these processes were mainly employed for detoxification and for water, wastewater, and soil treatment, but due to their ability to promote the cleavage of chemical bonds within the lignocellulosic structure, they have been applied as pretreatments to enhance the overall efficiency and yield of bioconversion processes.[10]

For this reason, this review:

- Comprehensively discusses the properties and composition of LCB and
- Illustrates the research progress on various oxidative pretreatments together with some recently developed technologies and the primary mechanism of oxidative pretreatment to enhance cellulose digestibility.

Finally, we highlight the applicability and economic feasibility of LCB valorization and emphasize its major challenges together with future directions.

2. LCB: overview and its valorisation potency

The potential yearly production of total primary biomass is estimated to be 1260 EJ per year, which decreases to 200–500

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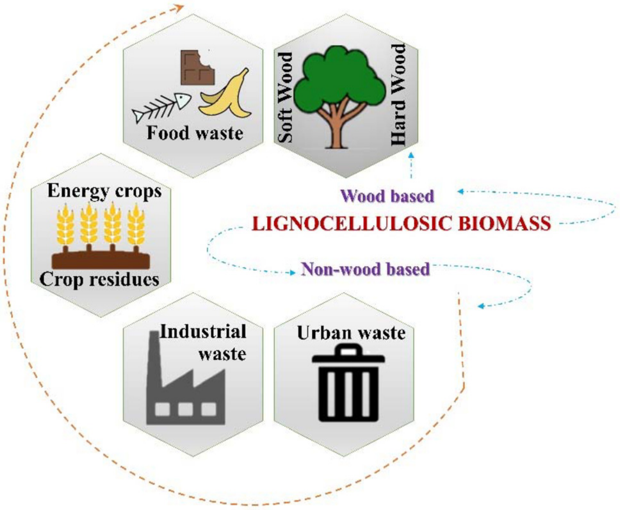

Fig. 1 Sources of LCB.

EJ per year[17] considering some constraints in its realistic technical availability and sustainable use, including socio-economic limitations and policy-drivers. Focusing on LCB, its content is estimated to be around 180–200 billion tons globally, although the literature highlights that more effort should be devoted to collecting data on a global scale as well as national and regional levels.[18,19]

Although biomass is recognized as a promising renewable source, bio-based products have not yet been completely integrated into society, which is possibly due to their relatively higher cost compared to fossil-based products.

As shown in Fig. 1 and 2, LCB includes various sources, such as forestry and agricultural residues, the organic fraction of municipal solid waste, and energy crops, and is primarily composed of carbohydrates (cellulose and hemicellulose) and lignin, with these three biopolymers arranged in non-uniform three-dimensional structures,[19] as follows:

- Cellulose, which makes up the majority of the carbohydrate content and forms long, oriented microfibrils that can combine to form longer and larger fibrils;
- Hemicellulose, which is composed of amorphous, branched polysaccharides that attach to the cellulose fibrils; and
- Lignin, which is a complex crosslinked macromolecule, binding the biomass structure together and strengthening the cell wall.

The composition and structure of these components vary depending on the type of biomass. The total carbohydrates (cellulose and hemicelluloses) account for about 70% of biomass, and their bonds with lignin contribute to the resistance of biomass to chemical and biological degradation.[20]

Consequently, pretreatments play a crucial role in enhancing the accessibility to the biomolecules in LCB. Indeed, due to its characteristics of hydrophobicity, enzyme adsorption, and heterogeneous composition, lignocellulose is highly recalcitrant to biological degradation by enzymes and micro-organisms, requiring high energy-demanding and costly pretreatments to enhance its chemical and physical characteristics for valorization.[16] The aim of pretreatments is to decrease the resistance of biomass by breaking down the complex structure of carbohydrates and lignin, deconstructing lignin and hemicellulose, increasing the surface area and porosity, and thereby enhancing the conversion efficiency.[21] However, it has to be considered that due to the different origins of biomass, its composition and structure may be diverse, requiring specific treatments, for example, woody biomass is more recalcitrant to enzymatic attack compared to herbaceous biomass, and thus requires more severe decomposition conditions.[22]

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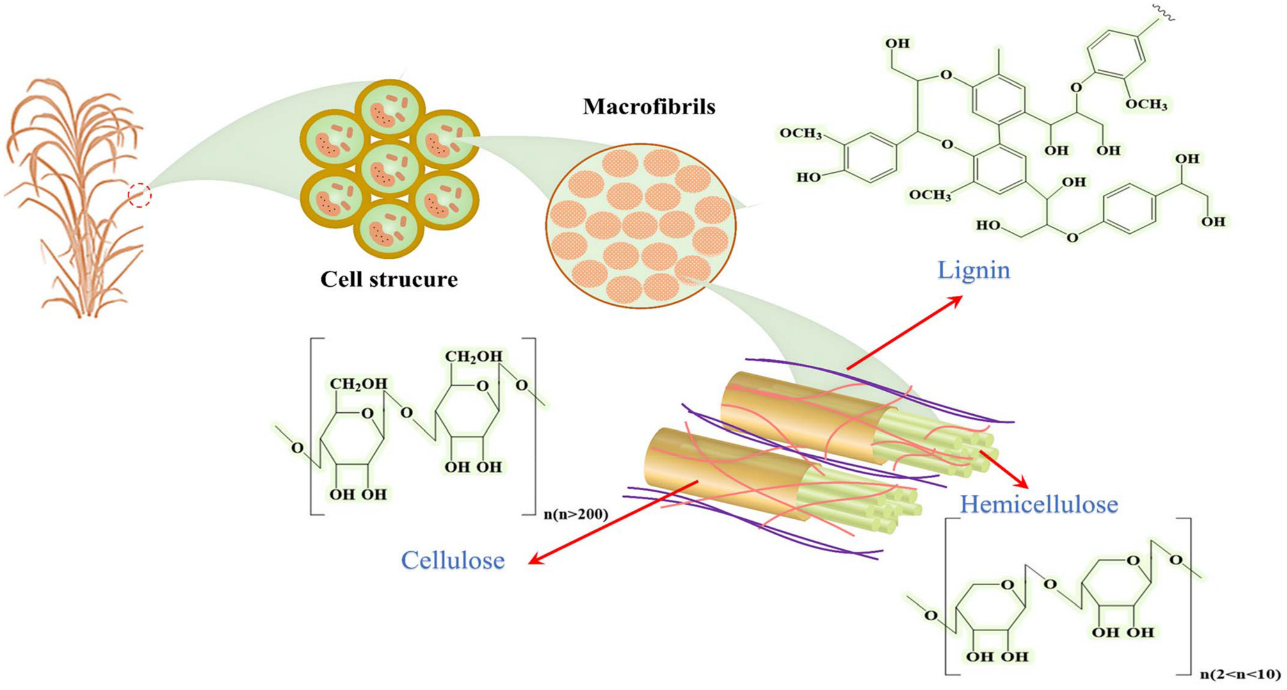

Fig. 2 Structure of LCB.

3. Advancement in oxidative pretreatment of LCBs

LCB, as a sustainable and renewable resource, holds immense potential for producing biofuels, biochemicals, and bioproducts. However, its complex structure makes it challenging to achieve efficient valorization processes. Recently, significant improvements have been made in developing oxidative pretreatments that effectively disassemble intricate lignocellulosic matrices, enhancing the accessibility to cellulose and hemicellulose.

These advanced oxidative processes, which can be divided into non-catalytic processes and catalytic systems, offer distinct advantages, such as mild operating conditions and cost-effectiveness.[23] In particular, the use of low-cost oxidizing agents and reduced quantity of chemical reagents has emerged as a favourable approach. These agents facilitate the formation of free radicals, which play a crucial role in the removal of lignin and enhancing the effectiveness of the treatment. A comparison of the sustainability of various oxidative pretreatments is presented in Table 2.

3.1. Wet air oxidation

Wet air oxidation (WAO) is based on the use of air in combination with water at elevated temperatures and pressures. Over time, WAO has been proven to be effective with various types of biomasses, making them more suitable for subsequent processing.[24] In particular, this process can break down biomass into two distinct parts, including a solid portion rich in cellulose and a liquid fraction consisting of water-soluble hemicellulosic sugars.[25]

The key parameters of WAO are the nature of the biomass followed by temperature, reaction time and air pressure. Commonly, this process is carried out at temperatures in the range of 125 °C to 200 °C with air pressures in the range of 0.3 to 3.5 MPa.[26] Although the temperatures employed in this method may seem high, the process is exothermic, thus guaranteeing a reduction in the energy required. Also, the intro-

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Table 2 Comparison of the sustainability of various oxidative pretreatment processes

		Sustainability aspect						
S. no	Oxidative pretreatment	Environmental impact	Energy consumption	Chemical usage	Byproduct generation	Catalyst recovery	Process complexity	Scale-up feasibility
1	Wet air oxidation	Moderate-high	High	Low	Organic acids, furans, phenols	—	Limited	Moderate
2	Photocatalytic oxidation	Moderate	—	Low	Reactive oxygen species	Yes	Moderate	Limited
3	Fenton oxidation	Moderate	—	Moderate	Iron sludge, acidic conditions	Limited	Moderate	Moderate
4	Hydrogen peroxide oxidation	Moderate	Moderate	Moderate	Metal containing waste	Limited	Moderate	Moderate
5	Peracetic acid oxidation	Moderate	Moderate-high	Limited	Acidic conditions	Limited	Moderate	Moderate
6	Persulfate oxidation	Moderate	Low	Moderate	Sulfate ions	Limited	Low-moderate	Moderate
7	Ozone oxidation	Moderate-high	Moderate-high	Moderate	Ozone byproducts	Limited	High	Limited
8	Sonochemical oxidation	Moderate-high	Moderate-high	Moderate	Oxidation byproducts	Limited	High	Limited
9	Electrochemical oxidation	Moderate	Moderate-high	Moderate	Oxidation byproducts	Yes	Moderate	Limited
10	Hydrodynamic cavitation coupled advanced oxidation process	Moderate-high	High	Moderate	Oxidation byproducts	—	Moderate-high	Limited
11	Radiation-induced oxidation	Moderate-high	Moderate-high	Low	Reactive oxygen species	—	Moderate-high	Limited
12	Reusable chemical oxidation	Moderate	—	Low-moderate	Reactive oxygen species	Yes	Moderate	Limited
13	Other combined oxidation process	Moderate	Moderate-high	Moderate-high	Oxygenated compounds	Yes	Moderate-high	Limited

duction of oxygen in the process leads to rapid degradation reactions, enabling the production of organic acids through hydrolysis and oxidative processes.[27] Furthermore, the use of high pressure enhances the solubility of oxygen, facilitating increased contact between oxygen and the treated organic matter, and thereby promoting an increase in the oxidation rate. In the WAO process, there are mainly two reaction outcomes, *i.e.*, complete oxidation, leading to the formation of CO_2 and H_2O as the final products, and partial oxidation, resulting in the production of intermediate organic compounds.[28] In this process, free radicals play a fundamental role, where their generation is favored by high-pressure and temperature conditions, and are essential for the subsequent destruction of lignocellulosic biomass. The formation of these radicals begins when oxygen reacts with the least stable CH bonds of an organic compound. The fundamental mechanism of this process is based on the generation and propagation of free radicals. Here, a detailed description of the reactions involved is presented, as follows:

- Generation of free radicals: initially, under high-pressure and temperature conditions, oxygen reacts with the weakest C–H bonds in organic compounds, generating free radicals. This process is described by the following reaction:

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \tag{1}$$

- Decomposition of hydrogen peroxide: the rapid decomposition of hydrogen peroxide (H_2O_2) produces hydroxyl radicals ($HO^{\bullet}$), which are highly reactive:

$$H_2O_2 + O_2 \rightarrow HO_2^{\bullet} + {}^{\bullet}OH \tag{2}$$

- Formation of peroxy radicals: organic radicals react with molecular oxygen to form organic peroxy radicals ($ROO^{\bullet}$):

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \tag{3}$$

- Hydrogen abstraction: organic peroxy radicals abstract a hydrogen atom from other organic compounds, forming organic hydroperoxides (ROOH) and new organic radicals:

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{4}$$

- Formation of additional radicals: hydroperoxy radicals ($HO_2^{\bullet}$) and hydroxyl radicals ($HO^{\bullet}$) interact with C–H bonds in organic compounds, generating further organic radicals:

$$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O \tag{5}$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2 \tag{6}$$

- Formation of stable products: the radicals formed react with each other to form stable products through covalent bond formation:

$$2ROO^{\bullet} \rightarrow ROOR^{\bullet} + {}^{\bullet}O_2 \tag{7}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{8}$$

These reactions illustrate how, through the propagation and interaction of various radicals, lignocellulosic biomass is gradually degraded into simpler and more stable compounds.

The use of catalysts and promoters can further facilitate these reactions, allowing a reduction in the high pressure and temperature conditions normally required for the process.[7] The chemical transformations involve all three key components within biomass.

Through solubilization and hydrolysis, hemicelluloses are fragmented into monomeric sugars, such as xylose and arabinose, which are characteristic products of this degradation and typically found in the liquid phase. In this case, the solubilization and hydrolysis rates are significantly influenced by the temperature and reaction time. Higher temperatures and longer duration tend to reduce the concentration of sugars, which is probably due to their decomposition under less favourable conditions. The temperature affects the solubility of oxygen, and with an increase in the saturated steam pressure above 100 °C, lignin removal is accelerated but the solubilization of hemicellulose is reduced. Longer reaction times favor the recovery of cellulose and lignin, whereas pressure has a minor impact on cellulose recovery but influences the solubilization of hemicellulose and removal of lignin.[29] Alternatively, lignin undergoes fragmentation and oxidative changes, ultimately decomposing into CO_2, water, and water-soluble carboxylic acids such as formic acid and oxalic acid.[30] Finally, cellulose is partially degraded, making it more susceptible to enzymatic hydrolysis.[31] Furthermore, high-temperature water acts as an acid agent, facilitating the hydrolysis of biomass through an increase in hydrogen ions and a subsequent decrease in the pH of the reaction mixture.[32]

WAO has been proven to be highly effective to separate rice straw components. The optimal conditions identified for this process include a temperature of 185 °C, an air pressure of 0.5 MPa, and a treatment duration of 15 min.[33] Under these conditions, 89% lignin was removed and 66.97% cellulose was recovered in solid form. Moreover, in the resulting liquid fraction, relatively high concentrations of glucose and xylose were achieved, even under mild pH conditions, which is favorable for subsequent fermentation processes.[34] The effectiveness of WAO was also demonstrated in a mixed LCB composed of rice straw and wheat straw in a 1 : 1 mass ratio.[35] The experiments were conducted by varying several key parameters, and the highest enzymatic conversion efficiency (63% by weight compared to 19% in the untreated biomass) was achieved after pretreatment under the conditions of 195 °C, 0.5 MPa bar and 10 min.

Another study[36] explored the application of WAO in common reed (*Phragmites australis*), achieving the most favorable outcomes at a temperature of 195 °C for a duration of 12 min. This treatment resulted in the solubilization of 51.7% hemicellulose and 58.4% lignin, with 87.1% cellulose remaining in its solid state. Subsequent enzymatic hydrolysis of the pretreated fibres using the same method resulted in a high conversion rate, with 82.4% cellulose transformed into glucose. In a study conducted by Irmak *et al.*,[28] the influence of temperature (150–250 °C) and pressure (500–1500 psi) on lignin depolymerization through WAO was investigated. Commercial alkali lignin was used as a representative sample, and the degradation/oxidation products of WAO treatment were identified to assess their potential. The depolymerization efficiency of alkali lignin was compared to that of lignins extracted from corn stover and cedar under identical WAO conditions. Isovanillic acid emerged as the primary product of WAO at 150 °C and oxygen pressure of 1000 psi. Elevated temperatures (200 °C and 250 °C) and oxygen pressures (1000 and 1500 psi) led to the generation of more oxidized products, predominantly carboxylic acid-derived compounds. The findings indicated that alkali lignin exhibited greater susceptibility to depolymerization compared to lignins derived from corn stover and cedar.

These findings underscore the versatility and efficacy of WAO in biomass fractionation and biofuel production. To degrade lignocellulose, a combination of several pretreatments can be integrated with WAO, such as chemical pretreatments like organosolv, alkaline treatment, and vapour explosion,[37–40] to increase the production of monosaccharides by enzymatic hydrolysis. Furthermore, the addition of catalysts can reduce the required operating conditions and increase the reaction rates. Generally, the lignin conversion rate and production of aromatic aldehydes are significantly higher when using catalytic procedures compared to non-catalytic techniques.[41] Alkali pretreatment can aid in the removal of lignin and uronic acid from hemicellulose with minimal damage to cellulose. Hydrogen peroxide possesses greater oxidative power than oxygen and can accelerate the degradation of lignocellulosic material.[42] Thus, wet air oxidation has emerged as a promising technique for the solubilization and subsequent oxidation of organic compounds using oxygen under high temperature and pressure conditions; however, its limitations, including high energy consumption and potential corrosiveness, raise critical questions about its long-term sustainability. A comparison of the sustainability of various pretreatment processes is provided in Table 2. Nevertheless, with the integration of new technologies and development of specific catalysts, coupled with the use of advanced predictive models, there is the potential to overcome these challenges, thereby expanding the application possibilities of WAO and enhancing its efficiency in environmental and industrial treatment scenarios.[43]

3.2. Photocatalytic oxidation

Photochemical mechanisms rely on the utilization of UV and visible light as an energy source. The absorption of UV light can cause the deterioration of biomass, although this process requires a significant amount of time.[44,45] Therefore, in the photocatalytic process, photocatalysts are employed to enhance the efficiency of biomass oxidation. Photocatalysts can be classified as heterogeneous or homogeneous.[46]

In reactions involving homogeneous photocatalysts, the photocatalysts and reactants coexist in the same phase, typically including soluble acids, bases, and transition metal compounds. However, despite their high photocatalytic activity, these catalysts are less utilized due to their high cost and difficult separation at the end of the process, often limiting their application in the conversion of lignin. In contrast, when heterogeneous photocatalysts are employed, these photocatalysts and the reactants are in different phases, thereby resolving the inherent separation issue in homogeneous systems. In heterogeneous photocatalysis, semiconductors are particularly significant due to the narrow bandgap between their valence and conduction bands.[47]

Heterogeneous catalysts include activated carbon-based materials, organometallics, and metallic sulfides. Among them, TiO_2 is favored due to its cost-effectiveness, stability, and availability; however, it primarily absorbs ultraviolet light. Consequently, researchers addressed this limitation by employing strategies such as metal and non-metal doping and surface modifications.[48]

Photocatalytic oxidation (PO) utilizes light to activate a photocatalyst, initiating specific chemical reactions. Photocatalysis occurs when a photocatalyst absorbs a photon with energy equal to or greater than its bandgap energy. The photocatalyst absorbs light in the visible and ultraviolet spectrum, creating excited electron–hole pairs, and leading to the generation of reactive oxygen species (ROS). ROS interact with the substrate adsorbed on the surface of the photocatalyst, facilitating the formation of essential free radicals such as alkyl radicals and hydroperoxides, which are crucial for biomass conversion (Fig. 3A).[49]

Indeed, when a photocatalyst (Z) absorbs a photon ($h\nu$), an electron (e^-) is excited from the valence band to the conduction band, resulting in the formation of a positive hole (h^+) in the valence band:

$$Z + h\nu \rightarrow Z(e^-) + Z(h^+) \tag{9}$$

The positive hole (h^+) in the valence band is highly reactive and can oxidize water (H_2O) or hydroxide ions (OH^-), producing hydroxyl radicals ($^{\bullet}OH$), which play a crucial role in the subsequent reactions:

$$Z(h_{VB}{}^+) + H_2O \rightarrow Z + {}^{\bullet}OH + H^+ \tag{10}$$

$$Z(h_{VB}{}^+) + OH^- \rightarrow Z + {}^{\bullet}OH \tag{11}$$

These hydroxyl radicals ($^{\bullet}OH$) are potent oxidizing agents that attack and oxidize lignocellulosic biomass, leading to its degradation:

$$^{\bullet}OH + LCB \rightarrow \text{oxidized } LCB^{\bullet} \tag{12}$$

Simultaneously, the excited electron (e^-) in the conduction band can reduce molecular oxygen (O_2) to form superoxide radical anions ($O_2{}^{\bullet-}$). These superoxide radical anions can be further reduced to form hydrogen peroxide (H_2O_2).

