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## Carbohydrate pulp in lignin-first biorefineries: properties and applications: a perspective review

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The shift toward sustainable lignocellulose biorefineries has raised interest in lignin-first technologies, which aim to valorize lignin while preserving the carbohydrate pulp. While much attention has been devoted recently to lignin depolymerization, the fate and potential of the resulting carbohydrate pulp under these lignin-first technologies remain comparatively underexplored. Achieving full valorization of both lignin and carbohydrates is essential for the successful implementation of lignin-first biorefineries. This review provides a critical overview of the current state-of-the-art in carbohydrate pulp obtained from lignin-first processes, with a particular focus on Reductive Catalytic Fractionation (RCF). The influence of process parameters on the chemical composition, structural integrity, and morphological features of the pulp is discussed. In addition, this review highlights recent advances in pulp applications, including biological and chemical conversion, and outlines emerging opportunities in material and fiber valorization. To our knowledge, this is the first review to place carbohydrate pulp at the center of lignin-first research, identifying challenges and proposing future directions to fully integrate pulp valorization within the lignin-first biorefinery concepts.

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### Green foundation

1. This review integrates advances in lignin-first biorefining with the understanding of pulp properties and applications. It outlines how lignin, pulp, and solubilized sugars can be covalorized within a unified lignin-first framework, promoting sustainability and supporting a circular bioeconomy.
2. By discussing how process parameters in lignin-first biorefineries, such as solvent type, temperature, and additives, affect pulp properties, this review identifies routes to produce high-quality, sulfur-free pulp under energy-efficient conditions while generating lignin suitable for value-added uses beyond combustion. These insights highlight greener alternatives to kraft and sulfite processes that reduce toxic chemicals (SO<sub>2</sub> and H<sub>2</sub>S) and environmental emissions.
3. The review provides a comprehensive framework linking catalytic biomass valorization to fiber applications, bridging two fields and guiding the design of sustainable lignocellulosic biorefineries aligned with circular economy principles.

## 1. Introduction

The development of sustainable alternatives to traditional fossil-based resources has led to extensive research into biomass-derived materials. Lignocellulosic biomass, which is sourced from forestry and wood waste as well as agricultural residues, can serve as an alternative carbon source to fossil fuels.<sup>1,2</sup> Lignocellulosic biomass is primarily composed of carbohydrate

polymers such as cellulose (35–55%) and hemicellulose (20–40%), as well as lignin (10–30%).<sup>3</sup> The diverse nature of these polymers offers significant potential for a wide range of applications such as biofuels, chemicals, and biopolymers. However, this very heterogeneity also presents a challenge when it comes to fractionating or separating the individual components for efficient use in various chemical processes.

Carbohydrate pulp is one of the most commonly used renewable materials in industries such as paper production, textile manufacturing, and bioethanol production. Traditional pulping methods, including kraft, sulfite, soda, and organosolv processes, focus on separating the carbohydrate fibers by effectively removing the lignin. However, the lignin produced through these conventional techniques, which is known as technical lignin, tends to have a recalcitrant structure, primarily due to condensation reactions that occur during the pulping process. This altered structure makes the lignin

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difficult to use in high-value applications, limiting its potential for further utilization in more advanced and sustainable products.<sup>4</sup> Although lignin is the most abundant source of aromatic compounds on Earth, technical lignin is primarily burned in the recovery boiler for energy purposes.<sup>4,5</sup> As a result, there is a growing need for more sustainable technologies that can efficiently utilize all components of biomass, particularly lignin, to unlock its full mass potential.

Existing commercial pulping operations can be regarded as carbohydrate-centric technologies, where the primary focus is on the production of pulp, rather than the isolation of lignin. In contrast, the lignin-first biorefinery represents an innovative approach that seeks to fractionate, depolymerize, and stabilize lignin while carefully preserving the integrity of the carbohydrate pulp.<sup>6,7</sup> These include catalytic reduction, as seen in Reductive Catalytic Fractionation (RCF), or by utilizing protective chemistries such as aldehydes in Aldehyde-assisted Fractionation (AAF) or diols in Diol-assisted Fractionation (DAF).<sup>7</sup> These strategies effectively avoid the lignin condensation reactions that usually hinder its subsequent utilization. By preventing such condensation, the resulting lignin is characterized by a reduced molecular weight ( $M_w$ ), an abundance of functional chemical groups, and elevated guaiacol (and syringol) monomer yields. These attributes collectively enhance its suitability for a broad spectrum of high-value applications, including the manufacture of polyesters, epoxy resins, adhesives, and other advanced materials.<sup>8,9</sup> Besides these established technologies, there are other emerging technologies such as Dithionite-assisted Organosolv Fractionation (DAOF),<sup>10–12</sup> Oxidative-Catalytic Fractionation (OCF),<sup>13–15</sup> and Arylation-based stabilization techniques.<sup>16,17</sup> Lignin-first biorefinery approach not only overcomes the limitations of traditional lignin processing but also substantially

broadens the scope for lignin to be harnessed as a versatile and economically valuable resource in diverse industries.<sup>18</sup>

