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Mechanochemical Reactions in Lignocellulosic Materials: A Review

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Abstract: Mechanochemistry investigates the chemical changes induced by mechanical energy in a substance. However, the potential of mechanochemical reactions in lignocellulosic materials has been overlooked in the application of mechanical treatments such as grinding, milling, and ultrasound, despite its recognition as a means of chemical activation in solid-state physics and polymer chemistry over the past decade. Therefore, it is crucial to consider the alteration of morphology and chemical composition that may result from mechanical treatments, as these treatments can lead to the formation of mechano-radicals that engage in multiple secondary reactions with one another. In theory, mechanochemistry has the potential to facilitate simplistic and sustainable chemical processes by reducing or eliminating the use of potentially harmful chemicals in cellulose fibrillation. This review article provides an overview of how mechanochemistry influences fibrillation, with the goal of promoting a more comprehensive understanding of the mechanism and its effects. By examining the role of mechanochemistry in the fibrillation of lignocellulosic materials, this review highlights the potential for sustainable and environmentally friendly cellulose fibrillation processes. The insights presented in this review article will be valuable to researchers and practitioners interested in the development of sustainable materials and processes.

Keywords: Mechanochemical; lignocellulosic materials; cellulose fibrillation; mechano-radicals

1. Introduction

Lignocellulosic materials are plant-derived materials containing cellulose, hemicellulose, and lignin, which are abundant and widely available, making them attractive for various renewable energy, biofuels, and bioproducts applications. Cellulose, the most abundant organic polymer on earth, possesses unique physical and chemical properties, making it an ideal material for many applications. Hemicellulose is less rigid than cellulose and plays a critical role in maintaining the structural integrity of the plant cell wall. Lignin, a complex polymer composed of various phenolic compounds, provides strength and rigidity to plant cell walls and is highly resistant to degradation [1]. Typically, lignocellulosic materials are obtained from agricultural or forestry waste, such as corn stover, sugarcane bagasse, and wood chips, and undergo mechanical or chemical processing to extract the cellulose and hemicellulose components. Despite their abundant availability and potential for sustainable and renewable applications, lignocellulosic materials' complex structure and composition pose unique challenges for processing and utilization [2].

The study of mechanochemical reactions in lignocellulosic materials is crucial due to its potential to enable novel processing and utilization routes for these sustainable resources [3]. Mechanochemical reactions occur when mechanical forces, such as

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grinding, milling, or shearing, are applied to solid-state materials, leading to unique chemical and physical changes that are not typically observed in conventional chemical reactions [4]. One promising application of mechanochemical reactions in lignocellulosic materials is the production of nanocellulose, a material with a high surface area and unique properties. Mechanochemical processes can break down cellulose fibers to the nanoscale, which can be more environmentally friendly than conventional chemical methods. Additionally, mechanochemical reactions can improve enzymatic hydrolysis and bioconversion of lignocellulosic materials by disrupting the plant cell wall, making the cellulose and hemicellulose components more accessible to enzymes [5]. Moreover, mechanochemical reactions can be used to develop functional materials, such as cellulose derivatives with tailored properties, and activate lignocellulosic materials for energy production [6]. Therefore, studying mechanochemical reactions in cellulose fibrillation can unlock new processing and utilization routes, leading to a range of sustainable applications in various fields.

This article presents the current state-of-the-art mechanochemistry applied to cellulose fibrillation, covering the fundamental principles of mechanochemistry, its use in processing and utilizing lignocellulosic materials, and discusses challenges and future directions for this field. Additionally, the review will highlight the challenges posed by mechanochemical processes in lignocellulosic materials, including the impact of mechanical forces on the material's chemical and physical properties, and their scalability for industrial applications.

2. Pulping of lignocellulosic materials

Pulping is a process used to convert wood or other fibrous materials into pulp, which can be further processed into paper and other cellulose-based products (Fig. 1). Mechanical and chemical pulping are two methods used to achieve this, and each has its advantages and disadvantages. The choice of method depends on the specific requirements of the product being produced, as well as other factors such as cost, availability of raw materials, and environmental impact [7].

Mechanical pulping involves grinding and refining wood logs or chips to produce pulp. The process includes debarking and chipping the wood logs, mechanically grinding the wood chips using grinders and refiners, cleaning the pulp using screens and centrifugal cleaners to remove any impurities, and sometimes bleaching the pulp to produce a brighter product. Although mechanical pulping is a fast and efficient process that produces pulp with high yield and low energy consumption, the pulp produced is often low in strength and brightness and is not suitable for high-quality paper products [8].

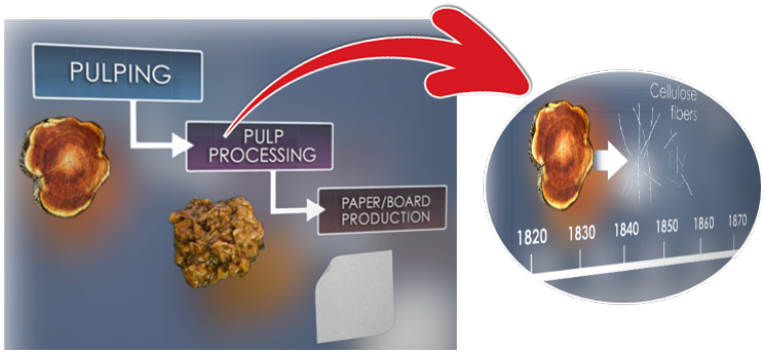

Figure 1. Mechanical pulping of refined fibrous materials into pulp for paper making. Adopted from - Vector Solution [9]

Chemical pulping involves the use of chemicals to break down the lignin in wood and separate the fibers [10]. Kraft pulping is the most used chemical pulping process and involves cooking the wood chips in a solution of sodium hydroxide and sodium sulfide (Fig. 2A), washing the pulp to remove any remaining chemicals and impurities, and bleaching the pulp to produce a brighter product. Sulfite pulping is a less common method that uses sulfurous acid and other chemicals to break down the lignin in wood. The process includes cooking the wood chips in a solution of sulfurous acid and other chemicals, washing the pulp to remove any remaining chemicals and impurities, and bleaching the pulp to produce a brighter product (Fig. 2B). Chemical pulping produces pulp with higher strength and brightness than mechanical pulping, but the process is more energy-intensive and produces more waste [11].