Hydrogen peroxide (H_2O_2) can react with superoxide radical anions ($O_2{}^{\bullet-}$) or electrons, generating additional hydroxyl radicals. These hydroxyl radicals ($^{\bullet}OH$) are highly reactive and can induce the complete or partial degradation of lignocellulosic biomass:

$$^{\bullet}OH + LCB \rightarrow \text{degraded } LCB^{\bullet} \tag{13}$$

In the absence of electron acceptors such as O_2 or H_2O_2, the electrons and holes within the photocatalyst can recombine, dissipating the absorbed radiation energy as heat, and thereby reducing the overall efficiency of the photocatalytic reactions:[50]

$$e^- + h^+ \rightarrow \text{heat} \tag{14}$$

The sustainability of PO is noteworthy, given that it operates at moderate temperatures (between 20 °C and 80 °C) and

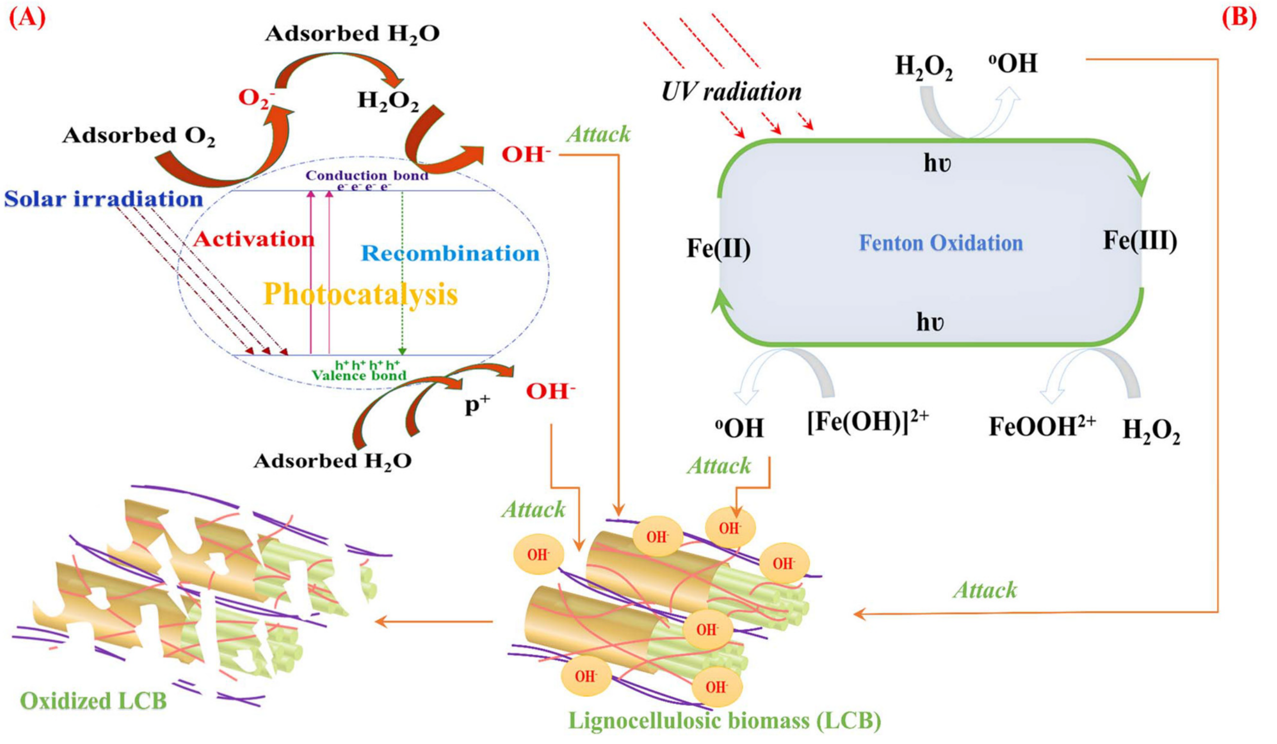


Fig. 3 Reaction mechanism of (A) photocatalytic oxidation and (B) Fenton oxidation.

pressures, it does not require toxic chemical reagents and it is associated with low energy consumption. In this case, selecting the appropriate light source is essential for maximizing the efficiency of the photocatalyst, while minimizing the energy consumption. Besides, optimizing the pH, reagent concentration, and reaction time is also important to enhance the product yields and minimize the generation of undesired byproducts.[50,51] Additionally, although not always required, the use of oxidizing agents, *i.e.* hydrogen peroxide (H_2O_2), oxygen (O_2), and persulfate ($S_2O_8{}^{2-}$),[52] can enhance the photocatalysis efficiency and process selectivity. H_2O_2 has been employed successfully for the selective oxidation of lignin, yielding phenols. Alternatively, O_2 has been utilized for the selective oxidation of cellulose, producing gluconic acid.[53] Persulfate can be employed as an oxidizing agent to enhance the efficiency of a photocatalytic reaction. Indeed, a study[54] demonstrated how persulfate facilitates the cleavage of the C–C bonds within lignin, promoting the generation of sulfate radicals. As a result of this process, valuable aromatic compounds were obtained.

The combination of photochemical oxidation and EO yielded synergistic effects, particularly in the oxidation of lignin into valuable products such as vanillic acid.[55] This approach is efficient to transform lignin into valuable chemicals. PO selectively breaks down lignocellulose, forming substrate-based radical intermediates engaged in various reactions, including single-electron and electron and proton transfer. These reactions play a crucial role in breaking the Cα–Cβ and C–O bonds, which is essential for lignin depolymerization, resulting in the production of smaller aromatic compounds such as coniferyl alcohol, catechol, and vanillic acid.[56] Pretreatment with an iridium-based photocatalyst led to the efficient breakdown of the β-O-4 bonds, followed by C–O bond cleavage, yielding benzoic acid and other products.[57] Further research demonstrated the formation of oxidative lignin products such as vanillic, ferulic, benzoic, and *p*-coumaric acids, comprising 85% of the detected lignin oxidation products, using laboratory-produced TiO_2.[58]

PO can be standalone or coupled. For example, combining hydrothermal oxidation and PO to treat corn stalks enhanced the extraction and modification of lignin.[59] Hydrothermal treatment made it easier to separate and utilize lignin, while preserving the integrity of cellulose. After PO, the modified lignin exhibited a smaller particle size, developed pore structure, and large content of carboxylic groups, resulting in a significant increase by six-fold in safranin-T removal, an indicator of pollutant removal efficiency.

Furthermore, PO of cellulose and hemicellulose involves glycosidic bond hydrolysis, yielding simple sugars such as glucose, xylose, and arabinose. This hydrolysis can be achieved through a combination of photocatalysts and acid catalysts under moderate conditions. In a study,[60] gold nanoparticles supported on active zeolitic catalysts efficiently absorbed visible light, directly activating the catalyst sites without the need for extensive solvent heating. This study investigated the impact of factors such as temperature, light intensity, and wavelength on the conversion of cellulose into valuable chemicals. Under moderate conditions, the glucose and hydroxymethylfurfural yields exceeded 60% at 130 °C for 24 h.

Another study focused on the conversion of rice husk[61] using UV light, TiO_2, and H_2O_2. The resulting organic molecules have various industrial applications and can serve as chemical raw materials. These organic molecules can be classified into alkanes, alkenes, arenes, non-substituted and substituted alkanols, alkenols, phenols, alkanals, alkenals, benzaldehydes, ketones, carboxylic acids, esters, phthalates, nitrogen-containing and sulfur-containing organic compounds, and other species. Among them, alkanes, phthalates, ketones, and fatty acids are relatively abundant. Non-aromatic species primarily result from the degradation of waxes, cellulose, and hemicellulose, while lignin may serve as a precursor for aromatic species. In a recent study by Cao *et al.*,[62] they evaluated the effectiveness of photocatalysis for the valorization of bast fibers. The findings demonstrated that photocatalytic degumming significantly reduced the β-O-4 and β–β bonds in the lignin of hemp fibers from 32.0% to 10.7% and from 6.8% to 3.4%, respectively. Additionally, there was an increase in non-conjugated carbonyl and carboxyl groups (C=O), indicating the formation of more carboxyl groups in lignin due to its oxidation by photocatalysis. The combination of lignin and $ZnIn_2S_4$ produced more $^{\bullet}O_2{}^{-}$ radicals compared to lignin or $ZnIn_2S_4$ alone. This was attributed to the reduced recombination of h^+ and photoelectrons when lignin acted as a sacrificial agent for h^+. The proposed mechanism for lignin removal involves the production of photoexcited holes upon the irradiation of both lignin and $ZnIn_2S_4$, which directly oxidize the lignin structure together with $^{\bullet}O_2{}^{-}$. Furthermore, enzymatic hydrolysis of the hemp fibers pretreated with photocatalysis yielded a higher glucose concentration (38.3 g L^{-1}) compared to the fibers pretreated without illumination (24.2 g L^{-1}). These results indicate that photocatalysis under moderate conditions has great potential for degumming bast fibers.

Photocatalysis offers an effective method for converting lignocellulose and its derivatives using solar energy. Recent advancements have optimized various semiconductors, such as TiO_2, WO_3, Fe_2O_3, CdS, and Cu_2O, for efficient lignocellulose conversion. Modification strategies, including crystal structure design and metal/non-metal doping, have further enhanced the light utilization and system performance.[63] However, despite these advancements, most research remains at the laboratory scale, highlighting the need for further efforts towards industrial application. Additional research is essential to identify suitable photocatalysts and operating conditions to maximize the efficiency of integrated systems for biomass conversion.[64]

3.3. Fenton oxidation

Fenton oxidation (FO) is based on the reaction between H_2O_2 and ferrous iron (Fe^{2+}) in an acidic environment,[44] as shown in Fig. 3B. This reaction generates highly reactive free radicals, including hydroxyl radicals ($^{\bullet}OH$), which can modify the intricate structure of lignocellulose, as shown in Fig. 3B.

Consequently, hemicellulose and lignin are eliminated, while the accessibility to cellulose for subsequent enzymatic hydrolysis stages is enhanced.[65] The effectiveness of FO is influenced by parameters such as temperature, pH, H_2O_2 concentration, and iron source.

During the Fenton-based pretreatment, the generated hydroxyl radicals ($^{\bullet}OH$) play a crucial role in breaking down the complex lignocellulosic biomass. These radicals react with lignin and hemicellulose, making them more accessible for subsequent enzymatic action. This process involves a series of reactions, including dehydrogenation, hydroxylation, and redox reactions.

i. Generation of $^{\bullet}$OH radicals:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{15}$$

In this reaction, hydrogen peroxide reacts with ferrous ions under acidic conditions to produce ferric ions, hydroxyl radicals, and hydroxide ions. The hydroxyl radicals are highly reactive species, which attack lignocellulosic structures.

ii. Fe^{2+} regeneration reactions:

Regeneration of Fe^{2+} and formation of $HO_2^{\bullet}$ radicals:

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{16}$$

In this reaction, hydrogen peroxide reacts with ferric ions (Fe^{3+}) to regenerate ferrous ions (Fe^{2+}), forming hydroperoxyl radicals ($HO_2^{\bullet}$) and hydrogen ions (H^+).

Reaction between Fe^{3+} and $HO_2^{\bullet}$ radicals:

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{17}$$

Here, ferric ions react with hydroperoxyl radicals to regenerate ferrous ions and produce oxygen (O_2) and hydrogen ions.

Reaction between Fe^{3+} and superoxide radicals ($^{\bullet}O_2^-$):

$$Fe^{3+} + {}^{\bullet}O_2^- \rightarrow Fe^{2+} + O_2 \tag{18}$$

In this reaction, ferric ions react with superoxide radicals to regenerate ferrous ions and produce oxygen.

Reaction between Fe^{3+}, superoxide radicals, and water:

$$Fe^{3+} + {}^{\bullet}O_2^- + 2H_2O \rightarrow Fe^{2+} + 2H_2O_2 \tag{19}$$

In this reaction, ferric ions react with superoxide radicals and water to regenerate ferrous ions and produce hydrogen peroxide.

iii. Inhibitory (Scavenging) reactions:

Reaction between Fe^{2+} and $^{\bullet}$OH radicals:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH \tag{20}$$

Ferrous ions react with hydroxyl radicals to form ferric ions and hydroxide ions.

Reaction between H_2O_2 and $^{\bullet}$OH Radicals:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \tag{21}$$

Hydrogen peroxide reacts with hydroxyl radicals to form water and hydroperoxyl radicals.

iv. Additional scavenging reactions:

Reaction between $^{\bullet}$OH radicals and H_2O_2:

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{22}$$

Hydroxyl radicals react with hydrogen peroxide to produce water and hydroperoxyl radicals.

Reaction between $^{\bullet}$OH radicals and $HO_2^{\bullet}$ radicals:

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O^{\bullet} \tag{23}$$

Hydroxyl radicals react with hydroperoxyl radicals to form oxygen and water. However, during the regeneration phases of ferrous ions (Fe^{2+}), hydroperoxyl radicals ($HO_2^{\bullet}$), which are less effective in breaking down lignocellulosic structures, are also formed. This slower phase can impact the overall efficiency of the pretreatment. Additionally, scavenging reactions can consume the reactive radicals, reducing the effectiveness of the process. Thus, accurate management of the Fe^{2+} concentration is essential to minimize the consumption of $^{\bullet}OH$ radicals and maximize the pretreatment efficiency. Excess Fe^{2+} reacts with hydroxyl radicals, producing $Fe(OH)_3$, while excess H_2O_2 acts as a scavenger of hydroxyl radicals, reducing the reaction rate. Therefore, optimizing the operational parameters is important to prevent enzyme activity inhibition and ensure efficient delignification.[66,67]

Typically, the pretreatment is conducted at moderate temperatures, preferably below 55 °C.[68,69] However, favorable outcomes can be achieved at higher temperatures, such as 130 °C, by reducing the H_2O_2 concentration, thereby facilitating the hydrolysis and dissolution of cellulose.[70,71] Furthermore, it is critical to maintain the pH of the pretreatment environment in the range of 2.5 to 3.5 to prevent the precipitation of ferric ions, which can disrupt the reaction. The commonly utilized sources of ferrous iron include economical and highly soluble salts such as iron sulfate and iron chloride.[72–74]

FO affects the lignocellulose components differently, where the cellulose component is impacted with a higher retention rate compared to lignin and hemicellulose. Firstly, the non-crystalline regions of cellulose undergo structural alterations, significantly affecting the surface morphology of biomass. This provides limited improvement in cellulose digestibility. However, when combined with other pretreatments such as hydrothermal, alkaline, acid, and organosolv, it yields synergistic effects that enhance the overall efficiency of FO.[75–78] FO also influences lignin by promoting the cleavage of bonds in the aromatic framework and increasing the negative zeta potential of lignin, which reduces the adsorption of cellulose on lignin. Moreover, cellulose undergoes oxidation, resulting in the formation of short-chain cellulose and carboxylic groups, further enhancing the enzymatic hydrolysis efficiency.[79]

However, despite its mild reaction conditions and use of eco-friendly oxidants, no pilot-scale pretreatments involving FO have been reported due to the relatively high costs and logistical challenges associated with H_2O_2 transport. An alternative option is represented by the electrochemical FO process, which produces H_2O_2 *in situ* continuously, eliminating the need for its transport and storage, while enhancing the overall performance. In this context, the synergistic effects of pretreating sugarcane bagasse using the Fenton reaction and subsequent extraction with NaOH were investigated.[80] Initially, a solution containing Fe^{2+} was employed to hydrolyze sugarcane bagasse with enzymes, followed by a yeast fermentation phase. The optimal Fe^{2+} concentration was determined to be 20 mM, while the optimal pH and temperature were 2.5 and 55 °C, respectively. Interestingly, NaOH extraction followed by the Fenton reaction exhibited a more positive impact on the structure of biomass compared to the reverse sequence.

To enhance the fermentation efficiency, simultaneous saccharification and fermentation were employed. NaOH extraction resulted in higher ethanol production compared to the Fenton reaction. This outcome was attributed to the Fenton reaction causing a higher accumulation of Fe^{3+} ions, which inhibited the activity of β-glucosidase, thereby reducing the conversion of glucose into ethanol.[81] In another study, Kato *et al.*[82] examined how Fenton pretreatment influenced four types of biomasses including miscanthus, switchgrass, wheat straw, and corn stover, revealing that FO augmented glucose production from cellulose, signifying the enhanced enzyme accessibility. Lignin analysis showed a decrease in the insoluble lignin content in acid for the first three samples, together with a reduction in soluble lignin in acid for the first two, suggesting that FO may not degrade lignin like decomposer fungi but instead enhances the accessibility to cellulose by enzymes, possibly through lignin structure modification. A study pioneered[83] the investigation of the Fenton reaction pathway and Fe_3O_4 nanoparticles (NMs) in lignocellulose biotreatment. Fenton-assisted delignification and hemicellulose removal, through two different combination systems, significantly improved the fungal degradation and enzymatic hydrolysis of wheat straw. After a 10-day fermentation and 36 h hydrolysis, the sugar yields from the FO-treated wheat straw, NM-treated wheat straw, and raw wheat straw were 225.7, 128.9, and 105.8 g kg^{-1}, respectively. The selective delignification process was accelerated due to the increased activities of the ligninolytic enzymes manganese peroxidase (MnP), lignin peroxidase (LiP), and laccase (Lac) in both systems. FRP demonstrated superior results compared to Fe_3O_4 NMs in terms of fungal growth, enzyme activity, selective degradation, and saccharification, which is likely because the lignin and hemicellulose in the FO-treated wheat straw were partially removed. Further research is necessary to optimize the Fenton-like processes to enhance their effectiveness.

Sustainability is a significant facet of FO due to its utilization of relatively straightforward reagents such as H_2O_2 and Fe^{2+} (Table 2). However, it should be acknowledged that this process may produce iron-containing byproducts, which can become secondary pollutants. Thus, to mitigate this, heterogeneous iron-based catalysts have been devised, leading to reactions similar to Fenton-like processes. These reactions can increase the pH range but often increase the process costs and are primarily explored for degrading organic pollutants.[74] Also, meticulous control of the ferrous iron and H_2O_2 concentrations is critical for the success of this process, given that these parameters determine the generation of free radicals. These concentrations are significantly influenced by the type of biomass employed[75] and any previous pretreatments or treatments that may have altered the biomass.[84] Additionally, it is imperative for the peroxide to be fully consumed during the reaction, given that any residual presence can prove unfavourable to enzymes or microorganisms employed in subsequent degradation stages.[76]

3.4. Hydrogen peroxide oxidation

Pretreatment with H_2O_2 allows the removal of hemicellulose and lignin, making cellulose more accessible to enzymatic processes.[85] This process takes place in an alkaline environment with the pH typically set at 11.5, where H_2O_2 dissociates into a hydroperoxide anion, generating highly reactive oxygen radicals such as superoxide and hydroxyl radicals. These radicals play a crucial role as powerful oxidants, promoting the oxidative degradation of lignin, resulting in smaller and more manageable fragments.[86] This pretreatment is particularly effective in delignification, given that it leads to the cleavage of the ester, ether, and β-aryl ether bonds within lignin, significantly improving the solubilization of hemicellulose and optimizing the accessibility to cellulose. This translates into an improvement in enzymatic digestibility.[87]

The chemical reactions that occur during the hydrogen peroxide pretreatment of lignocellulosic biomass involve hydrogen peroxide in an alkaline medium. These reactions are important for generating reactive species, which break down the complex structures of lignin and hemicellulose. The detailed reactions are as follows:

i. Dissociation of hydrogen peroxide in alkaline medium:

$$H_2O_2 + H_2O \leftrightarrow HOO^- + H_3O^+ \tag{24}$$

In this reaction, hydrogen peroxide dissociates to form hydroperoxide anions (HOO^-) and hydronium ions (H_3O^+).