The lignin-first approach has traditionally been centered around prioritizing the development, properties, and applications of lignin, often at the expense of focusing on the carbohydrate pulp, despite carbohydrates being the dominant constituent in the lignocellulosic biomass. To achieve greater sustainability and circularity within biorefining processes, it is crucial to pursue the parallel, integrated development of both lignin and carbohydrates, addressing the challenges and opportunities associated with both components. In this context, stepwise strategies based on biomass pretreatment followed by catalytic transfer hydrogenolysis of the extracted lignin have also been reported,<sup>19–22</sup> highlighting important trade-offs between lignin monomer yield and carbohydrate preservation. However, the present perspective focuses on integrated and well-established lignin-first fractionation approaches. Although numerous reviews have extensively covered various aspects of lignin within the context of lignin-first biorefineries, particularly focusing on process advancements, material properties, and potential applications,<sup>7,10,23</sup> no review, to the best of our knowledge, provides a comprehensive and in-depth discussion on the fate of the carbohydrates and their distinct properties. This gap in the literature underscores the need for a more holistic approach that considers the simultaneous development of both lignin and carbohydrate streams to optimize the potential of lignocellulosic biomass in sustainable biorefining.

This review seeks to explore lignin-first biorefineries from a pulp-centered viewpoint, offering a detailed overview of the current quality of pulp produced through lignin-first approaches. The scope is therefore focused on three established lignin-first technologies, namely RCF, AAF, and DAF, owing to their higher level of maturity and the broader avail-



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ability of quantitative and comparable data regarding pulp properties. We comprehensively summarize the chemical, structural, and morphological properties of the pulp, with a focus on how various process conditions influence these attributes. In addition, we examine the reported applications and conversion pathways for pulp derived from lignin-first methods, while also identifying promising potential applications that remain underexplored. Finally, we address the technical challenges and knowledge gaps that persist in the field, providing insights and a forward-looking perspective to inform and guide future research endeavors in this area.

## 2. Conventional pulping techniques (non-lignin-first)

Pulping technology is ancient, with its origins tracing back to the Egyptians and Chinese civilizations.<sup>24,25</sup> The primary goal of pulping is to dissolve as much lignin from the raw material as possible while preserving the integrity of the wood fibers.<sup>26</sup> Pulping methods are generally classified into four categories: mechanical, chemical, semi-chemical, and biological. Mechanical pulping relies on physical forces to separate fibers, while chemical pulping uses chemicals to dissolve lignin and release cellulose fibers.<sup>25</sup> Semi-chemical pulping combines both methods in a two-stage process, applying physical force in conjunction with mild chemical treatment. Biological pulping typically involves the use of biological nutrients (fungi and enzymes) that soften the biomass and facilitate the removal of lignin.<sup>27</sup> The selection of the appropriate pulping method depends on the type of raw material and the desired properties of the resulting pulp.<sup>25</sup>

In the context of this review, conventional pulping refers to the well-established and widely utilized chemical pulping

methods that have been the cornerstone of the paper industry for many years. These techniques can be broadly categorized into alkaline pulping, such as soda and kraft, acid pulping, like sulfite pulping, and organic solvent pulping.

### 2.1 Alkaline pulping

Alkaline pulping, including kraft and soda processes, is characterized by selective lignin removal under basic conditions (pH 13–14),<sup>28,29</sup> with reduced effect on cellulose and relative depolymerization of hemicelluloses (depending on the type), preserving a substantial part of the polysaccharides fraction of biomass. Soda pulping was the conventional alkaline method, depending solely on NaOH<sup>30,31</sup> before the improvement through the addition of sodium sulfide (Na<sub>2</sub>S), leading to the kraft process. As a result of this selective chemistry, alkaline pulping tends to produce high holocellulose (*i.e.*, hemicellulose & cellulose pulp) with high yield and superior mechanical strength, making alkaline pulping the dominant route for paper and packaging applications.<sup>28</sup> Currently, the kraft process stands as the predominant industrial pulping technique globally,<sup>32</sup> contributing to an annual production of approximately 130 million tons of pulp,<sup>33</sup> accounting for roughly 66% of the total pulp production and for over 90% of the chemical pulp.<sup>34,35</sup>