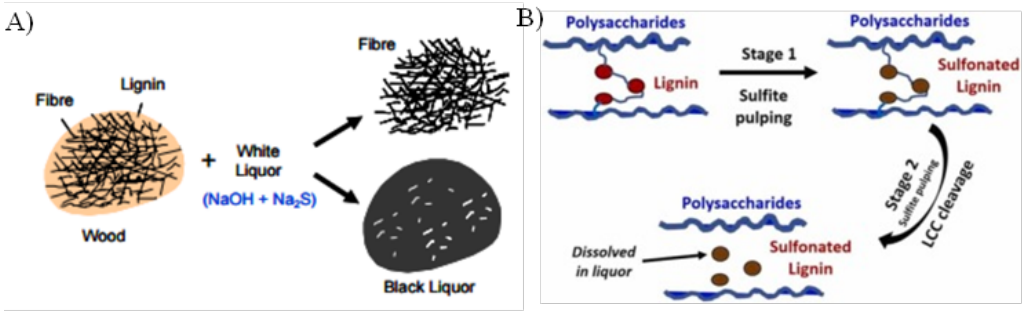

Figure 2. (A) Kraft and (B) Sulfite pulping for lignocellulosic depolymerization. Adopted from - Parvan [12] and Deshpande [13].

The mechanism of pulping involves breaking down the structure of the raw material to separate the fibers and remove any impurities. The specific mechanism depends on the pulping method being used, but there are some common steps in the process. These include fiber separation, lignin removal, washing and screening, and bleaching [14]. Fiber separation can be achieved through mechanical or chemical means, while lignin removal is achieved using chemicals that break down the lignin and separate it from the fibers. Once the fibers have been separated and the lignin removed, the pulp is washed to remove any remaining chemicals or impurities, and the pulp is then screened to remove any large or unwanted particles. In some cases, the pulp may be bleached to improve its brightness and color.

3. Mechanochemical reactions

Mechanochemical reactions involve the induction of chemical transformations in a substance by mechanical forces, such as grinding, milling, or ultrasonication [15,16]. These physical actions can generate high-energy intermediates, such as free radicals or ions, that participate in chemical reactions, leading to new products with enhanced properties and functionality. Mechanochemical reactions have garnered significant attention in recent years due to their potential for developing sustainable chemical processes and materials. Moreover, they offer a viable alternative to conventional chemical methods that often rely on the use of hazardous chemicals and solvents.

Mechanochemical reactions can occur in a variety of materials, including organic and inorganic solids, polymers, and biomolecules. They can also take place in both the solid state and solutions and can be induced by various mechanical means, such as shear, compression, and impact. Overall, mechanochemical reactions represent an exciting field of research with far-reaching applications in multiple disciplines. Further exploration and understanding of mechanochemistry could pave the way for the development of new,

sustainable processes and materials with applications in numerous industries, including pharmaceuticals, materials science, and energy.

During the mechanical pulping process, wood fibers are subjected to mechanical forces that break the chemical bonds within the wood structure, resulting in the formation of free radicals [17]. These radicals are highly reactive chemical species that play a crucial role in the breakdown of wood fibers. Mechanoradicals are formed through the cleavage of covalent bonds, which occurs due to the mechanical forces applied to the wood. This cleavage results in the formation of free radicals with unpaired electrons in their outermost shell (Fig. 3).

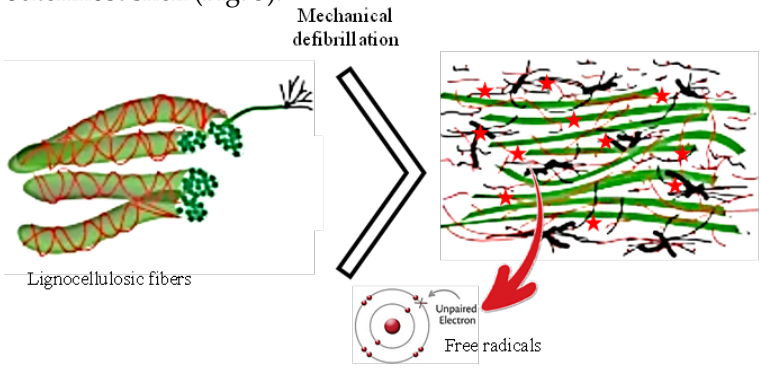

Figure 3. The figure illustrates the formation of mechano-radicals resulting from the cleavage of covalent bonds due to the mechanical forces applied to the wood. This process leads to the creation of free radicals, which have unpaired electrons in their outermost shell.

The mechanical pulping process involves the use of mechanical forces, such as grinding and refining, to separate the fibers from the wood. During this process, the cellulose, hemicellulose, and lignin molecules within the wood structure are broken down into smaller fragments, which then react with the free radicals to form new chemical compounds. Mechanoradicals are formed in the presence of oxygen, which acts as a catalyst, accelerating the rate of free radical formation [18].

The formation of radicals during mechanical pulping is critical to the process because they play a crucial role in breaking down the wood fibers. The free radicals react with the cellulose, hemicellulose, and lignin molecules, causing them to break down into smaller fragments. These fragments can then be further refined to produce pulp [19]. However, the formation of mechano-radicals can also contribute to the degradation of the pulp quality. When the radicals react with the cellulose and hemicellulose molecules, they can form carbonyl and carboxyl groups, which can reduce the strength and brightness of the pulp [20]. Therefore, it is essential to carefully control the formation and reactivity of the radicals during the pulping process to achieve the desired pulp quality. The optimization of the mechanical forces applied during pulping, the concentration of oxygen, and the use of antioxidants are some of the methods used to control the formation and reactivity of mechano-radicals during the process.

4. Mechanochemical reactions in lignocellulosic depolymerization

Mechanochemistry is a discipline that examines mechanical energy-induced chemical changes in a substance [21]. However, the mechanochemical reactions of lignocellulosic entities have always been disregarded in the application of mechanical treatments, e.g., grinding, milling, and ultrasound, even though it has already been widely acknowledged as means of chemical activation in solid-state physics and polymer chemistry since the past decade [22]. Therefore, alteration of morphology and chemistry composition should be addressed to which mechanical treatment may influence the

formation of mechano-radicals that engage in multiple secondary reactions with one another. Theoretically at least, providing the ability to establish simplistic and sustainable chemical processes, mechanochemistry has the potential to encourage minimal use, if any, of potentially harmful chemicals in cellulose fibrillation. This review offers an overview of how mechanochemistry affects fibrillation, ensuring a far broader understanding of the mechanism and its effects entailed.