Formation of superoxide and hydroxyl radicals:

$$H_2O_2 + HOO^- \leftrightarrow H^+ \, {}^{\bullet}O_2{}^- + H_2O \tag{25}$$

In an alkaline medium, the hydroperoxide anion reacts with hydrogen peroxide to produce superoxide (${}^{\bullet}O_2{}^-$) and hydroxyl radicals (${}^{\bullet}OH$), together with water.

Combination of superoxide and hydroxyl radicals:

$${}^{\bullet}OH + {}^{\bullet}O_2{}^- + H^+ \rightarrow O_2 + H_2O \tag{26}$$

Superoxide and hydroxyl radicals can combine to generate oxygen (O_2) and water.

General equation of H_2O_2 decomposition in alkaline medium:

$$H_2O_2 + HOO^- + H^+ \rightarrow O_2 + 2H_2O \tag{27}$$

For each mole of hydrogen peroxide added, 0.5 mol of oxygen is generated, provided no other compounds react with the radicals.

ii. Decomposition of H_2O_2 in the presence of transition metals:

Hydrogen peroxide is unstable under alkaline conditions and decomposes, especially in the presence of transition metals such as manganese, iron, and copper, leading to the generation of hydroxyl radicals and superoxides.

Formation of hydroxyl radicals:

$$H_2O_2 + M \rightarrow M^+ + {}^{\bullet}OH + OH^- \qquad (28)$$

Hydrogen peroxide reacts with a metal (M) to produce a metal ion (M^+), hydroxyl radicals, and hydroxide ions.

Formation of superoxides:

$$H_2O_2 + M^+ + 2OH^- \rightarrow M + {}^{\bullet}O_2{}^- + 2H_2O \qquad (29)$$

Hydrogen peroxide reacts with a metal ion (M^+) and hydroxide ions to produce the metal, superoxides, and water.

General equation for hydrogen peroxide decomposition:

$$2H_2O_2 + OH^- \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2{}^- + 2H_2O \qquad (30)$$

This reaction summarizes the decomposition of hydrogen peroxide, resulting in the formation of hydroxyl radicals, superoxide radicals, and water.[88,89]

Among the key parameters influencing the effectiveness of this process, pH plays a fundamental role given that it directly affects the formation of radicals. Additionally, critical factors in the treatment protocol include H_2O_2 concentration, treatment duration, and temperature.[90] Numerous studies have shown that the efficiency of lignin extraction is directly influenced by the concentration of H_2O_2. For example, mild concentrations of H_2O_2, such as 90 and 125 mg H_2O_2 g^{-1} of dry biomass of corn solver induced the oxidation of lignin side chain structures without significantly affecting the aromatic rings.[91] In contrast, a higher concentration of 250 mg of H_2O_2 g^{-1} of dry biomass resulted in more extensive depolymerization, with fragmentation of the aromatic rings. The pretreatment and reaction conditions are closely related to the type of biomass under examination. For instance, the optimal conditions for the delignification of cashew apple bagasse were identified by Correia *et al.*[86] as a 6 h treatment at 35 °C with a quantity of 61.92 mg of H_2O_2 g^{-1} of dry biomass. Alternatively, in the case of Jerusalem artichoke, the optimal conditions included a 2 h treatment at 50 °C with 72 mg H_2O_2 g^{-1} biomass.[92]

Also, the effect of increasing the process temperature has been analysed. Douglas fir was treated at a temperature of 180 °C, obtaining 22% delignification and the significant removal of 78% of glucomannan from hemicellulose.[85] These high temperatures can promote the formation of valuable organic acids through the depolymerization of hemicellulose, offering new opportunities to produce organic acids such as lactic acid, glycolic acid, succinic acid, and formic acid, in addition to improving the efficiency of cellulose-based biofuel or biochemical production. Furthermore, the potential of combining H_2O_2 oxidation with other pretreatments has been explored. As an example, wheat straw has been subjected to steam explosion, exposing it to steam in the temperature range of 200–220 °C and pressures between 15 and 22 bar.[93] Subsequently, the fibrous material was treated with a 2% H_2O_2 solution at 50 °C for 5 h, while maintaining a pH of 11.5. The initial pretreatment method resulted in a significant reduction in hemicellulose content and removal of approximately 11–12% of lignin. However, the subsequent process was observed to be highly effective, achieving an impressive lignin removal rate of 81–88%. In total, this two-stage approach successfully removed 92–99% of the original lignin from wheat straw. In another study, Morone *et al.*[94] experimented the combination of pressurized air oxidation at 0.6 MPa and 190 °C to reduce the required H_2O_2 quantity. This combined approach reduced the H_2O_2 concentration, simultaneously achieving a high lignin removal (77.29%) and significant cellulose retention (83.01%). Nevertheless, subjecting the material to elevated temperatures resulted in sugar breakdown and the creation of carboxylic acids, including acetic acid, leading to a notable alteration in the pH of the reagent, shifting it from pH 11.9 to pH 5.63. This pretreatment was effectively utilized for the fractionation of bamboo under mild conditions.[95] Utilizing 3.0% hydrogen peroxide, 68.29% lignin was removed, while retaining 90.72% glucan and 60.45% xylan. The glucan and xylan hydrolysis yields of the treated bamboo significantly increased, achieving 90.62% and 88.30%, respectively, which were much higher than that of raw bamboo. Additionally, 58.74% of dissolved lignin was recovered with high purity and beneficial properties for further applications in food and medicine.

Hydrogen peroxide oxidation pretreatment was applied to sugarcane bagasse at various temperatures to enhance enzymatic saccharification.[96] A positive correlation was found between hydrogen peroxide loading and glucose yield due to the extensive degradation of hemicellulose and lignin, which facilitated the accessibility to cellulose. The addition of Tween 80 further improved the glucose yield by stabilizing the enzyme activity. The highest glucose yield of 77.6% was obtained after pretreatment at 160 °C for 60 min with 6.25% hydrogen peroxide and Tween 8. Alkaline hydrogen peroxide pretreatment of lignocellulosic biomass has several sustainable advantages and some challenges. The pretreatment typically operates at moderate temperatures (25–70 °C) and ambient pressure, resulting in low energy consumption. Also, it does not produce toxic inhibitors such as furfural and HMF, which improves the efficiency of enzymatic hydrolysis. Besides, the chemicals used are readily available and the alkaline environment ensures sterile conditions, eliminating the need for antibiotics during hydrolysis.

However, this process can produce inhibitors due to the degradation of lignin, such as sodium acetate and phenolic acids, which can inhibit fermentation. Furthermore, large amounts of water are required to manage the high pH of the treated biomass.[89,96]

3.5. Peracetic acid oxidation

Peracetic acid (PAA) is an organic peroxide widely known for its potent oxidizing, disinfecting, bactericidal properties and selective delignification action.[96] Its chemical structure consists of a peroxide group (–OOH) bonded to an acetyl group

(CH_3CO–), imparting a high oxidative potential of 1.748 V. The peroxide bond (O–O) in PAA is relatively weaker compared to other peroxides, such as hydrogen peroxide, making PAA a highly effective oxidizing agent.[97] PAA is synthesized through a reaction catalyzed by sulfuric acid, involving H_2O_2 and acetic acid. The oxidative efficacy of commercial peracetic acid (PAA) can be improved using activators such as UV radiation, metal ions (Cu^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}), and carbon-based materials, which promote the generation of free radicals and enhance the degradation of organic compounds. PAA can also be generated *in situ* through an enzymatic pathway using a perhydrolase to catalyze the reaction between hydrogen peroxide and acetic acid or ethyl acetate, producing PAA directly during the pretreatment process. This approach is safer and less costly compared to chemical production.[98] PAA, as a potent oxidizing agent, primarily acts through the formation of hydroxonium ions, capable of attacking electron-rich sites in the structure of lignin, triggering a series of oxidative degradation reactions and generating water-soluble fragments. PAA functions as a delignifying agent by oxidizing the hydroxyl groups in the side chains of lignin to carbonyl groups, reducing the molecular weight of lignin and introducing hydrophilic groups, which facilitate the dissolution of lignin in water. It breaks β-aryl bonds in lignin, crucial for its polymeric structure, contributing to depolymerization. The dissociation of the peroxide bond in PAA generates free radicals such as acetoxyl and hydroxyl radicals, which further attack the bonds in lignin, breaking its internal bonds and forming low-molecular-weight compounds. Additionally, PAA oxidizes the phenolic groups in lignin to quinone groups, further weakening the structure of lignin. These reactions convert the functional groups in lignin into new chemical bonds, forming soluble organic acids and compounds. The oxidation of lignin produces acids such as hydroxybenzoic acid, maleic acid, and fumaric acid and their derivatives, aiding in the removal of lignin. The breaking of the β-aryl bonds and formation of carbonyl and carboxyl groups reduce the polymerization of lignin, fragmenting it into smaller, more degradable units. This conversion increases the polarity of the lignin fragments, making them more soluble in water, and prevents π–π interactions between the aromatic rings in lignin, disrupting its compact structure.[97]

This process induces substantial changes in the original biomass structure, creating furrows and increasing the exposure of cellulose, thus improving its accessibility to enzymes. The critical parameters affecting the efficiency of this process include PAA concentration, reaction temperature, exposure time, and biomass/PAA ratio. It is crucial to note that the temperature of this process must be maintained at moderate levels, preferably below 80 °C, to prevent the decomposition of paracetic acid. This condition, coupled with the absence of strong acids, constitutes one of the primary advantages of this pretreatment strategy.[99] The pretreatment duration may vary from minutes to several hours, depending on the biomass and specific conditions. Thus, the biomass/PAA oxidation ratio can be adjusted depending on the biomass characteristics and PAA concentration. The PAA concentration varies depending on the type of biomass used. It is worth noting PAA pretreatment has been proven to be effective on various biomasses, including hardwood such as oak,[100] sugarcane bagasse,[101] and aspen wood.[96] Further studies on various biomasses have evaluated the effectiveness of this pretreatment for the production of second-generation biofuel. This treatment has effectively removed lignin, exposing cellulose and hemicellulose, thereby increasing saccharification without the accumulation of ethanol fermentation inhibitors. Furthermore, it has been observed that pretreatment enhances the absorption of hydrolytic enzymes, maximizing the yields of sugar. Therefore, this pretreatment method appears to be a promising strategy for reducing the production costs of second-generation ethanol.[102]

It is well-documented that PAA oxidation significantly enhances the digestibility of LCB, enhancing the accessibility of cellulose to hydrolytic enzymes. This increases the efficiency of converting cellulose to glucose, making the overall process more sustainable.[103] For example, the use of H_2O_2 and acetic acid resulted in the removal of over 80% of lignin, subsequently achieving an enzymatic saccharification rate exceeding 90%.[104] For example, sugarcane bagasse treated with PAA and $FeCl_3$ showed a significant improvement in glucose production. PHP pretreatment, combining phosphoric acid and hydrogen peroxide, effectively removed lignin and hemicellulose, improving the digestibility of cellulose and fermentable sugar production, while reducing the operational costs and environmental impact. The combination of H_3PO_4 and H_2O_2 under moderate conditions has been shown to be effective for the removal of lignin and hemicellulose, enhancing the biomass fractionation and subsequent cellulose hydrolysis, thus increasing the process efficiency and reducing the use of hazardous chemicals.[105]

The enzymatic *in situ* generation of PAA reduces the operational costs and risks associated with storing and transporting commercial PAA, eliminating the need for large quantities of chemical reagents and contributing to a more sustainable approach to lignocellulosic biorefineries. The disinfectant and bactericidal properties of PAA protect treated biomass from microbial contamination during storage and fermentation, improving the durability and saccharification of biomass. Additionally, PAA can depolymerize lignin to produce low-molecular-weight phenolic compounds, such as hydroxybenzoic acid and vanillic acid, which have commercial applications, adding value to biorefinery by-products.

However, the chemical production of PAA is expensive and poses safety risks due to its explosive and unstable nature, limiting its widespread application in the pretreatment of lignocellulose. Also, although the enzymatic production of PAA is advantageous, it is necessary to improve the activity and selectivity of perhydrolases to enhance the efficiency of PAA generation and further reduce the operational costs. Furthermore, the practical use of PAA is limited by the operational costs and the need for efficient recycling processes to reduce the consumption of large quantities of chemical reagents, which increases the overall costs.[98] Finally, PAA pretreatment can be employed alone or in combination with other pretreatment methods to optimize its effectiveness.

3.6. Persulfate oxidation

The persulfate (PS) oxidation process actively removes organic pollutants from the environment. Strong oxidizing radicals such as hydroxyl radicals (${}^{\bullet}OH$), PS radicals (${}^{\bullet}SO_4{}^{2-}$), and superoxide anions (${}^{\bullet}O^{2-}$) are generated through various PS activation processes and their role in lignocellulosic pretreatment is shown in Fig. 4 under milder conditions.[106] Among the generated radicals, the ${}^{\bullet}SO_4{}^{2-}$ radical has the prominent characteristics of longer half-life and greater stability. The PS-activated free radicals, nucleophilic species, and reducing species are crucial for breaking the bonds in lignin.[107] The electron transfer from transition metals, such as iron, manganese, and cobalt, together with the potential mechanisms are illustrated by the following equations:

$$S_2O_8{}^{2-} \rightarrow 2SO_4{}^{\bullet -}(\text{in the presence of heat/UV}) \tag{31}$$

$$S_2O_8{}^{2-} + Mn^{+} \rightarrow SO_4{}^{\bullet -} + M^{n+1} + SO_4{}^{2-} \tag{32}$$

$$SO_4{}^{\bullet -} + H_2O \rightarrow SO_4{}^{2-} + HO^{\bullet} + H^{+} \tag{33}$$

$$\text{Pollutants} + \text{oxidative radicals} \rightarrow \text{Products} \tag{34}$$

The PS system, which uses SO_4 as its key component, has the potential to be as efficient as or even better than the OH system.[108] During PS-based AOPs (PS-AOPs), peroxymonosulfate (PMS, HSO^{5-}) and peroxydisulfate (PDS, $S_2O_8{}^{2-}$) are activated, which have recently gained attention owing to their capacity to produce reactive oxygen species (ROS) with high redox potential, including ${}^{\bullet}OH$ (−2.8 V), $SO_4{}^{\bullet -}$ (−2.5–3.1 V), $O_2{}^{\bullet -}$ (−0.15 V), and singlet oxygen (${}^{1}O_2$, −2.2 V).[109] PS activation processes such as heat, ultrasound, radiation, alkali, and transition metals are highly preferred to generate ROS.[110]

However, some of these methods of activation have some drawbacks. For example, the necessity of external energy requirements for thermal and ultrasonic activation leads to high energy consumption under harsh reaction conditions. Also, there is a chance of inducing environmental pollution during PS activation using alkali.[111]

Additionally, carbonaceous materials have been employed as environmentally friendly catalysts to activate PS such as carbon nanotubes, carbon quantum dots, and redox graphene. However, the activation of transition metals releases metal ions, which may contribute to secondary pollution. Among the transition metals, Fe^{2+} can activate PS given that it is an inexpensive expensive transition metal. However, the Fe^{3+} produced during activation cannot activate PS, leading to a low reaction efficiency. In this case, Fe^{2+} can be effectively accelerated using UV irradiation, but the use of artificial light sources is energy -intensive.[112] Hence, a cost-effective ecologically benign renewable energy source, *i.e.*, solar energy, is utilized for the activation of PS. The combined solar/Fe^{2+}/PS pretreatment of rice straw was investigated, in which a rice degradation rate of around 16.50%, cellulose content of 52.39%, and reducing sugar concentration of 254.40 mg L^{-1} were observed within 120 min. In addition, the lignin content of about 36.83% was lower than that of the untreated rice straw. Corn straw was pretreated with sodium PS at 50 °C for 16 h, with a lignin removal rate of 77.18%.[113] Wheat straw was pretreated using three PS activation systems (alkali, heat and H_2O_2), showing that alkali-activated PS is an effective radical

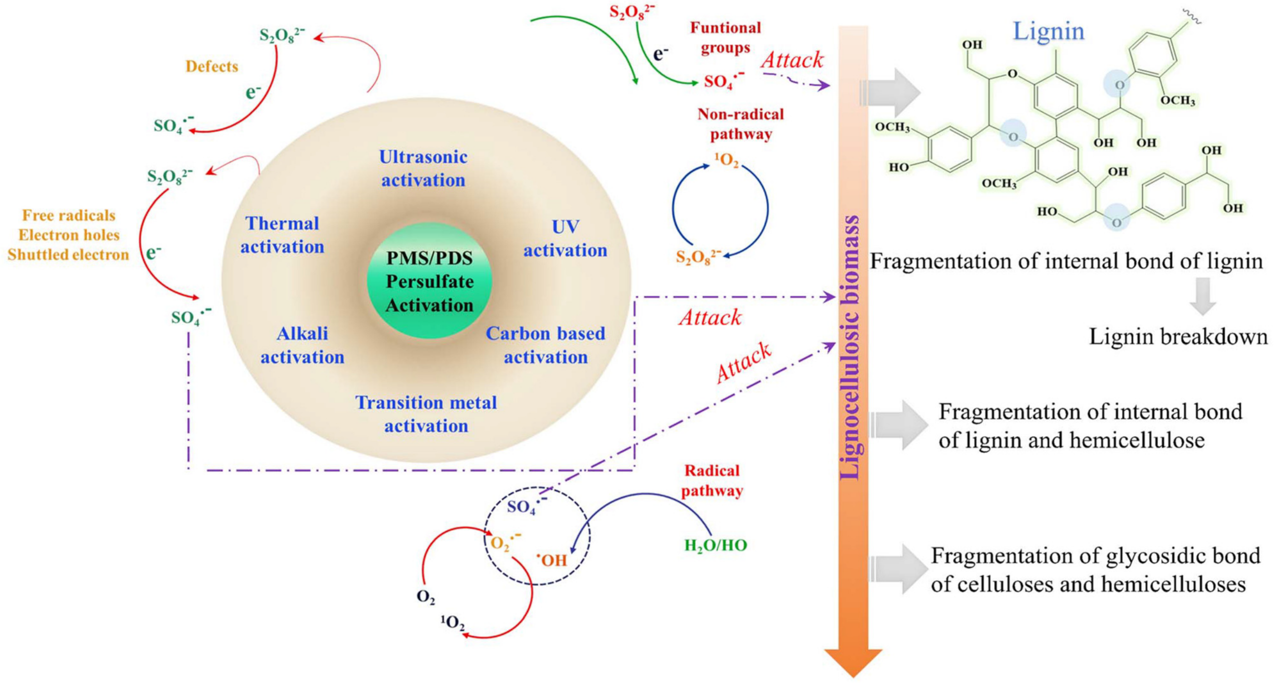


Fig. 4 Persulfate oxidation process.