During alkaline pulping, the carbohydrate fraction undergoes reactions that govern pulp yield and molecular integrity.<sup>28,29,36</sup> The main reaction mechanisms are shown in Fig. 1. The dominant reaction is the peeling reaction, which starts immediately upon contact with alkaline liquor, even at temperatures around 100 °C.<sup>28</sup> Peeling occurs at the polymer reducing end groups through  $\beta$ -elimination steps, causing stepwise depolymerization and dissolution of the carbohydrates.<sup>37</sup> This reaction predominantly affects hemicelluloses due to their lower degree of polymerization and higher substi-



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tution, whereas cellulose is far less impacted because of its high initial chain length and crystallinity.<sup>28,38</sup> Consequently, early yield losses in alkaline pulping are mainly attributed to hemicellulose degradation, while cellulose is largely retained.<sup>28</sup> In addition to the rapid peeling reaction, a much slower stopping reaction occurs, in which the reducing end group is stabilized as metasaccharinic acids, thereby inhibiting further peeling depolymerization. The likelihood of this reaction depends on the stability of the leaving group (OR<sub>3</sub> in Fig. 1). Stopping reactions are less frequent in cellulose and glucomannan hemicelluloses, where R<sub>3</sub> = H and the leaving group is a hydroxyl ion, than in xylan, which often contains more stable leaving groups such as acetate or deprotonated arabinose. Consequently, softwood hemicelluloses, rich in glucomannan, are more susceptible to peeling reactions than xylan-rich hardwood hemicelluloses under alkaline pulping conditions.<sup>28</sup>

At higher temperatures, typically above ~170 °C, random alkaline hydrolysis of glycosidic bonds may occur, mainly in the amorphous regions of cellulose microfibrils and hemicellulose.<sup>28</sup> This leads to chain scission, a reduction in cellulose degree of polymerization, and the formation of new reducing ends that can further undergo peeling. Nevertheless, alkaline hydrolysis is slower and less uniform than peeling, and its contribution to carbohydrate loss is limited.<sup>28</sup> In practice, the combined effect of peeling and alkaline hydrolysis results in an overall cellulose loss of about 10% in kraft and soda pulping.<sup>28</sup>

## 2.2 Acid pulping

Sulfite pulping, the oldest chemical pulping method, can be operated under acidic or neutral conditions, depending on the targeted pulp properties and end-use applications.<sup>39</sup> In acidic sulfite pulping, the cooking liquor typically operates at pH values between 1.5 and 4.0. The pulping liquor contains sulfite or bisulfite ions, commonly paired with calcium, magnesium, sodium, or ammonium as counter-ions.

From a carbohydrate perspective, the dominant reaction in acidic sulfite pulping is the acid-catalyzed hydrolysis of glycosidic linkages, which leads to extensive depolymerization of polysaccharides and the formation of soluble sugars in the pulping liquor,<sup>40</sup> with reaction mechanisms presented in Fig. 2.

Hemicelluloses are especially susceptible to acid-catalyzed hydrolysis due to their amorphous structure and higher accessibility, resulting in substantial losses during pulping.<sup>28</sup> However, hemicellulose reactivity is strongly dependent on its structural diversity across biomass types, including differences in backbone sugar composition, substitution, and degree of acetylation.<sup>41,42</sup> In hardwoods and grasses, hemicellulose is predominantly composed of glucuronoxylans and arabinans, which are rich in pentose sugars such as xylose and arabinose, and can undergo rapid acid-catalyzed depolymerization, often accompanied by the release of acetic acid from acetyl groups that further enhances hydrolysis rates.<sup>43,44</sup> In contrast, softwood hemicelluloses are mainly galactoglucomannans, which contain a higher fraction of hexose units and generally exhibit greater resistance to acid hydrolysis due to differences in backbone structure and substitution patterns.<sup>42</sup> For example, in softwood sulfite pulping, up to 70% of glucomannan and about 50% of xylan are removed from the solid pulp,<sup>28</sup> whereas in hardwoods, xylan removal is higher, typically exceeding 60% and reaching ~80%.<sup>45</sup> The dissolved carbohydrates are largely present as monomeric sugars, which may be further converted into degradation products such as furfural from pentoses and 5-hydroxymethylfurfural (HMF) from hexoses, depending on acidity, temperature, and cooking time.<sup>28,46</sup> Both chemicals may undergo polymerization forming humins.