Lignocellulosic materials, such as wood and agricultural waste, also contain cellulose along with hemicellulose and lignin. Mechanochemical reactions can occur in these materials as well, leading to a variety of interesting applications. One example is the use of mechanical force to break down the lignocellulosic structure, making it more accessible to enzymatic or chemical reactions. This process, known as pretreatment, is an important step in the production of biofuels and other value-added chemicals from lignocellulosic biomass [23]. Another example is the use of mechanochemical reactions to modify the lignin component of lignocellulosic materials [18]. Lignin is a complex polymer that provides structural support to plant cells but also makes it difficult to access cellulose and hemicellulose. By using mechanical force along with chemical treatments, lignin can be broken down or modified to improve the properties of the lignocellulosic material. Mechanochemical reactions can also be used to modify the properties of lignocellulosic materials for other applications, such as energy conversion/storage applications [24] and packaging [25]. By breaking down the cellulose and hemicellulose components, the resulting material can have improved flexibility, strength, or other desirable properties.

The mechanochemical mechanisms in cellulose, hemicellulose, and lignin involve a series of complex processes that can vary depending on the specific material and the conditions under which the mechanical force is applied. In cellulose, the mechanochemical reactions can involve the generation of mechanical stress that leads to the breaking of glycosidic bonds between the glucose monomers, resulting in the formation of reactive sites [26]. These reactive sites can then undergo further reactions, such as oxidation or reduction, which can lead to the formation of new chemical species. The presence of suitable catalysts or solvents can also facilitate the depolymerization of cellulose chains into smaller oligomers or monomers (Fig. 4) [27]. This ability has significant potential applications in the production of biofuels, pharmaceuticals, and other industrial products that require the use of oligosaccharides.

In hemicellulose, mechanochemical reactions can involve the depolymerization of the polysaccharide into smaller oligomers or monomers through the application of mechanical force along with a suitable catalyst or solvent (Fig. 5) [28]. The mechanical force can also break down the hemicellulose structure, increasing its surface area and making it more accessible for chemical reactions. Whereas, in lignin, the mechanochemical reactions can involve the breaking of the complex polymer structure, which can be achieved through mechanical force along with chemical treatments or enzymatic reactions. This can lead to the formation of new chemical species or modification of the lignin structure, resulting in improved properties. These products have significant potential for use in a variety of industrial applications, including the production of biofuels and chemicals.

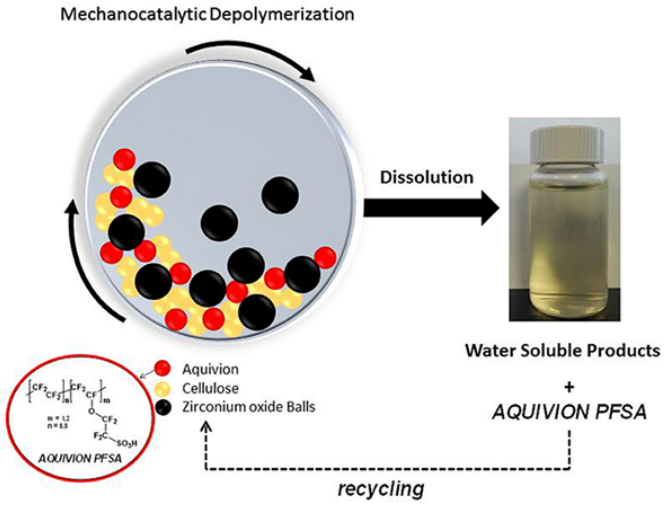

Figure 4. Depolymerization process of microcrystalline cellulose into oligosaccharides using Aquivion PFSA as a catalyst. Aquivion PFSA is a sulfonated perfluorinated ionomer that selectively breaks down the chemical bonds between the sugar molecules of microcrystalline cellulose, releasing oligosaccharides as a product. The selectivity of Aquivion PFSA allows for an efficient depolymerization process, without producing unwanted by-products. Adopted from - Karam et al. [29]

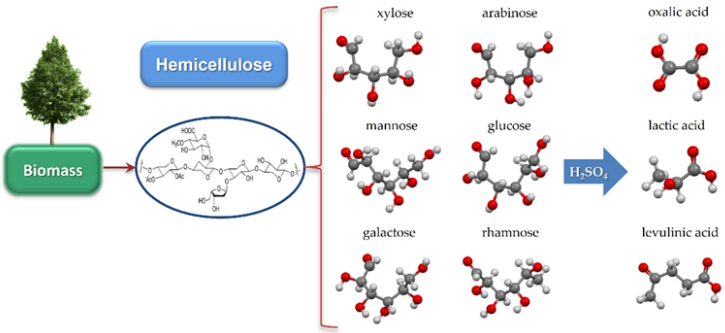

Figure 5. Scheme of the products obtained from the catalytic conversion of hemicellulose carbohydrate mixtures using a homogeneous H_2SO_4 catalyst in the liquid phase including various organic acids, such as oxalic, lactic, and levulinic acid. Adopted from - Sobus and Czekal [30]

4.1. Mechanistic of chemically assisted lignocellulosic depolymerization

In recent years, there has been renewed interest in the use of mechanical forces in various areas of chemistry, particularly in the acid-catalyzed depolymerization of lignocelluloses, which has opened new possibilities for biorefining. Herein, the chemical principles of the acid-catalyzed depolymerization of cellulose demonstrate how the use of mechanical forces can drive this reaction, making it a prominent example of a mechanochemistry application.

Recent DFT studies at the BB1K/6-31++G(d,p) level [31] and Car-Parrinello MD simulations combined with metadynamics have provided quantitative predictions of the pathways for the acid-catalyzed hydrolysis of cellobiose [32]. These studies offer valuable insights into the chemical obstacles that hydrolysis of cellulose faces. For example, the proton transfer from H3O+ to the glycosidic O site is hindered by the strong affinity of water towards H+ species. The protonation of the glycosidic O site is also complex due to its proximity to more basic O(2), O(3'), O(5), and O(6') sites. The basicity of the glycosidic O site varies upon structural distortion of the "cellobiose subunits" in the polymeric chains. Even upon successful protonation of the glycosidic O site, conformational changes are required to activate the C(1)-O(1) bond toward hydrolysis, as shown in Fig. 6. In conclusion, the studies provide important insights into the challenges of cellulose hydrolysis and offer potential solutions to overcome these challenges.