system for treating LCB. The presence of a greater content of sulphate radicals ($SO_4^{2-\bullet}$), hydroxyl radicals ($OH^\bullet$),[114] and superoxide anion radicals ($O_2^{\bullet-}$) in sodium PS activated by alkali system was observed, which improved the lignin removal efficiency to 25% and hemicellulose removal efficiency to 27%. PS pretreatments break the aryl C–O bonds in straw lignin, which can permeate the crystalline regions of straw cellulose. These radical species degraded lignin selectively and led to a high sugar yield. Various PS salts such as potassium PMS, PDS, sodium PS (SPS), and ammonium PS (APS) were used to treat sugarcane bagasse. Employing 1 mol L^{-1} PPMS, the maximum concentrations of the generated $OH^\bullet$ and $SO_4^{2-\bullet}$ were 4.32 and 2.68 mmol L^{-1}, 3.14 and 2.33 mmol L^{-1}, and 2.84 and 1.96 mmol L^{-1}, respectively. Thus, potassium PMS is capable of producing more free radicals than SPS and APS. Consequently, compared to the other PS salts, the potassium PMS-pretreated sugarcane bagasse demonstrated the highest sugar conversion rate of 90.29% and a lignin removal rate of 87.49%.[105] This potassium PMS was more selective for lignin degradation and could produce free radicals. This is possibly the most influencing factor pretreatment efficiency. To enhance the pretreatment efficiency of PS salt, inorganic salt additives ($CuCl_2$ and $FeCl_2$) can be used in combination with SPS salt, which maximizes the rate of lignin degradation rate and sugar conversion. The use of cheap, moderately reactive, and easy-to-handle reagents as additives made this process cost-effective and practically viable. The concentration of PS, concentration of the catalyst, the starting pH, and presence of organics and coexisting ions in the solution are all factors that influence the activation degradation of lignin by persulfate. However, there is a need for more research because the majority of current studies are restricted to lab tests. In this case, economic considerations should be examined throughout the actual treatment process, and factors impacting the efficiency of activated persulfate degradation should be identified using appropriate approaches.[115] Ultimately, to increase the effectiveness of sulfate radical-AOPs, more research on the reaction mechanism of double oxidation systems or combination activation technologies is required, together with the selection of targeted activation modes depending on the structure and properties of lignocellulosic biomass. Incorporating catalysts can accelerate persulfate oxidation, while reducing the required dosage and reaction time. Recent studies have explored the use of transition metal catalysts such as iron, manganese, and copper to improve the efficiency of persulfate oxidation. Utilizing environmentally friendly solvents as reaction media can enhance the sustainability of persulfate oxidation. The sustainability aspects of persulfate are provided in Table 2. Researchers have investigated the use of solvent systems such as deep eutectic solvents (DES) and ionic liquids to replace traditional organic solvents. Applying microwave or ultrasound irradiation during persulfate oxidation can intensify the reaction, leading to higher lignin removal rates and shorter treatment times. Integrating persulfate oxidation with other pretreatment methods such as steam explosion, alkaline treatment, and enzymatic hydrolysis can synergistically enhance the degradation of lignin and accessibility to cellulose. Delignification of lignocellulosic biomass using PS oxidation helps to improve the enzymatic hydrolysis of cellulose, production of high-value lignin-derived chemicals and is compatible with various lignocellulosic feedstocks, including agricultural residues and dedicated energy crops. This pretreatment is effective for degrading lignin and other recalcitrant compounds in biomass, it can be operated at ambient temperatures and pressures, and it does not require the addition of external chemicals.[116] However, it has relatively slower reaction kinetics compared to other oxidation methods, requires activation by heat, catalysts, or UV light for efficient oxidation and has limited selectivity, which may lead to the formation of undesirable byproducts. In addition, this pretreatment process is limited due to the potential degradation of cellulose at prolonged reaction times or high temperatures and the high cost of persulfate and challenges associated with scaling-up to industrial processes. Hence, future research is required for the optimization of the reaction conditions and catalyst systems to enhance the delignification efficiency, to assess integration with other pretreatment methods to achieve synergistic effects and exploring alternative oxidants or green solvents to improve the sustainability.

3.7. Ozone oxidation

Ozone is one of the chemical oxidants that reacts most strongly with substances (Fig. 5) that contain functional groups with a high electron density, such as those that in lignin. Consequently, enzymes can more easily access cellulose as a result of the breakdown of lignin. Furthermore, given that ozone is a selective oxidant, no appreciable carbohydrate losses occur. Another benefit is that ozonolysis can be performed at ambient pressure and temperature. Alternatively, significant ozone dosages may be required; therefore, the operating conditions must be optimised for cost-effectiveness. Considering its strong oxidative strength and ability to non-selectively decompose organic substrates, ozone has become popular as an ecologically sustainable oxidant, particularly for compounds with conjugated double bonds and functional groups with high electron densities. Ozone is unstable in water, and the pH of the water is crucial because hydroxyl radicals ($^\bullet OH$), a potent oxidising agent with an oxidation potential of 2.33 V, are produced when ozone decomposes in an alkaline environment. Ozone, a potent oxidant, oxidizes lignin *via* the Criegee mechanism, which attacks and breaks down alkene molecules (double bonds) to produce low-molecular-weight byproducts, while having little effect on the components of cellulose and hemicellulose, as shown in Fig. 5. Compared to other oxidants, ozone reveals a faster pace of oxidation reaction for the breakdown of lignin.[117] Besides the cellulosic and hemicellulose components of LCB, ozone attacks lignin, which releases soluble substances with lower concentrations, such as organic acids. Mostly, the lignin polymer is converted to carboxylic acids by oxidizing agents having aromatic rings, which prevents the growth of microorganisms. However, because it requires costly oxidizing agents, this

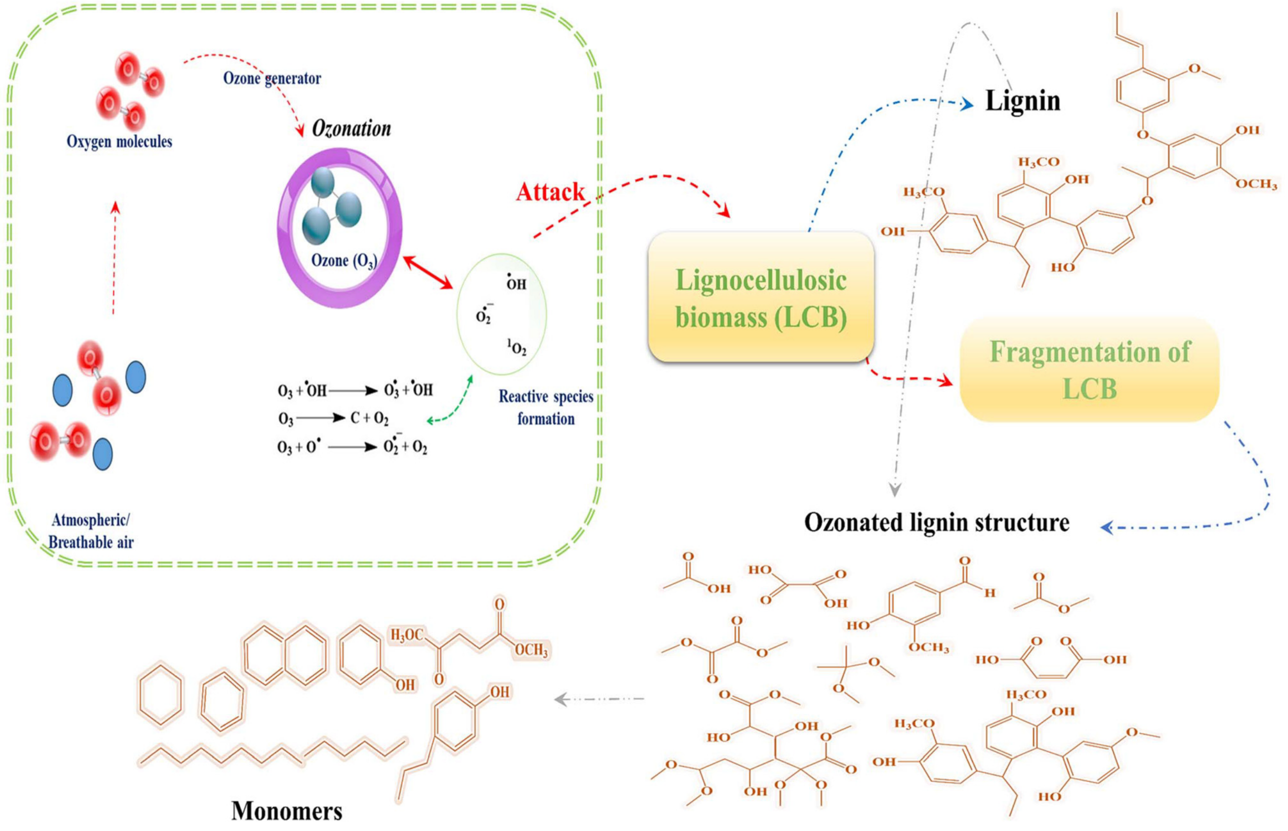


Fig. 5 Reaction mechanism of ozonation process.

approach has not piqued the interest of industry players or researchers compared to other approaches.

Parameters including the size of LCB particles, moisture content, dosage of ozone, and reactor design impact the effectiveness of ozone pretreatment. For the effective diffusion of ozone, moisture is essential, but a too much moisture content may obstruct the biomass pores and enhance the mass transfer resistance. Also, the size of the lignocellulose particles impacts the effectiveness of the ozone pretreatment, where smaller particles have higher delignification and more readily destroy carbohydrate components. The energy consumption is significantly affected by the ozone dose, reaction time, ozone concentration, and gas flow rate. Additionally, the reactor design has the potential to improve the effectiveness of ozone treatments. An appropriate reactor design is required to enhance the contact between the ozone and biomass for better mass transfer and reaction outcomes. The synthesis of ozone demands a high energy input (36 MJ kg^{-1} of ozone) and large doses for pretreatment (9 kg O_3 per ton dry biomass) to create 63 kg ethanol. According to the research by Osuna-Laveaga *et al.*,[118] much greater ozone dosages of 100–300 kg O_3 per ton dry biomass were required to provide a sugar yield of40–50%. Therefore, the energy input and ozone consumption in ozone oxidation must be reduced for it to become a sustainable and feasible pretreatment method. Depending on the substrate and process variables, LCB can be successfully delignified using ozone. Numerous reaction mechanisms have been postulated, such as selective interactions involving carbon–carbon double bonds, attacks the aromatic centres, and glycosidic bond cleavage. Due to their higher electron densities, olefinic, aromatic, and phenolic chemicals are more likely to react with ozone. The substituents affect both the reactivity and the reaction path. Ozone degrades a portion of the total lignin by attacking partially acid-insoluble lignin and turning it into acid-soluble lignin. Research on the ozone oxidation of bagasse sugarcane revealed a 66.8% decrease in acid-insoluble lignin, an increase from 3.13% in the raw material to 7.21%, and an overall decrease in the total lignin by 39.6%. Pretreatment of flax fibre processing waste with gas-phase ozone could greatly increase the delignification rate and digestibility by 31.9% and 16.3%, respectively.[119]

In the paper and pulp industry, the kinetics of lignin removal using pure oxygen have been thoroughly investigated. The delignification process is better described by the first-order kinetic model and the pseudo-first-order kinetic model because of the low lignin content in pulp, its homogenous distribution, and simple access to lignin. Yun[120] reported the use of oxygen and caustic treatments to remove lignin from pulp, demonstrating a first-order reaction rate in the absence of hexuronic acid. Also, pseudo-first-order reaction rate kinetics for ozone bleaching on dry materials in an oven and at room temperature was reported. A lignin model with phenolic β-o-4-

type guaiacylglycerol-β-guaiacyl ether at 160–200 °C was demonstrated using a pseudo-first-order reaction rate. Using Mn-molybdovanado-phosphate polyoxoanion (HPA-5-MnII) as a catalyst, globulus kraft pulp was treated and first-order reactions were used to elaborate the delignification of corn stover. Mbachu and Manley[121] discovered first-order kinetics for the breakdown of lignin by studying the ozonolysis of spruce wood in aqueous acid medium at ambient temperature. The wheat straw ozone delignification kinetics in this instance adheres to a pseudo-second-order reaction. This correlates well with the encouraging findings of the correlation coefficient, R^2, which was higher than the value given in the pseudo-first-order model of 0.9977. Numerous pretreatment techniques combining ozone and other pretreatments have currently been developed to further enhance the digestibility of cellulose and lignin, including ozone-alkaline, ozone-acid, and ozone-subcritical water pretreatments.[113] When an additional process is combined with ozone pretreatment, outstanding synergistic results can be seen. The main benefits of this process are the significant lignin removal, the absence of harmful inhibitor development, and the ability to process at room temperature and pressure. Also, this pretreatment acts as a platform for the generation of valuable chemicals from lignin. However, this approach is not economically feasible because it requires large amounts of ozone. Also, ozone generation requires specialized equipment and energy-intensive processes and it has limited solubility in water to achieve the efficient mixing required for effective oxidation. Furthermore, its process efficiency is limited due to the generation of potentially harmful ozone byproducts, equipment complexity and safety considerations. Hence, further investigation on the development of more efficient ozone generation and delivery systems is required to enhance the overall biomass conversion.

3.8. Sonochemical oxidation

Ultrasonic irradiation technologies generate mechanoacoustic (physical) and sonochemical (chemical) effects. Consequently, the local pressure drops due to the rarefaction and compression of the acoustic pressure in the liquid during ultrasonication. Microbubbles develop as the local pressure within the aqueous phase drop below the saturated vapour pressure. The microbubbles absorb ultrasonic energy, develop, and collapse once they reach their maximum size. The abrupt collapse of these microbubbles is known as cavitation, as presented in detail in Fig. 6. The acoustic cavitation of microbubbles, hydromechanical shear force, turbulence, and agitation assist the ultrasound delignification of LCB. The cleavage of lignin and xylan networks is facilitated by the chemical impact of ultrasound, which encourages the breakdown of water molecules into hydroxyl radicals. This procedure promotes delignification, breaks down the crystal structure of cellulose, improves the heat and mass transport, and promotes the solubilization of organic materials. Throughout the course of the treatment process, the application of ultrasonic irradiation causes sono-

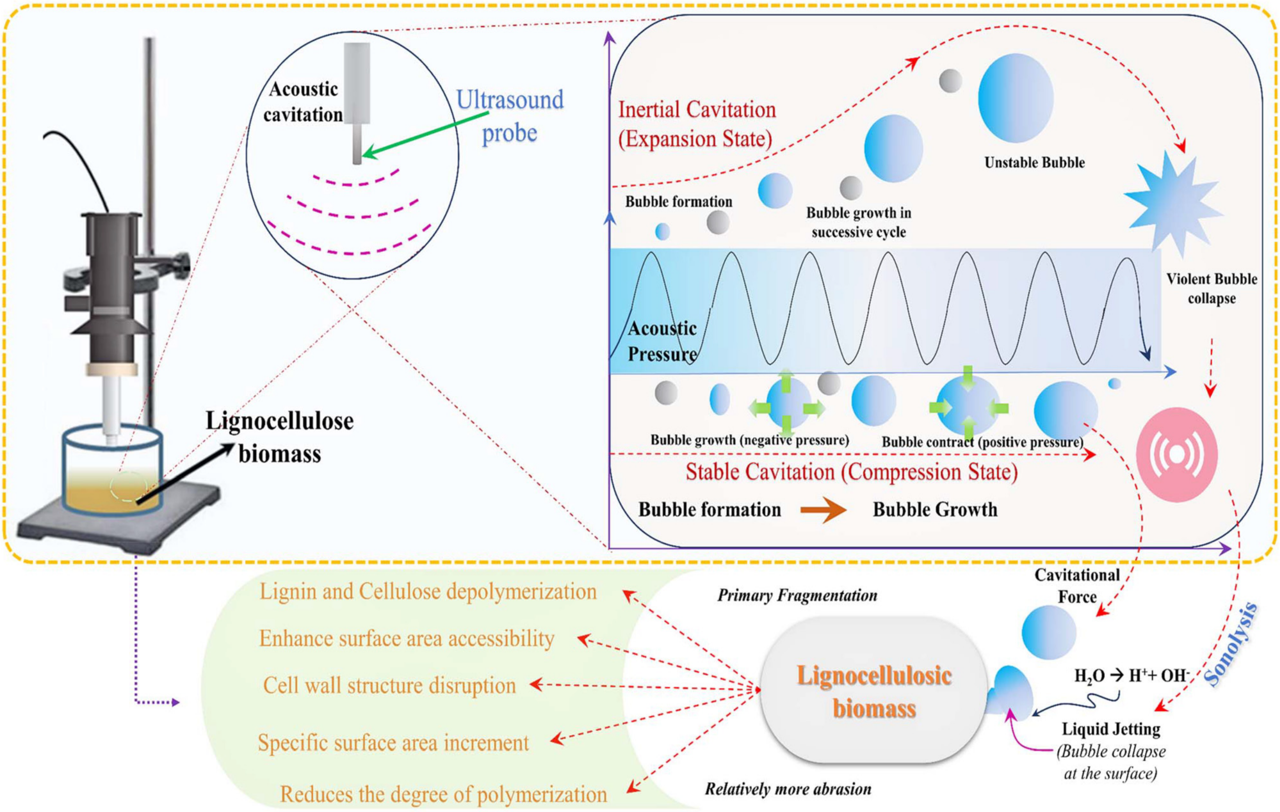


Fig. 6 Underlying mechanism of the ultrasonication process.

chemical and mechano-acoustic reactions, which result in the delignification and surface erosion of lignocellulosic biomass. Lignin and hemicellulose are released through the homolysis of the lignin-carbohydrate linkages caused by sonication.

The C–C bonds in aromatic rings of lignin are cleaved at the α position, while the C–H bonds are prone to disruption. The breaking of this link causes the production of macroradicals. The cooperation between these macroradicals and cavitation-produced radicals such as $^{\bullet}$H and $^{\bullet}$OH initiates the depolymerization of lignocellulosic material, was as presented in detail in Fig. 6. For better efficiency, milder conditions such as a shorter duration, atmospheric pressure, neutral pH, and ambient temperature are desirable. Ultrasonic irradiation is a potential auxiliary approach that can be integrated with chemicals to address these contradictory needs during valorization. The use of dilute acid in pretreatment is restricted owing to its failure to remove lignin. Therefore, it is encouraged to employ ultrasonication to increase the effectiveness of diluted acid pretreatment.[122] According to earlier research, the delignification of grass using ultrasound and diluted acid pretreatment increased from 33% to 80.4%. The most lignin was eliminated when ultrasonic irradiation was coupled with diluted hydrochloric acid pretreatment.

During combined alkaline and ultrasonic pretreatment, the lignin concentration in rice straw was reduced by about 4.70%. An innovative energy-saving technique that can be used to improve the economic feasibility of ultrasonic irradiation during the pretreatment is the use of the thermal energy lost in cavitation bubbles. In the case of ficus fibres and tow, ultrasound-assisted alkaline H_2O_2 pretreatment could remove lignin to a maximum of 88%; however, lignin removal for ficus pulp was reported to be 79%. Rice straw was pretreated with BmimCl-HCl and AmimCl-HCl using ionic liquids, and the addition of ultrasound increased the lignin removal rate by 18.06–19.33%.[123] Ultrasound may improve the deep eutectic solvent system by solubilizing lignin to a maximum of 48.15% (w/w), as shown by Malaeke *et al.*[124] Due to the removal and destruction of the waxy layers by ultrasound treatment and silica deposited on the surface of LCB, lignin was highly soluble. The delignification and biomass liquification of fruit and vegetable residues could reach as high as 72% when ultrasound was used in conjunction with surfactants such as sodium dodecyl sulphate.[125] Thus, together with the heat and mechanical effects of ultrasonic waves, cavitation breaks down the LCB matrices, reduces the particle size, and improves the local mass transfer. Also, when paired with the appropriate solvents, ultrasound application can also improve the delignification efficiency of thermal and chemical reactions. Furthermore, the thermal resilience of cellulose is enhanced by ultrasound, where cellulose extracted using ultrasound-mediated solvent pretreatment showed greater breakdown temperatures than cellulose extracted using non-ultrasound procedures.

The effects on various parameters, including time (operating range of 15–90 min), alkali concentration (0.25 M–2.5 M), solvent loading (1 : 15–1 : 30 w/v), temperature (50–90 °C), power (40–140 W), and duty cycle (40–70%) at a fixed frequency of 20 kHz, have been extensively studied in the utilisation of the combination of NaOH and ultrasound. An ultrasonic horn was designed to operate at its best under the following conditions: 1 M NaOH concentration, 1 h treatment duration, 70 °C operating temperature, biomass loading ratio of 1 : 20, 100 W ultrasonic power, and duty cycle of 70%, which yielded a delignification degree of 67.30%. Lower delignification was found in a comparative investigation employing conventional and ultrasonic bath-assisted alkaline treatment, with the corresponding values of 48.09% and 61.55%, respectively. The initial enzymatic rate of cellulose was significantly improved by ultrasound-assisted tetrabutylammonium hydroxide pretreatment (79.39 mg g^{-1} h^{-1}), and a decrease in sugar yield of 426.6 mg g^{-1} was obtained after 48 h.[126] Due to its distinct features, pretreatment using affordable aqueous ionic liquids and ultrasound can be a promising method in bio-refineries. Several possibilities exist for developing novel, efficient, and eco-friendly processes by designing the sonochemical parameters, and currently research is focusing on scaling-up and holistic economic and ecological sustainability analyses, which are still lacking. The advantages of this possess are that it enhances the reaction kinetics and mass transfer through acoustic cavitation, operates under mild conditions with no additional chemical reagents required and can be easily integrated into existing pretreatment processes. However, its disadvantages include the requirement of specialized equipment capable of generating high-intensity ultrasound, limited scalability due to high equipment cost and energy requirements and the possibility of equipment fouling and erosion over time. Also, scaling up sonication pretreatment processes for industrial applications may be challenging due to the limitations in ultrasonic reactor design, cavitation control, and uniformity of treatment. Besides, prolonged exposure to high-intensity ultrasound waves may cause degradation or modification of the biomass components, leading to changes in the chemical composition and potential loss of valuable products. Hence, the development of scalable sonication reactor designs and strategies for efficient energy transfer and cavitation control is essential for transitioning sonication pretreatment from laboratory-scale to industrial-scale operations. However, although the sonication pretreatment of lignocellulosic biomass holds great promise for improving biomass conversion processes, further research is needed to address its limitations and optimize its application for industrial-scale biorefinery operations. In this case, collaboration among researchers, engineers, and industry stakeholders will be key to driving innovation and advancing the field of sonication pretreatment.

3.9. Electrochemical oxidation

The lignin electrochemical oxidation (EO) process exhibits several benefits, as follows:

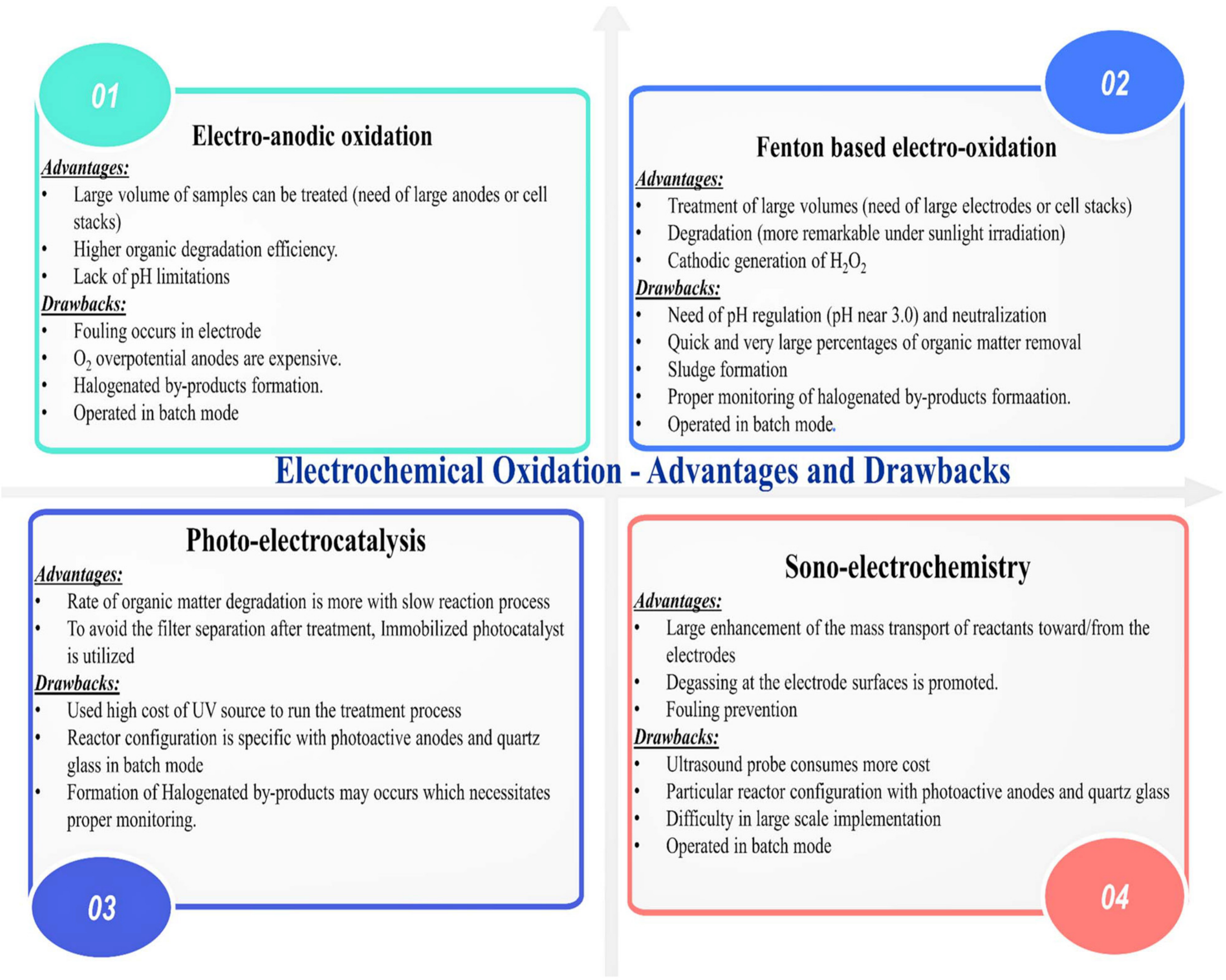
- No stoichiometric oxidants are necessary in EO, and typically H_2O is the only byproduct;

- The electrochemical reactions are carried out without the use of delicate chemicals under mild conditions; and

- The electrode potential or current intensity can be used to precisely control the rate of lignin degradation.

Consequently, in an EO system, high selectivity for the desired deconstruction can be achieved. To further achieve carbon neutrality, electrochemical lignin upgrading combined with renewable energy harvesting is a promising strategy. Depending on the anode material and the type of electrolyte of support used, electrochemical oxidation operates based on the application of an electric current or a potential difference between two electrodes (the cathode and anode), with the potential to generate hydroxyl radicals or other oxidizing species. Thus, both direct and indirect forms of electrooxidation are possible; in the former, the pollutant is removed at the anode through a charge transfer reaction, whereas in the latter, the pollutant is removed by the species generated during the oxidation of the water or electrolytes in the solution. Due to its environmentally friendly attributes, apparent robustness, and scalability, the EO of waste stream lignin has been regarded as promising technology to produce aromatic fine chemicals. The advantages and drawbacks of several EO process are presented in detail in Fig. 7. During the electrocatalytic oxidation of lignin, electrons can directly interact with the C–C bond of the reactant to cleave the reactant and produce free radical intermediates, thereby converting lignin into products.

Nickel-based anodes produce high-value fine compounds such as vanillin and acetovanillone, but Ni electrodes show great stability and have few corrosion problems. 3D materials such as stainless steel mesh and Ni foam have been employed to increase the yield of vanillin and lignin degradation. Opening loops, breaking ether bonds, and demethylation are some of the routes for lignin degradation proposed for use with titanium-based electrodes. Dimensionally stable anodes (DSA) such IrO_2, PbO_2, and SnO_2 have been employed in studies to oxidize lignin *via* the *OH produced on the anode surface. To degrade lignin under 500 mA cm^{-2}, IrO_2-based electrodes, such as $Ti/RuO_2–IrO_2$, $Ti/TiO_2–IrO_2$, and $Ti/Ta_2O_5–IrO_2$, demonstrated the maximum stability and increased activity.[127] They were also employed because PbO_2-based electrodes have a high potential for oxygen evolution. In the EO



Electro-anodic oxidation

Advantages:
- Large volume of samples can be treated (need of large anodes or cell stacks)
- Higher organic degradation efficiency.
- Lack of pH limitations

Drawbacks:
- Fouling occurs in electrode
- O_2 overpotential anodes are expensive.
- Halogenated by-products formation.
- Operated in batch mode

Fenton based electro-oxidation

Advantages:
- Treatment of large volumes (need of large electrodes or cell stacks)
- Degradation (more remarkable under sunlight irradiation)
- Cathodic generation of H_2O_2

Drawbacks:
- Need of pH regulation (pH near 3.0) and neutralization
- Quick and very large percentages of organic matter removal
- Sludge formation
- Proper monitoring of halogenated by-products formaation.
- Operated in batch mode.

Photo-electrocatalysis

Advantages:
- Rate of organic matter degradation is more with slow reaction process
- To avoid the filter separation after treatment, Immobilized photocatalyst is utilized

Drawbacks:
- Used high cost of UV source to run the treatment process
- Reactor configuration is specific with photoactive anodes and quartz glass in batch mode
- Formation of Halogenated by-products may occurs which necessitates proper monitoring.

Sono-electrochemistry

Advantages:
- Large enhancement of the mass transport of reactants toward/from the electrodes
- Degassing at the electrode surfaces is promoted.
- Fouling prevention

Drawbacks:
- Ultrasound probe consumes more cost
- Particular reactor configuration with photoactive anodes and quartz glass
- Difficulty in large scale implementation
- Operated in batch mode

Fig. 7 Advantages and drawbacks of several electrochemical process.

system, the investigation focused on the electrochemical breakdown of maize stover lignin in a 1 M NaOH solution between the Cu/Ni–Mo–Co cathode and the Pb/PbO_2 anode. Hydroxyl radicals first broke down or cracked the larger lignin molecules into smaller intermediates. Then, the intermediates were hydrogenated by H atoms, which saturated the molecular bonds in the intermediates and produced new chemicals. The hydroxyl radical for lignin oxidation degradation was produced by the Pb/PbO_2 electrode.[128] Due to their solubility in lignin and electrical conductivity, deep eutectic solvents (DES) and ionic liquids (IL) are considered good solvents for electrochemical oxidation. The outcome of the electro-catalytic oxidation of phenolic lignin model compounds was examined using a protic IL.[129] A methanol/choline chloride-based DES was used by Yu *et al.*[130] to enhance the solubility and depolymerization of lignin in corncob biomass. By combining EO with lignin fractionation, it was possible to reduce the production of waste and increase the economic feasibility of lignin valorisation. The decomposition of the wheat straw lignin unit structure was carried out electrocatalytically by oxidation on Pb/PbO_2 and reduction on alloyed material cathodes with various catalytic activities in alkaline solution. Gas chromatography was employed to monitor the maximum lignin yields from guaiacol and acetovanillone using the highest yield of compounds of the guaiacyl class, and it was found that the alloyed steels produced the best results in lignin and decomposition under ideal circumstances. Using solvents, sulphuric acid (SA), ammonia (AM), sodium hydroxide, and distilled water, a study examined the effects of bio and electrochemical processes on rice straw pretreatment. The total volatile fatty acids (tVFAs) in the electrochemical pre-treatment with sodium hydroxide (ENA) and sulfate-reducing bacteria (EBA) was 163.48 ± 10.49 mM according to the results. At 0.218 ± 0.10 mM g^{-1} of substrate, hydrogen was generated by the electrochemical process and there was no discernible gasification in the SA and AM electrochemical pre-treatments. The accessibility of the biomass to enzymes for the recovery of value-added products was enhanced by the ECP system.[131] Focusing on lignin, hemicellulose, and cellulose, a study examined the fragmentation and hydrogen generation of lignocellulosic biomass. The findings demonstrated that although cellulose is difficult to react, lignin and hemicellulose readily react with POM. Lower than the minimal potential needed for water electrolysis, the initial potential for hydrogen production for lignin and cellulose was 0.5 V and 0.6 V, respectively. The conversion efficiency of vanillin was 96.81%, whereas the average Faraday efficiency for hydrogen production from lignin was 95.93%. The conversion ratio of hemicellulose was 8.21% for alcohol compounds and 96.77% for ester compounds. In addition, the experiment showed the complete regeneration of the catalyst in the presence of an anode electric field, offering new information on the conversion of lignocellulosic biomass into chemicals and hydrogen energy.[132] To obtain an economic benefit from biomass electro-oxidation, mass manufacturing must move from the laboratory. This demands higher integration and scalability under stable, high-current operating circumstances and overcoming the limits of single block electrodes. In this case, compact and highly fluid integrated reactor designs have been developed recently for organic oxidation processes at industrial currents. These platforms provide larger reaction areas for multiphase reactions, and when combined with cathodic reactions, such as large-scale hydrogen production, they enhance the yield of organic products, while using less energy. Thus, emerging intelligent industrial models can open up new avenues for industrial applications.

3.10. Hydrodynamic cavitation-coupled advanced oxidation process

A growing field of research is the development of innovative pretreatment technologies for LCB. Consequently, hydrodynamic cavitation (HC), which involves the formation of oxidative species in the medium as one of its main effects, is an emerging option for addressing restrictions in the pretreatment step. Cavitation is a phenomenon of vapor/gas bubble formation within the bulk liquid, which agglomerate, and then collapse, was as shown in detail in Fig. 8. It is a highly complex process controlled by many factors. A series of occurrences are shown, including the nucleation, expansion, and collapse of the bubble cavities.[133] Similarly, heat and mass transfer occur between the bubble aggregates and the main liquid, producing cavitation noise and sonoluminescence. However, thorough experimental research is still being carried out to learn more about the dynamic behaviour of cavitation bubbles. Cavitation is undesirable in industrial operations but advantageous when utilised in a controlled environment, such as in biomass pretreatment. By creating shock waves and microcurrents, it is possible to break lignocellulosic fibres and adjacent organic molecules.[134] Furthermore, developing a simplified system improves the removal of lignin from biomass given that it is carried out under mild circumstances, such as short-operations. This technique encourages the hydrolysis of carbohydrates in less time, at a cheaper cost, and with the formation of fewer fermentation inhibitors. In fact, HC produces higher yields during the subsequent enzymatic hydrolysis when it is used in conjunction with an alkali pretreatment. Hence, time is the vital parameter in this pretreatment. The major advantage of using the HC process is its shorter time (*e.g.*, 10 min process time) compared to other cavitation processes, such as ultrasonication, which requires 70 min.[135] Also, to enhance the performance efficiency of HC, an innovative development of adding chemical reagents for efficient lignin removal was investigated recently. HC-assisted alkali pretreatment of reed took 41.1 min for 53.4% lignin removal with the maximum yield of reducing sugars of 326.3 g kg^{-1} of biomass. Applying the HC-assisted alkali method to sugarcane bagasse, 97% glucan hydrolysis yield was achieved in 24 h.[136] Various modes of operation were examined, such as alkaline liquor reusability in the HC-assisted process, which involved simply gathering the solid part of the pretreated sugarcane after retrieving the remaining solution after alkaline pretreatment in each subsequent batch. Also, alkaline H_2O_2 solution

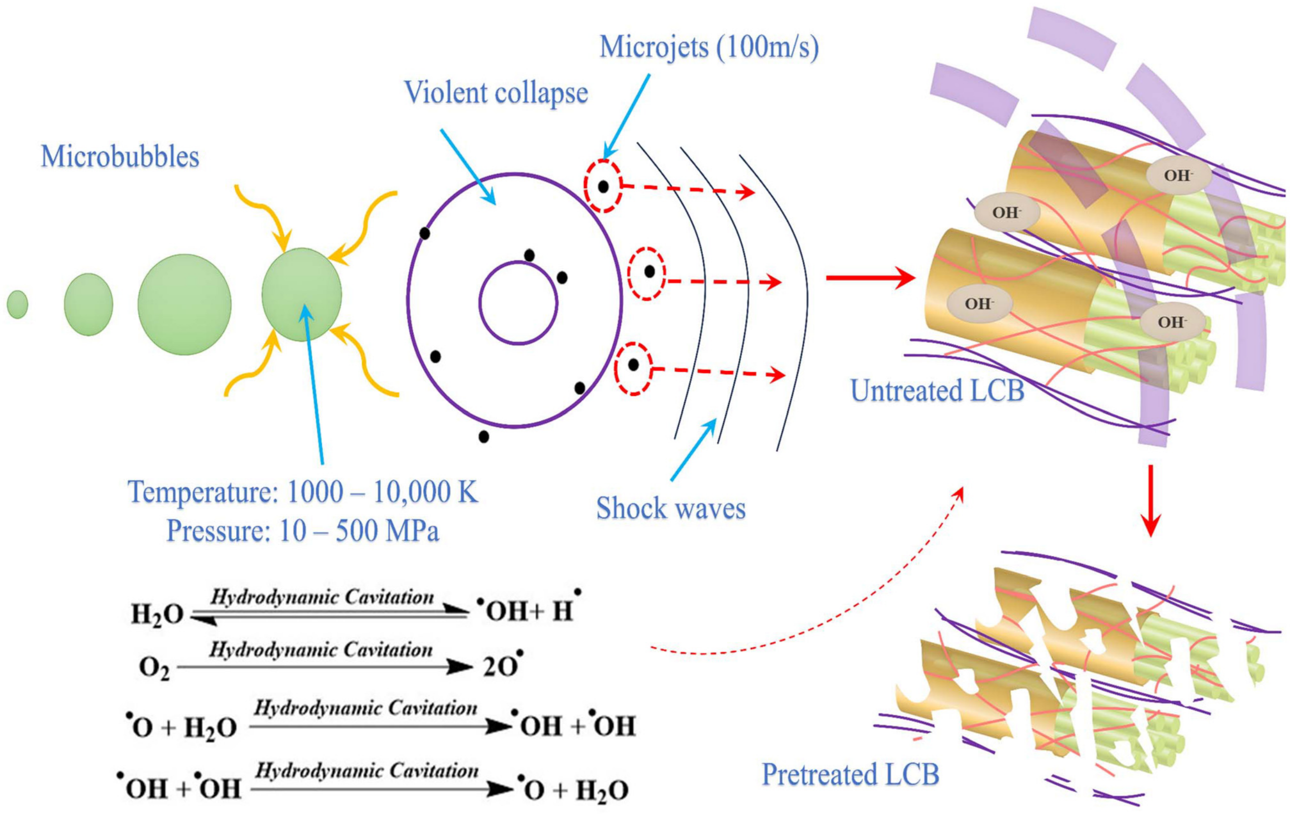


Fig. 8 Hydrodynamic cavitation-coupled advanced oxidation process.

was used in HC-assisted pretreatment, which was repeatedly recirculated for 10 min at 60 °C. After pretreatment, the liquid fraction was retrieved and used again in a subsequent batch process. The higher productivity of continuous processes provides an additional pretreatment option in biorefineries. Acid-catalyzed steam explosions, ionic liquids, sodium hydroxide, and double screw extruders with acid solutions have all been used in these processes. A continuous process was developed using a suspension containing 1% sugarcane bagasse in an alkaline solution during HC-assisted alkaline pretreatment.[137] This process produced 34 g of glucose/100 g of biomass and 18 g of xylose/100 g of biomass. Another crucial factor to consider is the high pH of the liquor produced by HC, which has not yet been researched. The generated liquor may undergo oxidation or degradation due to the removal of lignin, which can produce 2-methoxyacetophenone, 4-hydroxybenzoic acid, vanillin, vanillic acid, coumaric acid, and other chemicals. The major advantages of this pretreatment are its low energy consumption, efficient mixing and mass transfer, operation at ambient temperature, eco-friendly operation, and easy scalability. However, it has the drawbacks of easy wear and tear of the cavitation reactor, not suitable for all types of biomasses, use of complex equipment, bubble coalescence and instability and require safety concerns. Limited research teams evaluated this biomass processing technique, primarily showing an increased reducing sugar yield with HC pretreatment, often incorporating alkali for a synergistic effect. Compared to ultrasound, HC reactors are easily scaled up for industrial applications and require much less input energy but has a limitation in maintaining consistent cavitation conditions and chemical distribution. Thus, the development of advanced cavitation reactor systems capable of efficient persulfate activation and reaction control and selection of novel catalyst systems or additives to enhance the process selectivity and sustainability are appropriate research aspects to be considered in the future.