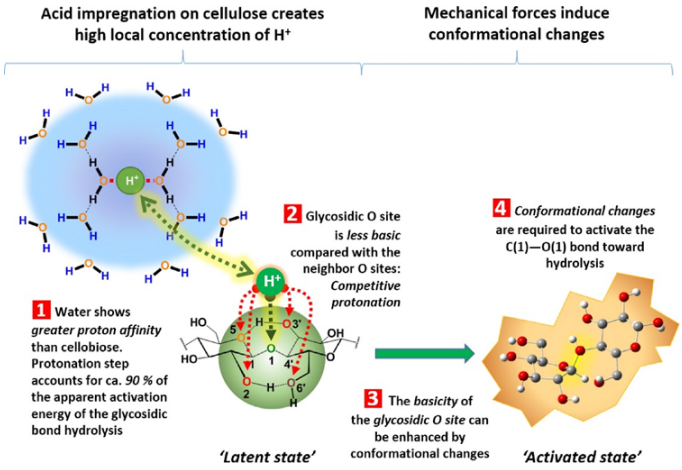

Figure 6. The use of mechanocatalysis, a method of using mechanical forces to activate chemical reactions, to overcome the chemical barriers of cellulose hydrolysis. Steps 3-4 of mechanical forces can activate the "latent state" of protonated cellobiose subunits in the cellulosic chain, inducing conformational changes necessary for the cleavage of the glycosidic linkage. Adopted from - Shüth et al. [33]

Shüth et al. [33] suggest that mechanical forces activate the protonated cellobiose subunits in the cellulose chain, inducing conformational changes necessary for glycosidic linkage cleavage. This idea is supported by previous studies on cellobiose hydrolysis. Experiments impregnating cellulosic substrates with strong mineral acids have shown improved conversion rates, suggesting that mechanical forces assist in activating the latent state. However, directly after impregnation, a significant amount of water-soluble products are formed, indicating that the use of mechanical force may not be necessary for depolymerization [34]. Attempts to increase the yield of water-soluble products by prolonging the impregnation step or aging the acid-impregnated cellulose have failed. Instead, aging leads to the carbonization of the substrate. Even exposure to high temperatures results in carbonization, indicating that mechanical force is crucial for effective depolymerization, as shown in Fig. 7.

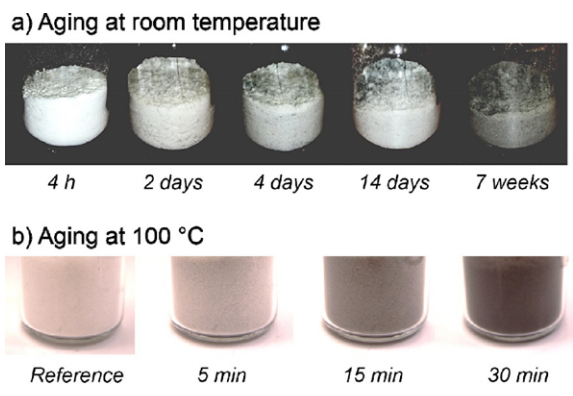

Figure 7. (a) The change in color of α-cellulose impregnated with H2SO4 during aging was investigated. When the impregnated α-cellulose was kept at room temperature, its color changed from white to dark gray over time. (b) Similarly, when the impregnated α-cellulose was aged at a temperature of 100 °C for 0.5 h, it also turned black. This color change indicates that the α-cellulose undergoes carbonization upon aging, rather than hydrolysis. The black powders obtained from the aging process are insoluble in water. This suggests that aging does not contribute to the depolymerization of cellulose into water-soluble products. Adopted from - Shüth et al. [33]

The hydrolysis of cellulose is heavily dependent on conformational changes, which are induced by mechanical forces acting on the protonated cellobiose subunits within the cellulosic chain [31,32]. Experimental evidence shows that the impregnation of strong acid on the cellulosic substrate accelerates the conversion of cellulose, but mechanical forces are still required for complete depolymerization to water-soluble products. DFT calculations suggest that the necessary conformational changes can be induced by mechanical forces that cause the glycosidic linkages to adopt a distorted environment favorable for hydrolysis [31]. These results indicate that conformational changes are crucial for the hydrolysis of the 1,4-β-glycosidic bonds and that mechanical forces aid in the activation of the 'latent state' of acid-impregnated cellulose. It is important to note that the acid-impregnated substrate is thermolabile, and depolymerization is not driven by hot spots created by the friction of balls-balls and balls-walls inside the mill vial. The acid-impregnated substrates should be stored at -20 °C to avoid substrate decomposition upon storage.

4.2. Mechanistic of mechano-radicals generation in cellulose fibrillation

The use of the Electron Spin Resonance (ESR) technique confirms the occurrence of mechano-radicals in lignocellulosic materials. This is due to the application of mechanical stress on semi-crystalline samples that results in non-homogeneous deformation and dissociation of various chemical bonds, such as carbon-oxygen and carbon-carbon bonds. The mechanical energy breaks the intramolecular forces holding the cellulose chains together, leading to homolytic and/or heterolytic rupture in the amorphous regions and the creation of free radical sites. The presence of these highly reactive radicals leads to various chemical transformations, including disproportionation, hydrogen abstraction, and radical rearrangements. No ESR signals should be detected until mechanical operation occurs [35,36].

Mechano-radicals are formed in lignocellulosic materials as a result of applied mechanical stress, leading to the dissociation of carbon-oxygen, carbon-carbon, and other chemical bonding. This is primarily due to non-homogeneous deformation caused by shear force exceeding the intramolecular forces that keep the celluloses bound together, resulting in homolytic and/or heterolytic rupture of the cellulose chain. Free radical sites are created, especially in amorphous regions, as a result of this chain rupture. Until mechanical operation occurs, no Electron Spin Resonance (ESR) signals should be observed. These radicals are highly reactive and engage in several chemical transformations, including disproportionation, hydrogen abstraction, and radical rearrangements.