3.11. Radiation-induced oxidation

High-energy ionising radiation, such as gamma rays and electron beams, can modify the structure of LCB by causing chemical reactions to disrupt its bonds. Recently, this technology has attracted significant interest, particularly to pretreat LCB to generate liquid biofuels. The most popular radioactive employed are cobalt-60 and cesium-137. The disruption of the intermolecular hydrogen bonds makes a gateway for irradiation to reduce the intra- and inter-molecular bonds in cellulose. The movement of radiation from the sealed source bombards the structure of LCB.[138] Gamma radiation transfers its energy to the biomass component through radiation collision, causing the atom to lose an electron and become ionised. Consequently, both short-lived and long-lived radicals are produced, leading to the disintegration of biomass through chain scission and crosslinking. These radicals change the crystallinity of cellulose and the biomass surface structure and increase its surface area. For instance, after being exposed to 480 kGy of radiation, the size of cotton cellulose polymers can shrink by 80 times. The mechanism of the radiation-induced oxidation of cellulose consists of the following phases:

- Ionization:

$$RH \rightarrow RH^{+} + e^{-} \tag{35}$$

- Recombination:

$$RH^{+} + e^{-} \rightarrow RH^{*} \tag{36}$$

- Fragment formation and decomposition with preferential cleavage of the C(1)–H and C(4)–H bonds of the glucopyranose ring:

$$RH^{*} \rightarrow R^{\bullet} + H \tag{37}$$

- Abstraction of hydrogen from other carbon atoms by the hydrogen atoms:

$$RH + H \rightarrow R^{\bullet} + H_2 \tag{38}$$

- Decomposition of the unstable $R^{\bullet}$ radicals with cleavage of the glucosidic bond to produce terminal radicals with scission of the glucopyranose ring.
- The scission of the glucopyranose ring results in the formation of CO_2 (or CO) and of polymeric compounds containing terminal carbonyl or carboxyl groups.

Miscanthus biomass can be hydrolyzed for smooth hydrolysis with 1200 kGy of Co-60 isotope gamma radiation, yielding greater reducing sugars. The potential of gamma radiation technology for pretreating several forms of biomass, such as jute fibre, poplar sawdust, wheat straw, and cotton cellulose, has been investigated. Gamma radiation was used to pretreat rice straw in 1% NaOH,[139] resulting in lower xylan and lignin concentrations, a 60% (100 kGy) increase in cellulose content, and no discernible inhibitor formation. According to a study on the effects of gamma irradiation on empty fruit bunches, pretreatment decreased the amount of lignin and increased the amount of cellulose. Pretreatment of softwood required a dosage of 40 kGy, whereas for hardwood, a greater dosage of 90 kGy was required. This study also found that the species-dependent nature of the gamma-ray pretreatment necessitated a greater dosage. Due to its long half-life of 5.26 years, the cobalt isotope (Co-60) is more frequently employed for industrial-scale irradiation procedures.

Another type of irradiation for pretreating biomass is electron-beam irradiation (EBI). The energy ranges of industrial electron accelerators are typically categorised into low (80–300 keV), middle (300–5 MeV), and high (over 5 MeV) categories.[140] LCB is subjected to a high-voltage stream of electrons. By altering the dose of radiation given during this pretreatment, the electron energy can be managed and adjusted. The released high-energy electrons move into the LCB structures and transmit energy within them. As a result of the LCB being oxidised, the heating process initiates the chemical and thermal reactions in the biomass, including the depolymerization of cellulose and the creation of a carbonyl group. It has also been noted that exposure to an irradiation beam causes the biomass components to crosslink. Additionally, biomass subjected to electron beams showed a decrease in mechanical strength. This may be because the hydrogen bonds between the chains of cellulose are broken, causing it to become less crystalline and more amorphous.[141] A recent study examined the electron beam radiation efficiency on various types of LCB such as rice straw, bamboo, oil palm, fruit bunches, and kenaf. Overall, most of the results showed that considerable cellulose breakdown was seen after the technique. According to a study on the EBI of hybrid grass biomass, the biomass glucose output increased by 59% compared to the untreated sample. This is comparable to the resulted reported in study by Bak *et al.*,[142] in which it was found that EBI could boost the energy and enzyme digestibility of rice straw. One of the key variables in the process is the EBI dosage. According to a study on the EBI of bamboo chips at different dosage in the range of 0.5 to 50 kGy, the pretreatment dose between 0 and 50 kGy achieved considerable cellulose breakdown. Additionally, the study found no appreciable changes in the hemicellulose concentration. Compared to gamma-ray irradiation, EBI, which uses electrically accelerated electrons of >200 keV, is more practical, environmentally benign, and cost-effective. Hence, EBI can replace gamma-ray irradiation.

Microwaves are also employed to pretreat biological materials by absorbing water, fats, or sugars, and transferring energy to organic molecules, generating heat. Through the disruption of the chemical bonds in the lignocellulose structure caused by this localised heating, lignin is depolymerized, hemicellulose is released into the aqueous medium, and cellulose is more amenable to enzymatic hydrolysis. The biomass that needs to be pretreated is submerged in an aqueous medium and exposed to microwaves operating at 2450 MHz, 250–1000 W, and 70–230 °C for 5–120 min.[143] The dielectric properties of biomass significantly impact the effectiveness of the pretreatment, where the presence of moisture and inorganic materials can increase the microwave absorption capacity. Microwave pretreatment is frequently used with diluted acid or alkali to improve its performance efficiency. Microwave-assisted biomass pretreatment has been the subject of numerous reports on energy and cost analysis. Microwave pretreatment used five times less energy than pretreatment using high pressure. Similar research assessed the economic performance of pretreating corn stover with a microwave-assisted steam explosion to produce fermentable sugars, with an estimated cost of production of \$0.093 per kg of sugars under ideal circumstances.[144] The advantages of this oxidation process include it provides uniform and controlled irradiation for selective oxidation reactions, it can be operated under ambient conditions with no additional chemical reagents required and it also enables precise control of the reaction kinetics and product formation. However, its drawbacks, which can affect the efficiency of the pretreatment process, are the requirement of specialized equipment capable of generating and shielding radiation sources, limited availability of suitable radiation sources and reactor designs and radiation exposure concerns and safety considerations for operators and the environment. Also, the treatment efficiency is reduced due to certain limitation such as limited penetration depth of gamma radiation, necessitating treatment of thin biomass layers, the high capital costs associated with radiation equipment and safety measures and potential for cellulose degradation and formation of undesirable byproducts under prolonged radiation exposure. Thus, more research is required for the exploration of advanced reactor designs and process configurations to enhance the radiation efficiency and scalability. Also, the development of novel radiation shielding materials to improve the safety and reduce radiation exposure risks must be explored further.

3.12. Reusable chemical oxidation

The deconstruction of the biomass cell wall is a key component of the new lignocellulose pretreatment technology known as reusable chemical oxidation. This method has the advantage of being easily regenerable and reusable.[145] Reusable oxidants, also called electron carriers, can oxidize biomass made of lignocellulose in either acidic or alkaline media. Pretreatment increases the accessibility to cellulose by oxidizing and removing the hemicelluloses and lignin components using oxidized electron carriers. These oxidized electron carriers withdraw the electrons in LCB, which are subsequently reduced. These electron carriers can then be further transformed chemically or electrochemically into an oxidised state. The depolymerization of lignocellulose has been accomplished using a variety of electron carriers, such as polyoxometalates, iron salts, and organic redox compounds. Polyoxometalates (POMs), especially heteropolyacids, are protonic acids with diverse and stable structures. Due to their potent acidity and redox characteristics, they have been extensively used in catalysis.[146] A POM-mediated integrated process for biomass pretreatment coupled with a liquid flow fuel cell (LFFC) was proposed for efficient electricity production at low temperatures. LCB was oxidised using three different Keggin-type POMs in a strong acidic medium. Delignification and xylan dissolution were visible after pretreatment. The use of organic redox couples as electron carriers in combinative biomass pretreatment for electricity generation is feasible to encourage the removal of lignin. Methylene blue (MB) pretreatment was applied in an alkaline medium, where breakdown of the cell wall of wheat straw was visible.[34] Recently, the effectiveness of maize stover fermentation, which was preoxidised with three different electron carriers, including phosphomolybdic acid, $K_3[Fe(CN)_6]$, and MB, was assessed by Wang *et al.*[147] The best enzymatic digestibility was found in the maize stover pretreated by MB in alkaline medium, with glucan and xylan conversion rates of 97% and 72%, respectively, and a total fermentable sugar concentration of 87 g L^{-1}.[148] Pretreatment of reusable oxidants is a cutting-edge, developing field in an active stage of research. Using appropriate electron carrier pairs, it is possible to simultaneously generate electricity under mild conditions and deconstruct lignocellulose, which is not possible with other pretreatments. However, pretreatment using a reusable oxidant is still in the lab phase. Hence, further investigation of this type of regeneration of oxidants is recommended. Besides, more research is needed on the pretreatment performance of the reusable oxidant following multiple regenerations. Recently, evidence that regenerated $FeCl_3$ performs similarly to fresh $FeCl_3$ in terms of pretreatment was reported,[149] and there was no discernible drop in enzymatic glucan conversion. The determination of the electron carrier stability for recycling is crucial when considering the economic advantages of the system. Hence, together with the traditional goal of achieving a better pretreatment performance, reagent screening and operational condition optimisation should also be considered in the realisation of the greater reuse of reusable oxidants.

(i) Advantages:

- Offers the potential for catalyst recovery and reuse, reducing operational costs.
- Minimizes waste generation and environmental impact compared to single-use catalysts.
- Can be tailored for specific biomass feedstocks and target products.

(ii) Disadvantages:

- Requires additional separation and purification steps for catalyst recovery.
- Catalyst stability and activity may decrease over multiple reaction cycles.
- Limited by the availability of recyclable catalyst materials and regeneration methods.

However, although recyclable oxidation offers significant potential for sustainable biomass valorization and chemical synthesis applications, addressing challenges related to catalyst stability, recovery, and selectivity will be crucial to realizing the full benefits of recyclable oxidation processes and advancing the transition towards a circular economy.

3.13. Other combined oxidation process

Many combinations of various oxidative techniques have been proposed for LCB pretreatment in the literature. For instance, AOPs for processing *Miscanthus* biomass using a mixture of ammonia and peroxide was investigated in Yu *et al.*[150] A fixed ammonia concentration of 30% (m/v) was used to test the effects of temperature (60–150 °C), peroxide loading (1–5% H_2O_2), and reaction duration (1–6 h), obtaining the ideal conditions of 5% H_2O_2 at 130 °C for a 4 h reaction time, removing 89% of the lignin. Fenton-assisted ultrasonic cavitation (UC) was investigated for the pretreatment of rice straw,[151] analysing the effects of various UC potencies, ranging from 200 to 600 W at a fixed frequency of 22 kHz, using a solution of 1.6 M H_2O_2, 0.4 M Fe^{2+}, at 25 °C during 3 h reaction. The lignin removal reached 70% under the optimal circumstances attained with 600 W. Fenton's reagent altered the specific surface area more effectively than ultrasonication alone, and this surface had less mechanical structure than the surface of the untreated biomass, according to the characterization. However, when

Fenton's reagent and UC were used together, the sugar yield after the enzymatic hydrolysis improved by 93% compared to separate use of the two methods. Thus, it was established that Fenton's reagent process, in combination with ultrasound cavitation, is a reliable and efficient procedure. With a 39% decrease in lignin content, the non-thermal plasma/Fenton treatment appears to be effective for rupturing the intricate lignocellulose structure. This treatment improved the hydrolysis of carbohydrate compared to the untreated sample, leading to a 2.25-times higher hexose yield. With 6.5 U g^{-1} of biomass enzyme and a 60 min runtime,[152] a 5% biomass load (corncobs) was treated achieving the highest level of delignification (47.4%) using less energy. A decrease in lignin (47.4%) and an increase in cellulose content (25.3%) were seen after the conditions were optimised. Therefore, the two-stage pretreatment method that combines HC and enzymatic pretreatment may be more effective. Combining ultrasound and sodium percarbonate pretreatment had a synergistic effect on cellulose digestibility and improved the oxidative delignification.[153] It was found that 50 W of irradiation with 0.8 mol L^{-1} of sodium carbonate and 1.2 mol L^{-1} of H_2O_2 produced the best results without producing the inhibitory product furfural. The ozonolysis of sugarcane bagasse in an alkaline medium (NaOH) with ultrasound irradiation was evaluated.[154] The yield of readily accessible cellulose increased to 94% due to this combined pretreatment in removing lignin and hemicellulose. According to Sun *et al.*,[155] pretreating bamboo biomass with a synergistic hydrothermal (HT) and alkaline deep eutectic solvent (ADES) combination was very successful for biomass fractionation and value-adding. The ideal HT-CM/25P pretreatment left the cellulose content (88.9%) intact, while eliminating lignin (93.1%) and hemicellulose (77.9%). A noteworthy percentage of xylan of 65.9% was converted into useful XOS through valorisation. A foundation for downstream use was shown by the branching composition of *O*-acetyl-4-*O*-methyl-glucurono-β-(1 → 4)-D-xylan in the regenerated hemicellulose structure. Similarly, the lignin structure was preserved effectively and a green SUPARDES pretreatment method increased the rates of cellulose saccharification and delignification. The *K*–*T* values and Langmuir adsorption kinetics provided insight into the mechanisms involved in lignin extraction and protection followed pseudo-first-order kinetics with an R^2 value in the range of 0.98–0.99.[156] A novel benchmark for lignocellulose fractionation and upgrading procedures was offered by a high-efficiency *in situ* lignin protection approach. The advantages of this method are as follows: the synergistic effects between different oxidation methods can enhance the reaction efficiency, allowing the selective oxidation of biomass components through complementary mechanisms.

Also, it offers flexibility in process design and optimization for specific biomass feedstocks and target products. However, it has certain disadvantages such as increased complexity and cost associated with integrating multiple oxidation methods, challenges in optimizing the reaction conditions and catalyst compatibility and limited understanding of the interactions and kinetics between combined oxidation processes. Further research on the process complexity, energy consumption, and catalyst compatibility will be essential for realizing the full potential of combined oxidative pretreatment processes and advancing towards sustainable and resource-efficient biorefinery technologies.

For each of the analysed pretreatments, some examples are reported in Table 3, illustrating the biomass feedstock, operating conditions, bioproduct generated and efficiencies.

4. Application of oxidative pretreatments

Oxidative pretreatments can effectively enhance the digestibility of cellulose, improving the energy recovery from LCB. The most common substrates to be treated are agriculture by-products. However, as biomass pretreatments, the majority of oxidative processes are still employed at the lab scale with very few examples of scaling up to the pilot or industrial level.

One of the mildest processes is WAO, whose application has great potential with the investigation of different reactor configuration technologies.[157] Its efficiency is influenced by the air pressure, temperature and reaction time, and also depends on the targeted biofuel.[158] WAO has been proposed to enhance the energy recovery from different feedstocks, such as improving the bioethanol production from rice husk,[36] increasing the glucose yields in treating wheat straw,[159] enhancing the enzymatic hydrolysis efficiency of a mixture of rice husk and wheat straw,[40] and improving the cellulose accessibility and digestibility of rice straw.[160] Adding alkali during the WAO of LCB allows increasing the amount of sugar obtained and decreasing the formation of acetic acids caused by the breakdown of hemicellulose: consequently, higher cellulose deconstruction, lignin and extractive removal and biomethanation potential were observed in the water treatment of hyacinth compared to WAO.[161] The efficiency of WAO can be also improved by using a catalyst. Compared to conventional WAO, this decreases the energy demand, given that higher rates of oxidation and milder operating conditions can be employed.[162] Also, the reaction time, and consequently the economic operating costs are reduced.[163] The catalysts employed to enhance the depolymerization and fragmentation of lignin, were reported by Ma *et al.*,[164] as follows:

- Transition metal ions, *i.e.* Cu(II), Fe(III), Mn(II and III), Co (II), and Zr(IV), and metal oxides, which increase the oxygen reactivity, and thus expedite the cleavage of β-O-4 and pinacol-type C–C linkages;
- Polyoxometalates, which were observed to activate molecular oxygen and oxidize lignin;
- Metallosalen and metalloporphyrins, which were demonstrated to be efficient in breaking ether linkages, and subsequently releasing phenolic aldehydes/ketones; and
- Vanadium group (V, Nb, Ta) catalysts, which were found to be effective in the catalysis of ether and C–C bond cleavage in lignin-containing pinacol structures.