The chain breakage of the cellulose backbone due to the formation of mechano-radicals is illustrated in Fig. 8. This is more likely to occur in the mid-chain of cellulose

than at the chain ends [36]. Crosslinks or joints between the cellulose molecules are known for high energy sites for chain rupture. The behavior of radicals in mechanically degraded cellulose molecules depends on the ambient conditions in which they are formed, especially temperature and oxygen attendance. Mechanochemical activation can facilitate various forms of bond cleavage, including radical formation, ring breaking, and chain-breaking, as shown in Fig. 9. The mechanical activation is expected to initiate ring and chain bond cleavages, while radicals-induced bond cleavage is attributed to the interaction between the free radicals and the cellulose molecules.

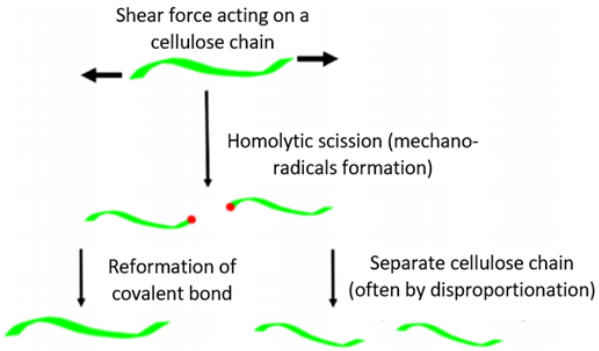

Figure 8. The process of mechano-radical formation in cellulose chain under shear force is illustrated in the schematic diagram presented. The figure depicts how the application of mechanical stress on cellulose leads to the formation of mechano-radicals by homolytic chain scission. These radicals are highly reactive, and they can engage in several chemical reactions, including the formation of new covalent bonds or disproportionation, which leaves the fractured cellulose chains separate. The mechano-radicals are formed primarily in the mid-chain region of cellulose, rather than at the chain ends. Adopted from - Solala et al. [37]

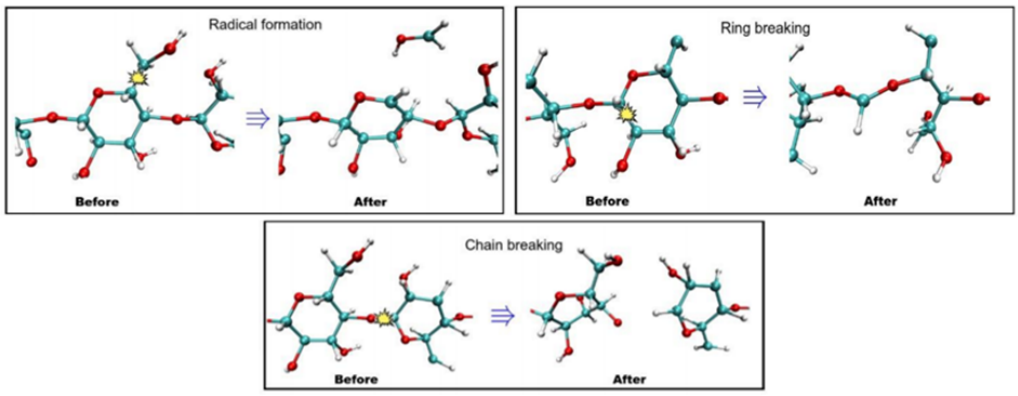

Figure 9. The presence of crosslinks or joints between the cellulose molecules is known to be a high-energy site for chain rupture. The behaviour of these radicals in mechanically degraded cellulose molecules is dependent on the ambient conditions in which they are formed, especially temperature and oxygen attendance. Furthermore, mechanochemical activation can facilitate various forms of bond cleavage, including the formation of radicals, ring-breaking, and chain-breaking. The mechanical activation is expected to initiate ring and chain bond cleavages, while the radicals-induced bond cleavage is attributed to the interaction between the free radicals with the cellulose molecules. Adopted from – Solala [36]

The cleavage of glycosidic bonds (depolymerization) in cellulose during mechanical treatment generates two radical sites. Previous studies have shown that milling of cellulose fibers produces three mechano-radicals, namely singlet, doublet, and triplet signals. The singlet signal arises from alkoxy radicals (Rcell—C4—O•), while the doublet and triplet signals correspond to carbon radicals located at C1 and C2—C3 positions, respectively. These doublet and triplet signals can react with oxygen molecules to form peroxy radicals (Rcell—C1—O—O•), which is not possible with the singlet signal. The cleavage of glycoside connections can occur via two different mechanisms under the impact of mechanical stresses, as shown in Eq. 1 and 2, resulting in the formation of alkoxyl and alkyl radicals. The alkoxy radicals of •C4—Rcell can interact with protons at the C4, C3, and C5 positions of a fresh cellulose segment. As denoted in Eq. 2, the singlet and doublet signals correspond to •O—C4—Rcell and Rcell—C1•, respectively. These reactive radicals induce the cleavage of the cellulose chain by interfering with carbon-carbon bonds along the cellulose backbone, causing chain scission. During this process, unwanted side reactions occur, constantly regenerating the radicals by hydrogen abstraction, a process known as chain propagation. When the C2—C3 bonds are broken, the resulting mechano-radicals exhibit triplet signals. While dehydrogenation at C2, C3, C4, and C6 positions can also generate free radicals as triplet signals, it is unlikely to occur under mechanical stress.

Rcell—C1—O—C4—Rcell → Rcell—C1—O• + •C4—Rcell (Eq. 1)

Rcell—C1—O—C4—Rcell → Rcell—C1• + •O—C4—Rcell (Eq. 2)

*Where Rcell is a cellulose molecule

4.3. Effects of mechano-radicals formation in cellulose fibrillation

According to Solala et al. [35], the fractionation analysis showed that unbleached pulp underwent greater fibrillation compared to its bleached counterpart, resulting in less fibrous aggregation in its suspension. This could be attributed to the density of charge, which was found to be about twice as high in the unbleached pulp due to the presence of glucuronoxylans, a hemicellulose with carboxyl groups that contribute to the pulp's charge [38]. The charge density of pulp is known to affect its swelling and resilience in suspension, ultimately affecting the ease of mechanical processing [39]. Furthermore, Solala et al. [35] found that milling cellulose fiber in the presence of nitrogen or oxygen led to a greater reduction in the degree of polymerization in the presence of oxygen compared to nitrogen. The researchers proposed that this may be due to the scavenging of mechano-radicals by oxygen molecules, which reduces the likelihood of radical recombination and thus enhances the depolymerization activity.