Table 3 Some examples of various oxidative processes for the pretreatment of LCB involving delignification and bioproduct generation

Sn. no.	Pretreatment	Feedstock used	Operating condition	Outcomes	Ref.
1.	WAO	Wheat bran	Temperature of 170 °C and pressure of 12 bar	Xylose concentration of 4.33 g L^{-1}, increased to 13.75 g L^{-1} by using forward osmosis membrane to concentrate the pretreated liquor	179
2.	WAO	Rice husk and wheat straw	Temperature of 170 °C and 195 °C, pressure of 5 and 10 bar, reaction time of 10 and 20 min	Optimal conditions identified at 195 °C, 5 bar, 10 min, with cellulose convertibility of 63%, glucose yield of 22.6 g per 100 g of raw biomass, lignin removal of 51.8% and hemicellulose solubilization of 67.4%	27
3.	Alkaline peroxide-assisted WAO	Rice straw	Temperature of 160 °C and 190 °C, H_2O_2 concentration of 0.5 and 4.0 (w/v%), soaking time of 6 and 24 h	Highest concentration of sugars and acetic acid (1.2 g L^{-1}) at 190 °C, 0.5% H_2O_2, 24 h soaking time, corresponding to 71.86% of hemicellulose solubilization	180
4.	PO	Biomass-derived monosaccharides and macromolecular xylan	Fe-doped gallium nitride (GaN) treated by calcination as catalyst, 10 W of visible light	CO production rate of 385.74 μmol (g h) and lactic acid yield of 71.38% from xylose reforming and CO production rate of 923.21 μmol (g h) and lactic acid yield of 105.50 mg/200 mg_{xylane} from reforming of macromolecular xylan	181
5.	PO	Biomass-derived 5-hydroxymethylfurfural	Simulated sunlight irradiation (AM 1.5 G), graphitic carbon nitride impregnated niobium oxide as catalyst	Selectivity of 2,5-diformylfurane from 56% to >99% by including triethanolamine tertiary butanol	182
6.	FO	Mixed hardwood (*Quercus mongolica*, *Robinia pseudoacacia* L., and *Castanea crenata*) chips	$FeSO_4{\cdot}7H_2O$ and H_2O_2 (28%, w/w) used as Fenton reagent a moral ratio of 1 : 25 to 1 : 100	The optimal condition (0.01 g L^{-1} of glucose, 0.13 g L^{-1} of xylose and 0.26 g L^{-1} of acetic acid) for FO of mixed hardwood at a molar ratio of 1 : 25 and reaction time of 96 h	183
7.	FO	Rice straw	$FeSO_4{\cdot}7H_2O$ and $FeCl_2{\cdot}4H_2O$ and two types of Fe^{3+}-salt $Fe_2(SO_4)_3$ and $FeCl_3{\cdot}6H_2O$ were used for Fenton-based pretreatment	The highest lignin removal (from 83% in the untreated sample to 3.78) for pre-treatment with $FeCl_3{\cdot}6H_2O$ and H_2O_2 batch dose mode	184
8.	FO	Sugarcane bagasse	Fenton's reagent $FeCl_2{\cdot}4H_2O$ and H_2O_2 (30%, w/w)	Sugar concentration of the treated substrate reduced to 3- to 9-fold increase over that of the untreated one	54
9.	H_2O_2 oxidation	Sugarcane bagasse	Temperatures of 20 °C, 40 °C and 60 °C, reaction time of 6, 15 and 24 h, H_2O_2 concentration of 1%, 3%, 5%	Highest glucose yields after hydrolysis of bagasse pretreated with peroxide (309.3 mg g^{-1}) 20 °C, 24 h and 5% H_2O_2 concentration	185
10.	H_2O_2 oxidation	Rice hulls	H_2O_2 at concentration of 0%, 3.75%, 7.5%, and 10.0%, v/v, reaction time of 6 and 24 h	Highest yield of total sugars of 249 ± 1 mg g^{-1} at 7.5% H_2O_2 concentration, 35 °C and 24 h	186
11.	H_2O_2 oxidation	Sweet sorghum	5% (w/v) H_2O_2	78.84% ± 0.23% of acid detergent lignin removal, increase in cellulose content from 49.78% in the untreated substrate to 72.45%	187
12.	PAA oxidation	Eucalyptus	Temperature range of 110–150 °C, time reaction of 30–120 min, concentration of PAA from 1.0% to 3.0%	Delignification of 54.8% and more than 90% of the glucan recovery retained in the solid residue at 2% PAA, 140 °C, 60 min	188
13.	PAA oxidation	Wheat straw	PAA solution at pH 4.8, reaction was carried out at 85 °C for 45 min	Cellulose content increased from 35.6% in the untreated substrate to 67.1%, lignin decreased from 28.1% to 7.0%	189
14.	PAA oxidation	Chips of aspen (*Populus tremuloides Michx.*) wood	PAA solution (115 mM) for 6 h at 60 °C	Lignin content dropped to 11.6% after 3 h reaction and to 9.9% after 6 h reaction; glucose yield after saccharification of 95.0%	65
15.	PS oxidation	Sugarcane bagasse	Temperature: 80 °C, duration: 180 min, varied PS salt: *Sodium PS*: 1.6 mol L^{-1}, S/L ratio −1 : 20 (g mL^{-1}); *Ammonium PS*: 1.4 mol L^{-1}, S/L ratio of 1 : 20 (g mL^{-1}) *Potassium peroxymonosulfate*: 0.8 mol L^{-1}, S/L ratio 1 : 20 (g mL^{-1})	Reducing sugar yield = 67.98%; sugar conversion rate = 90.29%, lignin removal rate = 87.49% for PPMS, which was 2 to 3 fold times higher than the other PS salts	73
16.	PS oxidation	Rice straw	120 °C 2 h with 75 mM potassium PS concentration	Glucan recovery of 85.50%, lignin removal of 8.96%, enzymatic digestibility of 91%	190
17.	PS Oxidation	Wheat straw (*Triticum aestivum*)	Base activated, heat activated, and H_2O_2 (0.5, 1, 1.5, 2, and 2.5 mol L^{-1} concentrations of H_2O_2) activated PS, reaction times of 30, 80, 130, 180, and 230 min, reactant solutions of 0.05, 0.175, 0.3, 0.425, 0.55 mol L^{-1}	Maximum sugar yields of 66.8%, 49.4%, and 41.7% in base, heat, and H_2O_2 activated PS	79

Table 3 *(Contd.)*

Sn. no.	Pretreatment	Feedstock used	Operating condition	Outcomes	Ref.
18.	Ozone oxidation	Empty fruit bunch	160 g, 40 wt% moisture contents, 120 mg min^{-1} ozone for 90 min	Lignin removal = 78.0%	191
19.	Ozone oxidation	Sugarcane bagasse	Sugarcane bagasse moisture content of 30%, 50%, 70%, ozone concentration of 2%, 3%, 4% mol mol^{-1} in ozone/oxygen, ozone/oxygen flow of 30, 60, 72, 90 L h^{-1}, particle size higher than 4.76, between 4.76 and 1.25, lower than 1.25 mm	77.55% and 56.95% of glucose and xylose yields obtained at 50% moisture content, 2% mol mol^{-1} in ozone/oxygen, 60 L h^{-1} of ozone/oxygen flow, particle size lower than 1.25 mm	123
20.	Ozone oxidation	Wheat and rye straws	Moisture content from 20 to 40% w/w, particle size lower than 1 to 3–5 mm, ozone concentration from (2.7% to 3% w/w), air/ozone flow rate from 60 to 90 L h^{-1}, basic conditions from 0 to 20% NaOH	Enzymatic hydrolysis yield of 53–88.6% for wheat straw, with lignin content decrease from 17.1% to 13.5–11.2%; enzymatic hydrolysis yield of 36–57% for rye straw with lignin content decrease from 22.1% to 18.3–12.1%	192
21.	Sonochemical oxidation	Oil palm empty fruit bunch	500 mL of 2% H_2SO_4 aqueous solution with 50 g of biomass; power of 2 kW, frequency of 20 kHz, duration of 15, 45, 60 min, amplitude 15%, 60%, 90%, ambient temperature normal pressure	Highest xylose yield of 58% at 90% amplitude for 45 min	193
22.	Sonochemical oxidation	Olive tree pruning residues	Duration of 30, 60 and 120 min using an ultrasonic bath (420 W, 50/60 Hz, Selecta), temperature of 50 °C	Higher delignification with ultrasound application, lignin removal increased from 17.3% up to 45.6%	194
23.	Sonochemical oxidation	Corn bran	5 g of ground bran suspended in 50 mL of extractant (water and NaOH at 1% and 5%), sonic power of 100 W, duration of 5–10 min, at 30 °C, 50 °C, 60 °C, 70 °C	Highest yield of polysaccharide fractions (41.2%) with 5% NaOH as extractant, 50 °C and 10 min	195
24.	Electrochemical oxidation	Aspen lignin	Pb/PbO_2 anode, stainless steel wire mesh cathode, DC 20–90 mA cm^{-2}, temperature 30–90 °C, reaction time 0–8 h	88% lignin decomposed within 5 h; maximum content of 4-methylanisole (64.9 g kg^{-1} lignin) at 50 mA cm^{-2}, 50 °C, in 2nd h; maximum yield of styrene (1.8 g kg^{-1} lignin) and 2,6-dimethoxyphenol (9.48 g kg^{-1}) at 60 mA cm^{-2}, 50 °C in the 2nd hour	196
25.	Electrochemical oxidation	Kraft lignin	Ni (300 A m^{-2}), DSA-O_2 (500 A m^{-2}) and PbO_2 (500 A m^{-2}) electrodes	15%, 17%, 7% of lignin conversion yield, 63%, 64%; 56% of vanillin conversion yield, 1%, 4%, 5% of vanillic acid conversion yield with Ni, DSA-O_2, and PbO_2, respectively	197
26.	HC	Sugarcane bagasse	Pressure of 200 kPa, 300 kPa and 400 kPa, throat lengths of Venturi tube of 1.5, 3.0 and 5.0 mm, throat diameters of Venturi tube of 1.5 mm and 2.0 mm, addition of NaOH from 1% to 5%	Under optimal conditions (4.90% of NaOH, 2.03% solid weight percentage in liquid in 58.33 min of process) 58.46% of cellulose, 14.34% of hemicellulose, 14.03% of lignin (lignin removal of 56.01%) with a solid recovery of 66.06%	198
27.	HC	Sugarcane bagasse	Inlet pressure of 3 bar, concentration of NaOH of 0.3 mol L^{-1} and H_2O_2 of 0.78% (v/v), 7.5 min at 60 °C	Glucan hydrolysis yield of 80%, hemicellulose removal of 54.47%, lignin removal of 54.4%	96
28.	HC	Reed	Centrifugal pump (1.5 kW), pressures of upstream and downstream at 0.6 and 0.06 MPa	Solid recovery of 76.4%, glucan recovery of 97.8%, lignin removal of 42.3%	199
29.	Radiation-induced oxidation	*Miscanthus floridulus*	^{60}Co-γ radiation source intensity of 9.99×10^{15} Bq at 2.0 kGy h^{-1} dose rate, specific levels of absorbed doses 0, 400, 600, 800, 1000, and 1200 kGy	Scarce influence on lignin content (highest decrease from 21.30 in the untreated biomass to 19.70 in biomass irradiated at 1200 kGy)	200
30.	Radiation-induced oxidation	Rice straw	Electron beam irradiation with doses of 7.6, 20, 50, 80 and 90 kGy	Xylan and lignin losses of mass of 5–12% and 1–7%	101
31.	Radiation-induced oxidation	Rice straw	Microwave power from 480 to 800 W, irradiation time from 4 to 12 min, sodium chlorite concentration from 0.4 to 3.0%, bleaching time from 1 to 5 h	Delignification percentage from 63.15% to 94.15%	201
32.	Wet oxidation pretreatment	Softwood (*Picea abies*)	200 °C for (10 min at neutral pH) followed by enzymatic hydrolysis (72 h)	79% of sugar yield used as biochemical products	206
33.	Ozone oxidation	Maize stover	(Conc. 2.8%, 1 h, 60 L h^{-1} flow rate) and enzymatic hydrolysis	80% of glucose used as biochemical products	207
34.	Fenton oxidation	Corn stover	(1000 mmol L^{-1} H_2O_2 + 10 mmol L^{-1} $FeSO_4$) and enzymatic hydrolysis	67.61% of glucose used as biochemical products	208
35.	PAA oxidation	Wheat straw	Alkaline peroxide pulping followed by mild peracetic acid (85 °C for 45 min)	36%–60% of nano and microfibrils, eco-friendly products, pharmaceutical application	146

Table 3 *(Contd.)*

Sn. no.	Pretreatment	Feedstock used	Operating condition	Outcomes	Ref.
36.	Wet oxidation pretreatment	Beech wood	Wet oxidation followed by enzymatic saccharification and fermentation processes	75.9 g L^{-1} of ethanol used as biofuel	209
37.	Fenton oxidation	Sugarcane bagasse	2 mol L^{-1} $FeCl_3$ in an autoclave at 120 °C enzymatic hydrolysis; $FeCl_3$ can be regenerated in a liquid flow fuel cell (LFFC)	70% electricity used as energy	108
38.	Ozone oxidation	Empty fruit bunch	(160 g, 40 wt% moisture contents, 120 mg min^{-1} ozone for 90 min)	Lignin degradation is 78 wt%, & maximum glucose yield of 12 wt%; used as biochemical products	148
39.	Microwave oxidation	Miscanthus and switchgrass	Microwave (120 °C under 800 W) + sub-critical treatment; gasification	65%–71% hydrogen used as biofuel	210
40.	Microwave oxidation	Cauliflower (*Brassica oleracea var. botrytis*) and cabbage (*Brassica oleracea var. capitata*) Leaves	Microwave irradiation (350 W microwave irradiation for 30 min) and biomethanation	Methane-0.271 L g^{-1} VS removed used as biofuel	211
41.	Ultrasound oxidation	*Agave durangensis* leaves	Ultrasound and enzymatic digestibility	Inulinase – 4 U mg^{-1} and cellulase – 0.297 U mg^{-1} used for cosmeceutical applications	212

Another promising treatment is represented by ozonolysis, which has been shown to be a successful method for treating different types of LCB, such as sugarcane bagasse, cereal straws, wheat straw, rye straw, eucalyptus, maple, oil palm frond and empty fruit bunches, especially on a small scale; however, scaling up on an industrial level is limited by the high costs of ozone.[165] The main parameters influencing the efficiency of ozonolysis are as follows:[166]

- Reactor design, which can be based on a perfectly mixed or plug flow configuration and should be optimized to maximize the contact between the ozone and biomass, enhancing the process performance.

- Moisture content, which acts as the mass transport medium and plays a role in the generation of radicals; however, the transfer of ozone mass is restricted at a too low moisture content, leading to inadequate reaction with biomass, whereas a too high-water concentration can involve the formation of a layer of water, which obstructs the pores of the biomass, increasing the process time with the decomposition of ozone into hydroxyl radicals.

- Particle size, given that ozonolysis is a process based on surface reaction.

Due to its advantage of operation at low-medium temperatures, oxidation based on Fenton reactions or hydrogen peroxide is under investigation. In detail, FO is also feasible for operation with a relatively high solid loading, with the further benefit that in presence of light radiation (photo-Fenton advanced oxidative process), the degradation of recalcitrant organic materials becomes faster with low operating cost due to the use of a renewable energy source.[11] FO for LCB treatment has been mainly investigated in combination with hydrothermal treatment to evaluate the effect of these processes on the enzymatic hydrolysis efficiency of wood chips.[79,167] The influence of Fenton reactions on enzymatic hydrolysis was also tested to assess the effect of this pretreatment on anaerobic digestion, where an increase in biogas production with a significant methane content was observed.[168] Enzymatic digestibility is also affected by the use of catalysts. For example, Fe_3O_4 magnetite nanoparticles increased the enzymatic digestibility of reed stem and rice straw by 177% and 87%, respectively, with the additional advantage that nanoparticles can be easily separated using a magnetic method, and then recycled.[169] As mentioned above, a further approach to enhance the Fenton reaction performance was observed to be the combination with ultrasound, which allowed the highest release of reducing sugars with levels 4 and 1.5 times higher than untreated straw and Fenton reagent-pretreated straw without ultrasound, respectively, to be achieved. This result was ascribed to the ability of ultrasound to disrupt the cellulose structure and increase the pore volume and surface area, while Fenton's reagent selectively degraded hemicellulose and lignin through the generation of hydroxide free radicals.[151]

Concerning hydrogen peroxide oxidation, this process is significantly influenced by the H_2O_2 concentration, biomass loading, pretreatment time and temperature.[165] One of the main advantages of this process is represented by the absence of residues given that hydrogen peroxide degrades into oxygen and water, reducing the need for further waste treatment.[170] Using alkaline hydrogen peroxide pretreatments has been demonstrated to increase the yield of sugars when combined with enzymatic hydrolysis by investigating several ligno-cellulosic substrates, *i.e.* rice husk, cashew apple bagasse, wood, artichoke, rice straw, agave bagasse, coconut husk, corn stover, banana rachis, corn cub, corn stover, sugar cane bagasse, Douglas-fir wood, *Miscanthus*, sorghum, Virginia mallow, and switchgrass.[49,171] Testing the process on corn stover for subsequent enzymatic saccharification to monomeric glucose and xylose, it was suggested to increase the biomass loading, decrease the H_2O_2 loading, prolong the pretreatment time and maintain the pH to increase the process efficiency and reduce the economic costs.[172]

Regarding sonochemical oxidation, the available literature primarily focuses on the use of ultrasonic technology with horn-based systems operating below 50 kHz, with different studies carried out on the pilot scale.[173] Different substrates have been tested, *i.e.* sugarcane bagasse to assess the effect of sono-chemical oxidation to enhance ethanol production,[174] fresh olives and olive leaves, peels of pomegranate, eggplant, jabuticaba, mango, citrus, grape pomace and skin, forest wood wastes, sugarcane bagasse, groundnut shells, pistachio shell, coconut coir, corn cob, corn stover and sorghum stalk.[173,175] It was observed that acoustic phenomena can enhance both the enzymatic activity and anaerobic digestion performance.[176] However, there are opposing views on the feasibility of this process; indeed, some authors highlighted that the high energy demand of this pretreatment is not counter-balanced by its benefits at the lab scale,[177] whereas others observed that it may be energetically and economically feasible if employed on a large scale with commercial technologies.[178] Finally, it has been reported that to accelerate the hydrolysis of hemicellulose, ultrasound treatments can be also combined with microwaves.

HC has been tested on different scales including lab, pilot and large to assess its potential for increasing biogas and biomethane production, lignin removal, saccharification efficiency, and cellulose enhancement considering several feedstocks, *i.e.* corn stover, wheat straw, sugarcane bagasse, and grass silage.[202] The main factors affecting the process are the bubble size and life of the so-called bubbles, which represent the distance traveled before their collapse and the cavitator size and geometry.[92] HC reactors can be classified as follows:[151,203]

- Non-rotating reactors, such as orifice plates and Venturi pipes, which are versatile and easy to operate but characterized by a low efficiency due to the high pressure connected, severely restricting the flow and
- Rotating reactors, which generate cavitation in a region through the use of high-velocity propellers and show a higher efficiency compared to non-rotating reactors.

Another classification is based on the operational conditions, according to which pulsating HC reactors, which operate in cycles, continuous HC reactors, and shear-induced HC reactors can be distinguished.[203] PS advanced oxidation is mainly employed to reduce organic pollutant contamination in water and soil, whereas its application as lignocellulose pretreatment has scarcely been investigated, especially on a large scale.[204] For example, the effect of different PS pretreatments was investigates to test the enzymatic saccharification efficiency of sugarcane bagasse,[73] changes in biomass composition, lignin removal, and glucan yield in the treatment of wheat straw,[79] and increase in the decomposition of maize straw.[205]

Finally, the use of electrochemical oxidation and reusable oxidants to treat biomass is still very limited and in the research stage.[122] Table 3 presents details the various applications of oxidative pretreatment for LCB biorefining. Some biorefinery bioproducts such as glucose, xylose, methane, hydrogen, gluconic acid, enzymes, and organic acids can be produced during various oxidative treatments. The generated bioproducts have various applications in the pharmaceutical industry, cosmetics, self-care products, animal and bird feed, nutritional supplements, *etc.* The development of eco-friendly and efficient biomass pretreatment technologies can bring the concept of sustainable biorefineries to reality. Based on the evaluation of various pretreatment methods, the optimal procedure can be chosen to improve the crystallinity of cellulose, overcome the resistance of LCB, and guarantee the highest possible recovery of sugars and other bioproducts with industrial significance.[211,212] The obstacles in the efficient pretreatment of biomass include issues related to cost-effectiveness, energy-efficiency, and environmental sustainability. These issues are currently impeding the integration of biomass as feedstocks in biorefinery methodologies.