In the case of the unrefined sample, the presence of phenoxy radicals can be attributed to their different chemical history. Specifically, these radicals are formed during the bleaching stage using either chlorine dioxide or hydrogen peroxide as reported in previous studies [40–42]. On the other hand, for the fibrillated sample, the free radical content is closely linked to the degree of fibrillation and thermal activation. However, given that the maximum temperature during mechanical fibrillation was only about 60-80 °C, it is unlikely that radical formation occurred during this process. This is because the thermal modification of cellulose in wood usually takes place over several hours at temperatures ranging from 180-250 °C [35].

Electron Spin Resonance (ESR) spectroscopy was utilized to determine the concentration of free radicals in the samples. This technique relies on detecting unpaired electrons (radicals) through their interaction with magnetic fields. EPR tests were conducted around a week after mechanical treatment to allow for stabilization of the free

radicals formed initially and prevent significant contribution to the radical content [43]. The free radical content in the samples is influenced by both the degree of bleaching and mechanical treatment applied to the pulp. The ESR spectra of unbleached pulp showed a significant singlet signal indicating the formation of alkoxy radicals (R–O•) due to glycosidic bond rupture between C1 and C4. These cellulose-derived free radicals typically react with residual lignin to form very stable phenoxy radicals. In the absence of lignin, these free radicals are more likely to react rapidly with oxygen molecules to form stabilized phenoxy radicals (Rcell—C1—O—O•), leading to a higher radical content in fully bleached pulps.

The formation of mechano-radicals during milling was found to be influenced by temperature, with a singlet signal being detected from samples milled at higher temperatures. The reactivity of the mechano-radicals may be related to the poor diffusion of oxygen in cellulose fiber at lower temperatures. Previous research has shown that amorphous regions are preferentially disrupted at room-temperature milling compared to cryo-milling [44]. As bleaching and fibrillation continued, the degree of polymerization was expected to decrease, with lignin-containing pulp having higher cellulose chain concentration than fully bleached pulp. The presence of lignin in the pulp promotes fibrillation by scavenging radicals. However, in the absence of lignin, or with traces present, more cellulose radicals could engage in recombination reactions, resulting in crosslinking that counters fibrillation [45].

5. Challenges and future directions of mechanochemical reactions using lignocellulosic biomass

There is a growing body of evidence that mechanochemical reactions may be used to induce chemical changes in lignocellulosic materials. However, there are several challenges that must be addressed before its full potential can be realised. Inefficient mechanochemical reactions are hampered by the variety and complexity of lignocellulosic materials, which are characterised by complicated networks of cellulose, hemicellulose, and lignin, along with impurities. Research in the future should concentrate on finding ways to modify the structure of biomass to improve its reactivity and accessibility. To make the lignocellulosic matrix more receptive to mechanochemical processes, one may use pretreatment or genetic engineering [46]. More work has to be done to decipher structure-function correlations and design biomass feedstocks more suited to mechanochemical reactions in the future [47]. Selective bond cleavage and the promotion of desired chemical reactions may be achieved by the careful alteration of cellulose, hemicellulose, and lignin.

The success of mechanochemical reactions in lignocellulosic materials depends critically on the reactivity and accessibility of the target components. However, cellulose and lignin are generally limited in their reactivity due to their recalcitrance. The integration of several mechanochemical methods is a necessary step for the future. Researchers may improve the effectiveness of mechanochemical reactions by combining methods like mechano- and photo-chemical reactions [48]. Selective bond cleavage and the promotion of desired chemical changes in biomass components may be facilitated by this integrated strategy.

Understanding the mechanisms and developing better procedures requires characterising the transformations that occur in lignocellulosic materials during mechanochemical reactions [49]. Significant analytical problems are presented, however, when attempting to analyse structural changes, chemical transformations, and intermolecular interactions in complex biomass matrices. Improving our ability to characterise complex systems at the molecular level is essential for understanding

mechanochemical processes. To decipher the structural and chemical changes happening during mechanochemical processing, cutting-edge tools including spectroscopy, microscopy, imaging approaches, and computer modelling need to be developed. Process optimisation and control may be greatly aided by real-time monitoring strategies like in situ or operando analysis.

Energy efficiency and process economics must be considered when scaling up mechanochemical processes for industrial purposes. Mechanical milling or grinding procedures may be impractical for widespread use because of their high energy requirements [50]. The development of energy-efficient techniques for mechanochemical reactions in lignocellulosic materials should be the focus of future study. In order to minimise energy consumption and maintain the appropriate reactivity, the milling parameters rotating speed, milling duration, and milling medium may be optimised. Improving energy efficiency and expanding production potential may also be achieved via the use of alternate milling technologies and process intensification strategies.

Tailoring biomass structure, incorporating numerous mechanochemical approaches, creating catalysts and additives for enhanced selectivity, and improving characterisation techniques are all areas that need to be prioritised moving ahead. Full utilisation of mechanochemical processes in lignocellulosic materials will be facilitated by addressing these limitations and investigating these future possibilities. This will aid in the environmentally responsible manufacture of biofuels, chemicals, and high-tech materials, all of which contribute to sustainable biomass utilisation.

To modify reaction paths and increase selectivity in mechanochemical processes, catalysts and additives may be very useful tools. [46]. More work is needed to produce metal-mediated catalysts optimised for lignocellulosic materials and mechanochemical conditions [51]. Co-solvents and other additives have also been included [52], which can enhance the efficiency of mechanochemical reactions by improving mass transfer and reducing energy barriers. Mechanochemical processes may be made more selective and efficient via research into the synergistic effects of catalysts and additives.

Research into the future should emphasis on perfecting and eventually industrialising mechanochemical processes. Among them are the development of more energy-efficient procedures and the optimisation of milling settings. The overall effectiveness and scalability of the process may be enhanced by exploring process intensification options like continuous flow systems or the incorporation of mechanochemical reactions with other conversion processes.

6. Conclusions

Mechanical treatment of lignocellulosic materials produces mechano-radicals that can initiate chemical reactions within the fibers. This can explain the differences in fibrillation efficiency observed between unbleached and completely bleached pulps, as the latter process not only removes lignin but also extracts hemicelluloses, affecting the charge density and fiber structure of the pulp. However, the highly reactive mechano-radicals quickly become different radical species or react with each other in radical recombination reactions, limiting their ability to initiate further reactions and potentially leading to the formation of new compounds that can affect the pulp properties. Further research is needed to fully understand the role of mechano-radicals in pulp processing and fibrillation, as the chemical reactions initiated by these species are complex and their lifetimes are relatively short.

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References

[1] A. Zoghlami and G. Paës, "Lignocellulosic Biomass: Understanding recalcitrance and predicting hydrolysis.," *Frontiers in Chemistry*. vol. 7, no. December, p. 2019.
[2] K. Eksiler, Y. Andou, and Y. Shirai, "Simple manufacture of surface-modified nanolignocellulose fiber via vapor-phase-assisted surface polymerization.," *ACS Omega*. vol. 3, no. 4, pp. 4545–4550, 2018.
[3] J. Lease, T. Kawano, and Y. Andou, "Esterification of cellulose with long fatty acid chain through mechanochemical method.," *Polymers*. vol. 13, no. 24, pp. 1–12, 2021.
[4] F. Shen, X. Xiong, J. Fu, et al., "Recent advances in mechanochemical production of chemicals and carbon materials from sustainable biomass resources.," *Renewable and Sustainable Energy Reviews*. vol. 130, no. 38, p. 109944, 2020.
[5] V.A. Barbash, O. V. Yaschenko, S. V. Alushkin, A.S. Kondratyuk, O.Y. Posudievsky, and V.G. Koshechko, "The effect of mechanochemical treatment of the cellulose on characteristics of nanocellulose films.," *Nanoscale Research Letters*. vol. 11, no. 1, p. 2016.
[6] K.S. Guiao, C. Tzoganakis, and T.H. Mekonnen, "Green mechano-chemical processing of lignocellulosic biomass for lignin recovery.," *Chemosphere*. vol. 293, no. January, p. 133647, 2022.
[7] T.K. Das and C. Houtman, "Evaluating chemical-, mechanical-, and bio-pulping processes and their sustainability characterization using life-cycle assessment.," *Environmental Progress*. vol. 23, no. 4, pp. 347–357, 2004.
[8] D. McDonald, K. Miles, and R. Amiri, "The nature of the mechanical pulping process.," *Pulp and Paper Canada*. vol. 105, no. 8, pp. 27–32, 2004.
[9] Vector Solutions, "Pulping and papermaking overview," https://www.vectorsolutions.com/course-details/pulping-and-papermaking-overview/c69ece9a-9583-e811-a985-02ec32550f44/.
[10] W.A. Laftah and W.A.W. Abdul Rahaman, "Chemical pulping of waste pineapple leaves fiber for kraft paper production.," *Journal of Materials Research and Technology*. vol. 4, no. 3, pp. 254–261, 2015.
[11] D. Mboowa, "A review of the traditional pulping methods and the recent improvements in the pulping processes.," *Biomass Conversion and Biorefinery*. p. 2021.
[12] M. Parvan, "Life cycle assessment of lignin recovery in a kraft pulp mill and its alternative ways of utilization," (2023).
[13] R. Deshpande, L. Sundvall, H. Grundberg, G. Henriksson, and M. Lawoko, "Structural basis for lignin recalcitrance during sulfite pulping for production of dissolving pulp from pine heartwood.," *Industrial Crops and Products*. vol. 177, no. November 2021, p. 114391, 2022.
[14] P. Bajpai, "Green chemistry and sustainability in pulp and paper industry.," *Green Chemistry and Sustainability in Pulp and Paper Industry*. pp. 1–258, 2015.
[15] T.K. Achar, A. Bose, and P. Mal, "Mechanochemical synthesis of small organic molecules.," *Beilstein Journal of Organic Chemistry*. vol. 13, pp. 1907–1931, 2017.
[16] G. Cravotto and P. Cintas, "Harnessing mechanochemical effects with ultrasound-induced reactions.," *Chemical Science*. vol. 3, no. 2, pp. 295–307, 2012.
[17] Z.H. Wu, M. Sumimoto, and H. Tanaka, "Generation of oxygen-containing radicals in the aqueous media of mechanical pulping.," *Journal of Wood Chemistry and Technology*. vol. 15, no. 1, pp. 27–42, 1995.
[18] E. Małachowska, M. Dubowik, P. Boruszewski, J. Łojewska, and P. Przybysz, "Influence of lignin content in cellulose pulp on paper durability.," *Scientific Reports*. vol. 10, no. 1, pp. 1–12, 2020.
[19] S.R. Djafari Petroudy, B. Chabot, E. Loranger, et al., "Recent advances in cellulose nanofibers preparation through energy-efficient approaches: A review.," *Energies*. vol. 14, no. 20, pp. 1–31, 2021.
[20] J. Perrin, F. Pouyet, C. Chirat, and D. Lachenal, "Cellulosic pulps : Effect on alkali resistance.," *BioResources*. vol. 9, no. 1, pp. 7299–7310, 2014.
[21] M.K. Beyer and H. Clausen-Schaumann, "Mechanochemistry: The mechanical activation of covalent bonds.," *Chemical Reviews*. vol. 105, no. 8, pp. 2921–2948, 2005.
[22] E. Boldyreva, "Mechanochemistry of inorganic and organic systems: What is similar, what is different?," *Chemical Society Reviews*. vol. 42, no. 18, pp. 7719–7738, 2013.
[23] G. Brodeur, E. Yau, K. Badal, J. Collier, K.B. Ramachandran, and S. Ramakrishnan, "Chemical and physicochemical pretreatment of lignocellulosic biomass: A review.," *Enzyme Research*. vol. 2011, no. 1, p. 2011.
[24] X. Liu, Y. Li, L. Zeng, et al., "A review on mechanochemistry: Approaching advanced energy materials with greener force.," *Advanced Materials*. vol. 34, no. 46, pp. 1–30, 2022.
[25] F. Cavalieri and F. Padella, "Development of composite materials by mechanochemical treatment of post-consumer plastic waste.," *Waste Management*. vol. 22, no. 8, pp. 913–916, 2002.