4.1. Routes in mechanistically-driven catalytic systems for enhanced biomass valorisation: rational design, process optimization, and future perspectives

For the effective valorization of biomass, it is essential to comprehend the underlying mechanisms of the reactions involved in biomass conversion and to design catalytic systems accordingly. An understanding of the bond breaking in lignocellulosic biomass and the creation of new bonds in the resultant products and intermediates can be gained by investigating the molecular mechanisms of oxidative pretreatment.[213,214] Furthermore, thermodynamic and kinetic studies are critical for understanding the energetics and reaction rates of these processes, allowing an enhancement in the process efficiency.[215] A summary of a full overview of the methodologies used to investigate these aspects is presented as follows:

Biomass structure analysis. Understanding the complex structure of lignocellulosic biomass, including cellulose, hemicellulose, and lignin, is crucial. This study focuses on specific bonds that are important for cleavage, namely ether linkages in lignin–carbohydrate complexes and carbon–carbon bonds inside the lignin aromatic units. Using sophisticated spectroscopic techniques such as mass spectrometry (MS) and nuclear magnetic resonance (NMR), the breakage of chemical bonds during oxidation can be closely monitored. In addition, a discussion of the critical role played by reactive oxygen species (ROS), such as hydroxyl radicals ($^{\bullet}OH$) and sulphate radicals ($SO_4^{\bullet-}$) in initiating and accelerating the bond breakage processes can be performed. Characterizing the distribution of cleavage products provides critical insights into their effects on the structure and composition of biomass. Utilizing techniques such as density functional theory (DFT), molecular dynamics (MD) simulations, and quantum chemical calculations can provide insights into the mechanisms of bond breaking in biomass components. These methods allow researchers to analyze the cleavage of glycosidic bonds in cellulose, ester linkages in hemicellulose, and β-O-4 linkages in lignin under oxidative conditions.

Reaction pathway elucidation. Investigating the mechanisms involved in biomass depolymerization, dehydration, hydrogenation, and deoxygenation is important. Kinetic studies, isotopic labeling experiments, and computational modeling can elucidate the reaction pathways and identify key intermediates. Molecular simulations and spectroscopic techniques such as nuclear magnetic resonance (NMR) spectroscopy enable the identification of reactive intermediates formed during oxidative pretreatment. By characterizing transient species such as radicals and carbocations, researchers can elucidate the pathways leading to new bond formations, such as the generation of aldehydes, ketones, and carboxylic acids from lignocellulosic biomass.

Catalyst–substrate interactions. Understanding the interactions between lignocellulosic biomass substrates and catalytic species is critical. Surface science techniques, such as X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR), help elucidate catalyst–substrate interactions and surface reactivity.

Kinetic and thermodynamic analysis. Characterizing the kinetics and thermodynamics of biomass conversion reactions provides insights into the reaction rates, activation energies, and equilibrium constants. The thermodynamic study calculates the Gibbs free energy change for oxidation reactions in lignocellulosic biomass pretreatment, assesses bond cleavage and formation processes, investigates the effects of temperature, pressure, and solvent composition on the reaction equilibrium and product distribution, and evaluates the thermodynamic stability of the intermediate species and their potential for further transformation or degradation. Similarly, kinetic studies aim to determine the reaction rate constants for individual oxidation steps, examine the impact of reaction parameters such as temperature, pH, and catalyst concentration on the kinetics, characterize the reaction order and mechanism, and identify the potential rate-limiting steps and kinetic bottlenecks affecting the process efficiency. Kinetic modeling and thermodynamic calculations guide process optimization and reactor design. Kinetic Monte Carlo simulations and reaction network modeling allow researchers to quantify the contributions of different reaction pathways in oxidative pretreatment. By integrating the experimental kinetic data with computational models, it becomes possible to predict the evolution of the reaction products with time and optimize the process parameters to achieve the desired product distributions.

Based on the above-mentioned investigation, the rational designing of catalyst systems can be developed. Developing tailored catalysts is essential for advancing particular biomass conversion processes. This entails choosing suitable metal or metal oxide catalysts, adjusting the particle size and shape, and maximizing the catalytic activity and selectivity. Also, optimizing the catalyst support, such as zeolites, mesoporous silica, and carbon compounds, improves the catalyst stability and dispersion. Integrating heterogeneous and homogeneous catalysis techniques results in synergistic catalytic activity and selectivity for biomass valorisation. Multifunctional catalyst design enables various biomass conversion processes to be mediated concurrently, rapid process operations and lower catalyst requirements. Advanced characterization techniques such as operando spectroscopy and high-throughput screening are being used to provide real-time insights into catalytic processes, enabling faster catalyst discovery and optimization. Developing catalysts with improved stability, recyclability, and resistance to deactivation is crucial for long-term process sustainability. Techniques such as catalyst regeneration, immobilization, and recovery systems are being explored to enhance the process economics and minimize waste. Biological and bioinspired catalysis offers opportunities for biomimetic biomass conversion processes and engineering enzymes and pathways. Lastly, integrating renewable resources such as biomass-derived feedstocks, bio-based solvents, and green hydrogen in catalytic processes promotes sustainability and reduces the environmental impact. Overall, biomass structure analysis methods provide valuable insights into the composition, architecture, and properties of lignocellulosic biomass. These techniques are essential for understanding the biomass structure–property relationships and optimizing biomass conversion processes for bioenergy, bioproducts, and biorefinery applications. Collaboration among academia, industry, and government agencies is essential for driving innovation in biomass valorization. Mechanistically-driven research initiatives bring together experts from diverse disciplines to tackle complex challenges and accelerate the development of sustainable catalytic systems and biorefinery processes. In conclusion, using mechanistic insight to build effective catalytic systems holds enormous promise for increasing biomass valorisation. By integrating fundamental insights with rational catalyst design concepts and process optimization methodologies, researchers can pave the path for the development of efficient and sustainable biorefinery technologies that can convert biomass into valuable fuels, chemicals, and materials.

5. Economic consideration

Economic feasibility is essential in lignocellulosic biomass pretreatment to make the process commercially viable. Resources can be conserved by identifying bottlenecks early on through their possibility evaluation. Despite the positive outcomes observed in pilot and lab settings, there is still a significant lack of academic research regarding process parameter optimization and the feasibility of bringing pretreatment to an industrial scale. Furthermore, to assure a green and economically viable energy pathway, the environmental impact related to the energetic valorization of biomass needs to be thoroughly evaluated.[216] This is important in examining the costs of the various steps of the entire LCB treatment process, which can assist in the estimation of the expense spent for the proposed method.

- The costs of the biomass,
- Equipment,
- Chemicals and power consumed
- Utilization of renewable anergy

are all factors to be considered in the pretreatment of LCB.

5.1. Factors impacting economic feasibility

Cost of biomass. LCB is very sustainable and its overall cost is about 22–85 $ per t, depending on accessibility and category. A positive relationship always exists between the cost of produced biomass and value-added product. The affordability of raw materials, handling expenses, energy utilisation efficacy, and the demand for renewable energy products are some of the variables that determine the possibility of using LCB for energy generation in an economically feasible way.

Equipment cost. Nearly half of the total cost of the production of lignocellulosic biofuels and biochemicals can be attributed to the pretreatment of heterogeneous biomass residues, as well as the expenses related to their collection, inventory, and transportation. Oxidative processes appear to be more expensive compared to non-oxidative treatments, considering both the investment costs, due to the need for additional equipment, and the operation expenses related to the high energy requirements.[217,218]

Chemicals, and power consumption. The high cost of oxidant agents poses a significant challenge in the widespread adoption of oxidative pretreatment methods for LCB recovery. Chemical consumption and energy costs are critical considerations when evaluating the economic feasibility of pretreatment methods. Besides investment costs, operational expenses, including chemical usage and energy consumption, need to be carefully assessed to accurately determine the overall cost-effectiveness of oxidative pretreatment approaches.

Utilization of renewable energy. Integrating renewable energy sources, such as solar power, presents an opportunity to reduce economic costs in oxidative pretreatment processes. Solar-driven oxidative methods demonstrate potential cost reduction compared to conventional approaches, benefiting from lower operating costs, minimal maintenance requirements, and environmentally friendly characteristics.

5.2. Considerations and prospects in economic assessment in oxidative pretreatment

A significant limitation in the widespread use of oxidative pretreatments in the recovery of LCB is represented by the high cost of the oxidant agents. Chemical consumption and energy costs are the two primary factors that need to be considered when selecting oxidative pretreatment, beside the investment costs, to determine operational expenses. The most basic photo-induced chemical oxidation method is the use of UV/H_2O_2, but given that it is not solar-driven, novel UV light sources will be necessary for its advancement. Photo-induced chemical oxidation methods such as photo Fenton and photocatalysis consume electrical energy to generate UV radiation to accelerate the treatment process. The electrical energy consumption can be calculated using the following formula:[219]

$$E = (P \times t \times 10^{-6})/V\ (C_{\mathrm{o}} - C_{\mathrm{f}}) \tag{39}$$

where P = rated power in UV lamp (kWh), t = irradiation time (h), V = volume of the sample (L) and C_{o} and C_{f} = the initial and final concentration of sample used, respectively (mg L^{-1}). This energy consumption is directly related to the treatment efficiency and energy cost. Renewables are also important in terms of both economic feasibility and environmental impact. For example, employing solar energy reduces the economic costs of photocatalysis pretreatment[220] and Fenton reaction when it is coupled with light radiation (photo-Fenton advanced oxidative process)[4] compared to other oxidative pretreatments. Utilising solar energy from photovoltaic cells is another potential development to be considered for the large-scale application of oxidative pretreatment. The primary advantage achieved in utilizing solar energy for pretreatment is cost reduction. These systems also benefit from being relatively solar-available, noiseless, having low maintenance and operating costs, and classified as clean energy. They can also generate energy in close proximity to the consumer. However, there are still problems with the limited market availability, high initial costs, the comparatively large installation area needed for these systems and geographic factors that affect solar irradiation. Furthermore, another issue in photo-induced chemical oxidation is that the relatively high turbidity of the sample can prevent radiation from penetrating far enough to oxidize the substrate optimally, necessitating an increase in radiation dose, and correspondingly higher energy requirements. This affects the efficiency of the treatment process. Thus, proper investigation is needed to avoid these drawbacks and better implement cost-effective solar-based photo-oxidation processes. Cost is typically the most important in FO processes. Although the solid catalysts in Fenton reactions usually have low concentrations, it is still important to consider the presence of precious metals, given that they can increase the cost of the catalyst and make its recovery and reuse more challenging.

Furthermore, due to their difficult and expensive production, oxidative agents with excellent performances reported in the literature are hardly ever considered for practical applications.

Another strategy to reduce the economic costs related to the oxidative agent involves controlling the consumption by identifying an optimal concentration, as shown in a study that investigated the effect of using FO on lignin decomposition and enhancement in the yield of hydrolysis glucan from treating garden biomass.[50] Additionally, the contribution of oxidants to the operating costs can be reduced by using reusable oxidants. Their use, especially when the process is based on organic redox compounds, is expected to be particularly promising and capable to be economically convenient on a large scale.[122] Considering the specific treatments, some comparisons are reported in the literature. Analysing the benefits of PS oxidation, it has been demonstrated that this process may reduce the economic cost by about 6 times compared to Fenton reaction.[79] Actually, the economic viability of PS oxidation has also been highlighted in treating straw residues to limit pesticide contamination.[163] The cost of EO is directly correlated with the applied current. This pretreatment has a significant impact on the investment cost. High electrical energy and electrode material costs are the major operational costs in the electrochemical oxidation process. Its energy consumption can be calculated as follows:[221]

$$\mathrm{EC} = (U \times I \times t)/[(C_{\mathrm{o}} - C_{\mathrm{f}}) \times V \times 10^3] \tag{40}$$

where EC is energy consumption (kW h per kg COD), U is the applied voltage (V), I is the applied current (A), t is the electrolysis time (h), and C_{o} and C_{f} are the initial and final COD (g L^{-1}), respectively, and V is the volume (L). A study confirmed the highest net profit of $ 119.29 for the electrochemical oxidation pretreatment of yard waste for biofuel generation during economic analysis.[176] Approximately, about 7 $ increment in net profit was achieved in electrochemically pretreated yard waste compared to the untreated yard waste during anaerobic digestion. This indicates the efficiency of this pretreatment process.

Regardless of all the lab-scale investigations on ozone, full-scale ozone-based biomass pretreatment has yet to be developed. Ozone generation has significant disadvantages when considering two aspects of the high cost of production presently and the significant quantity of ozone required for the process. However, over the past four years, the cost of producing ozone has steadily decreased due to technological advancements, falling by 30%. Currently, only 1.65 MJ of electrical energy is consumed for every 100 g of ozone, compared to the estimated 2.38 MJ.[222] Given that 100 g of ethanol is burnt to release 2.67 MJ, optimising the pretreatment conditions to minimise the ozone consumption and maximise the efficiency is necessary for an economically viable ozonolysis-based ethanol production process. Ultimately, this will result in lower costs. Similar findings were reported for the production of biogas from ozonated wheat straw.[223]

Physical oxidation processes, such as US, HC, and irradiation method, consume greater cost in the form of specific energy given that they requires constant energy input to run the pretreatment process, which may be very high for a long pretreatment time. The specific energy consumption can be calculated using the following formula:[224]

$$E_{\mathrm{spec}} = (P_{\mathrm{consume}} \times t_{\mathrm{p}})/(Q_{\mathrm{S}} \times T_{\mathrm{S}}) \tag{41}$$

where E_{spec} – is the specific energy (kJ kg^{-1} TS), P_{consume} – is the power consumed (kW), t_{p} – is the time taken for pretreatment (seconds), Q_{S} – is the sample quantity (L), and T_{S} is the – total solids utilized (kg). Bussemaker *et al.*[225] found that the sono-chemical pretreatment of sawmill chips and sawn logs requires ultrasonic energy, which accounts for 63% of the total electrical cost. This may result from the energy loss caused by shortcomings in the design of the ultrasonic reactor. A study examined the ultrasonic-assisted chemo pretreatment process for LCB from an economic perspective. Using a sonication-assisted chemo process lowered the manufacturing cost from $1001.00 per kg to $401.21 per kg.[225] The increase in pretreatment capacity significantly impacted the production costs. Compared to ultrasonic-assisted chemo methods, the higher cost of conventional sonic pretreatment is attributed to its longer time consumption. Unfortunately, the research on the way this method works, scaling – it up and comprehensive analysis of both economic and environmental sustainability still remains unsatisfactory. Despite the high initial cost, microwave pretreatment has a high capital turnover ratio. The initial investment for microwave pretreatment was evaluated to be $ 7000.[226,227] The capital cost can be returned in less than a year if the operation is assumed to run for 6000 h annually. Significantly, the advantages of microwave use compared to traditional techniques were also assessed, including quality gains, waste reduction, and decreased starch consumption. In the study by Kainthola *et al.*,[228] the pretreatment of rice straw using the AD process was investigated using a microwave. The results demonstrated that the net energy required for the pretreatment is less than the energy consumed, which is 3288.58 J g^{-1}. VS for pretreatment and 20 635.43 J g^{-1}. VS for net energy produced during the AD process. However, some of the drawbacks of MW include its high operating temperature and expense, batch mode of operation, lack of large-scale equipment, and the need for additional studies to determine its non-thermal effect on biomass.

Compared to other energy-source methods, HC technology offers low equipment and maintenance costs, which are a significant concern in the industry regarding emerging technology.[159] The only expenses associated with producing HC reactors, whether advanced rotational or non-rotational, are associated with the manufacturing process, raw materials, and low or moderate pressure pump and/or electrical motor. HC has demonstrated greater operational cost competitiveness when applied in the pretreatment of LCB or other uses compared to ultrasound, microwave, electric field, and ultraviolet pretreatment. The macroscopic heating effect, which can be utilised to preheat LCB and reduce the electrical consumption, is one of the secondary effects produced by HC, further improving its economic benefit. Additionally, HC lowers the viscosity and particle size of LCB, which reduces the energy needed for the pump. Consequently, HC is appropriate for pretreatments on an industrial scale.

From the perspective of the economy, using LCB can create job opportunities for rural development and reduce the reliance on fossil fuels. Although LCB is present worldwide, it is primarily found in forests and rural areas. Moreover, raw biomass, mainly agricultural biomass, cannot be preserved in the location of origin, is highly expensive to transport, and is humid and asymmetrical in size. Thus, considering these factors, to promise a consistent and reasonably priced biomass supply, issues in the supply chain management and logistics of biomass feedstock collection, transportation, and preservation must be resolved. The improved LCB conversion efficiency and costs have been largely attributed to technological developments in biomass pretreatment and other conversion processes.

However, considering the available literature, it is evident that only preliminary conclusions can be drawn on the economic feasibility of oxidative pretreatments. Indeed, considering that the majority of the analyses were carried out on the lab scale, the focus was on the operating costs, neglecting the equipment and maintenance contributions. Therefore, to carry out a comprehensive assessment of their economic and environmental viability, more effort is needed to scale up the configurations analysed in the literature for large-scale application.

6. Challenges, limitation and opportunities

As mentioned above, the main challenge in the widespread application of oxidative pretreatments to improve the LCB characteristics aimed at the recovery of biofuels and biochemicals appears to be the scalability of the process. Scaling up the different available processes and assessing their real-operating conditions will allow their comparison on a representative basis, considering technical, economic and environmental aspects. Another important aspect is related to the optimization of the working parameters. Indeed, depending on the process and substrate, different factors including temperature, pressure, oxidant concentration, reaction time, and capacity, significantly affect the efficiency of the process, and consequently its economic viability. Moreover, the possible integration of different pretreatments should be further investigated to identify possible synergisms and explore the effect of their interactions on the global efficacy of the process.

Additionally, the techno-economic analysis of oxidative pretreatments needs to be significantly extended. Indeed, technological and economic assessment is compulsory to achieve industrialization and commercialization. Finally, the environmental impact of oxidative pretreatments should be considered. Indeed, regarding oxidative pretreatments, few studies are available in the literature. WAO appears to be the most analysed using lifecycle assessment, highlighting that its use can decrease the environmental impact of processes aimed at recovering biofuels and/or biochemicals from biomasses.

7. Conclusion and future scope

LCB is recognized as one of the most promising alternatives to fossil fuels due to its abundance, local availability, reliability and carbon neutrality. However, given that the lignin content limits the accessibility to cellulose and hemicellulose, before the valorisation of LCB, pretreatments are needed to reduce its recalcitrance. This review presented a comprehensive analysis of the oxidative pretreatments, including the most recent and emerging technologies, also considering technical and economic aspects. The analysis highlighted that several gaps still need to be filled. Indeed, the majority of the works available in the literature were developed on the lab scale without presenting data for possible scaling up at the commercial and industrial levels. This makes a comparison among the available different pretreatments, together with the assessment of their economic feasibility difficult. Furthermore, it appears that an assessment of the environmental impact of oxidative pretreatments is almost completely neglected in the available literature. Therefore, future studies should focus on scaled up oxidative pretreatments and the analysis of their integration in biorefineries to assess their impact from an economic and environmental point of view on the valorization of LCB.

Author contributions

ADF – original drafting, SDF – literature survey, and original drafting, GSV – conception, design of work, and drafting of final manuscript, RBJ – resource, NM – resource.

Conflicts of interest

There are no conflicts to declare.

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