[26] E. Calcio Gaudino, G. Cravotto, M. Manzoli, and S. Tabasso, "Sono- and mechanochemical technologies in the catalytic conversion of biomass.," *Chemical Society Reviews*. vol. 50, no. 3, pp. 1785–1812, 2021.
[27] A. Shrotri, H. Kobayashi, and A. Fukuoka, "Cellulose depolymerization over heterogeneous catalysts.," *Accounts of Chemical Research*. vol. 51, no. 3, pp. 761–768, 2018.
[28] C.R.M. Monteiro, P.F. Ávila, M.A.F. Pereira, et al., "Hydrothermal treatment on depolymerization of hemicellulose of mango seed shell for the production of xylooligosaccharides.," *Carbohydrate Polymers*. vol. 253, no. October 2020, pp. 1–8, 2021.
[29] A. Karam, P.N. Amaniampong, J.M.G. Fernández, et al., "Mechanocatalytic depolymerization of cellulose with perfluorinated sulfonic acid ionomers.," *Frontiers in Chemistry*. vol. 6, no. MAR, pp. 1–9, 2018.
[30] N. Sobus and I. Czekaj, "Catalytic transformation of biomass-derived hemicellulose sugars by the one-pot method into oxalic, lactic, and levulinic acids Using a homogeneous H2SO4 catalyst.," *Catalysts*. vol. 13, no. 349, pp. 1–13, 2023.
[31] C. Loerbroks, R. Rinaldi, and W. Thiel, "The electronic nature of the 1,4-β-glycosidic bond and its chemical environment: DFT insights into cellulose chemistry.," *Chemistry - A European Journal*. vol. 19, no. 48, pp. 16282–16294, 2013.
[32] X. Liang, A. Montoya, and B.S. Haynes, "Local site selectivity and conformational structures in the glycosidic bond scission of cellobiose.," *Journal of Physical Chemistry B*. vol. 115, no. 36, pp. 10682–10691, 2011.
[33] F. Schüth, R. Rinaldi, N. Meine, M. Käldström, J. Hilgert, and M.D.K. Rechulski, "Mechanocatalytic depolymerization of cellulose and raw biomass and downstream processing of the products.," *Catalysis Today*. vol. 234, pp. 24–30, 2014.
[34] J. Hilgert, N. Meine, R. Rinaldi, and F. Schüth, "Mechanocatalytic depolymerization of cellulose combined with hydrogenolysis as a highly efficient pathway to sugar alcohols.," *Energy and Environmental Science*. vol. 6, no. 1, pp. 92–96, 2013.
[35] I. Solala, A. Volperts, A. Andersone, et al., "Mechanoradical formation and its effects on birch kraft pulp during the preparation of nanofibrillated cellulose with Masuko refining.," *Holzforschung*. vol. 66, no. 4, pp. 477–483, 2012.
[36] I. Solala, "Mechanochemical reactions in lignocellulosic materials," (2015).
[37] I. Solala, M.C. Iglesias, and M.S. Peresin, "On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on properties and applications.," *Cellulose*. vol. 27, no. 4, pp. 1853–1877, 2020.
[38] N.K. Bhardwaj, T.D. Duong, and K.L. Nguyen, "Pulp charge determination by different methods: Effect of beating/refining.," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. vol. 236, no. 1–3, pp. 39–44, 2004.
[39] J. Laine and P. Stenius, "Effect of charge on the fiber and paper properties.," *Paperi Ja Puu*. vol. 79, no. 4, pp. 257–266, 1997.
[40] D.W. Reeve, *Introduction to the principles and practice of pulp bleaching*., 1996.
[41] V. Tarvo, T. Lehtimaa, S. Kuitunen, V. Alopaeus, and T. Vuorinen, "Chlorate formation in chlorine dioxide delignification - An analysis via elementary kinetic modeling.," *Journal of Wood Chemistry and Technology*. vol. 29, no. 3, pp. 191–213, 2009.
[42] U. Germgård, *Bleaching of pulp*., 2009.
[43] E. Iller, A. Kukielka, H. Stupińska, and W. Mikolajczyk, "Electron-beam stimulation of the reactivity of cellulose pulps for production of derivatives.," *Radiation Physics and Chemistry*. vol. 63, no. 3–6, pp. 253–257, 2002.
[44] B. Stefanovic, K.F. Pirker, T. Rosenau, and A. Potthast, "Effects of tribochemical treatments on the integrity of cellulose.," *Carbohydr Polymer*. vol. 111, pp. 688–699, 2014.
[45] T. Dizhbite, G. Telysheva, V. Jurkjane, and U. Viesturs, "Characterization of the radical scavenging activity of lignins - Natural antioxidants.," *Bioresource Technology*. vol. 95, no. 3, pp. 309–317, 2004.
[46] A.M. Pérez-Merchán, G. Rodríguez-Carballo, B. Torres-Olea, et al., "Recent advances in mechanochemical pretreatment of lignocellulosic biomass.," *Energies*. vol. 15, no. 16, p. 2022.
[47] O. Advantages and C. Drawbacks, "Recent developments in mechanochemistry.," p. 2023.
[48] T. Friščić, C. Mottillo, and H.M. Titi, "Mechanochemistry for synthesis.," *Angewandte Chemie*. vol. 132, no. 3, pp. 1030–1041, 2020.
[49] M. Solares-Briones, G. Coyote-Dotor, J.C. Páez-Franco, et al., "Mechanochemistry: A green approach in the preparation of pharmaceutical cocrystals.," *Pharmaceutics*. vol. 13, no. 6, pp. 1–49, 2021.
[50] L.M. Tavares, "A review of advanced ball mill modelling.," *KONA Powder and Particle Journal*. vol. 2017, no. 34, pp. 106–124, 2017.
[51] A. Porcheddu, E. Colacino, L. De Luca, and F. Delogu, "Metal-mediated and metal-catalyzed reactions under mechanochemical conditions.," *ACS Catalysis*. vol. 10, no. 15, pp. 8344–8394, 2020.
[52] F. Cuccu, L. De Luca, F. Delogu, et al., "Mechanochemistry: New tools to navigate the uncharted territory of 'impossible' reactions,." *ChemSusChem*. vol. 15, no. 17, p. 2022.