Kraft and sulfite processes demonstrate fundamental mechanistic differences in their selectivity toward lignocellulosic components, which in turn govern the fate of the



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resulting pulp.<sup>47</sup> In the kraft (sulfate) pulping, the process targets lignin through nucleophilic cleavage of ether linkages (e.g.,  $\beta$ -O-4 bonds) under strongly alkaline conditions, leaving a significant portion of the hemicelluloses unaltered.<sup>40</sup> In contrast, acidic sulfite pulping targets hemicellulose to a greater extent, as acid-catalyzed hydrolysis preferentially cleaves glycosidic bonds in hemicelluloses and amorphous cellulose regions, while lignin is solubilized *via* sulfonation reactions due to increase of hydrophilicity. These pulps generally exhibit lower mechanical strength than kraft pulps but offer higher purity, making them particularly suitable for dissolving pulp applications and selected low-volume paper grades.<sup>40</sup> Therefore, while both processes aim to liberate cellulose fibers, kraft pulping emphasizes lignin removal with better preservation of carbohydrate integrity, whereas sulfite pulping induces more extensive carbohydrate degradation, particularly of hemicellulose.

### 2.3 Organosolv

Organosolv pretreatment is a chemical fractionation process that separates lignocellulosic biomass into its main components using organic solvents such as ethanol, acetone, or ethylene glycol (EG), often in combination with acidic or basic catalysts.<sup>48</sup> Under appropriately selected and typically mild conditions, organosolv processes can enable effective lignin solubilization while relatively preserving the cellulose fraction, whereas hemicellulose is more prone to hydrolysis, particularly under acidic conditions.<sup>49,50</sup> Operating temperatures generally range from 100 to 250 °C, depending on the solvent system, catalyst, and targeted degree of delignification.<sup>48,51</sup>

The fractionation mechanism primarily involves the cleavage of lignin-carbohydrate complex (LCCs) and ether linkages in lignin, especially  $\alpha$ - and  $\beta$ -O-4 bonds, which increases lignin solubility in the organic phase.<sup>52</sup> Solvent choice and catalytic conditions strongly influence both delignification efficiency and carbohydrate retention. Acid-catalyzed organosolv tends to yield better results in terms of lignin dissolution while also promoting the hydrolysis of hemicellulose into fermentable sugars.<sup>53</sup>

The organosolv medium actively governs carbohydrate reactivity through its influence on effective acidity, solvation of intermediates, and water activity.<sup>54</sup> The strength of Brønsted acids in mixed solvent systems depends strongly on solvent polarity and hydrogen-bonding capacity, which affect proton solvation and dissociation equilibria, thereby modifying hydrolysis and dehydration kinetics.<sup>54,55</sup> In mixed systems, organic co-solvents like  $\gamma$ -valerolactone do not compete with the sugar molecule for acidic protons as strongly as water does. This increases the effective proton activity (or Hammett acidity), allowing the catalyst to drive carbohydrate dehydration more efficiently at lower energy barriers in presence of the organic solvent.<sup>54,56</sup> The high-boiling and polar aprotic co-solvents (e.g.,  $\gamma$ -valerolactone or glycols) have been reported to lower activation barriers for acid-catalyzed transformations by stabilizing key intermediates, although such strong solvation and high boiling point can complicate downstream separation.<sup>54,57</sup> For example, pentose dehydration is favored in high-polarity, low-basicity aprotic solvents because they increase the effective acidity of the catalyst, while simultaneously reducing the water activity that leads to furfural degradation.<sup>58,59</sup>

Organosolv-pretreated biomass offers multiple valorization pathways. The cellulose-rich pulp can be directed toward fermentation or material applications, while the recovered lignin is typically sulfur-free and of relatively high purity, making it attractive for downstream conversion into materials and chemicals.<sup>60,61</sup> The hemicellulosic sugars released during pretreatment can also serve as feedstocks for fermentation processes, yielding biofuels and biochemicals.<sup>62</sup> However, the sustainability advantages of organosolv processes are highly conditional, depending on factors such as solvent selection, solvent recovery efficiency, energy demand, and process integration.<sup>63,64</sup>

Despite extensive research and early demonstration efforts, large-scale industrial implementation of organosolv technologies has remained limited.<sup>65</sup> Historical challenges include high solvent recovery costs, corrosion issues, and overall process economics, which contrast with the robustness and proven scalability of sulfur-based kraft and sulfite pulping.<sup>53,65</sup>

## 3. What is lignin-first technology?

Over the past few decades, various technologies have been developed to selectively extract and depolymerize lignin from lignocellulosic biomass, including organosolv,<sup>65–68</sup> ionic liquids,<sup>69</sup> and deep eutectic solvents.<sup>70,71</sup> Among these, organosolv has emerged as the most prominent and well-established approach, particularly tailored for second-generation biofuel production. A notable example is the Assam Bio-Refinery in India, which applies organosolv (ethanol) to fractionate bamboo for the production of second-generation bioethanol ( $\approx 49\,000\text{ t y}^{-1}$ ), alongside furfural and acetic acid as co-products.<sup>72</sup>

It is documented that intramolecular condensation reactions also occur during organosolv treatment, leading to the



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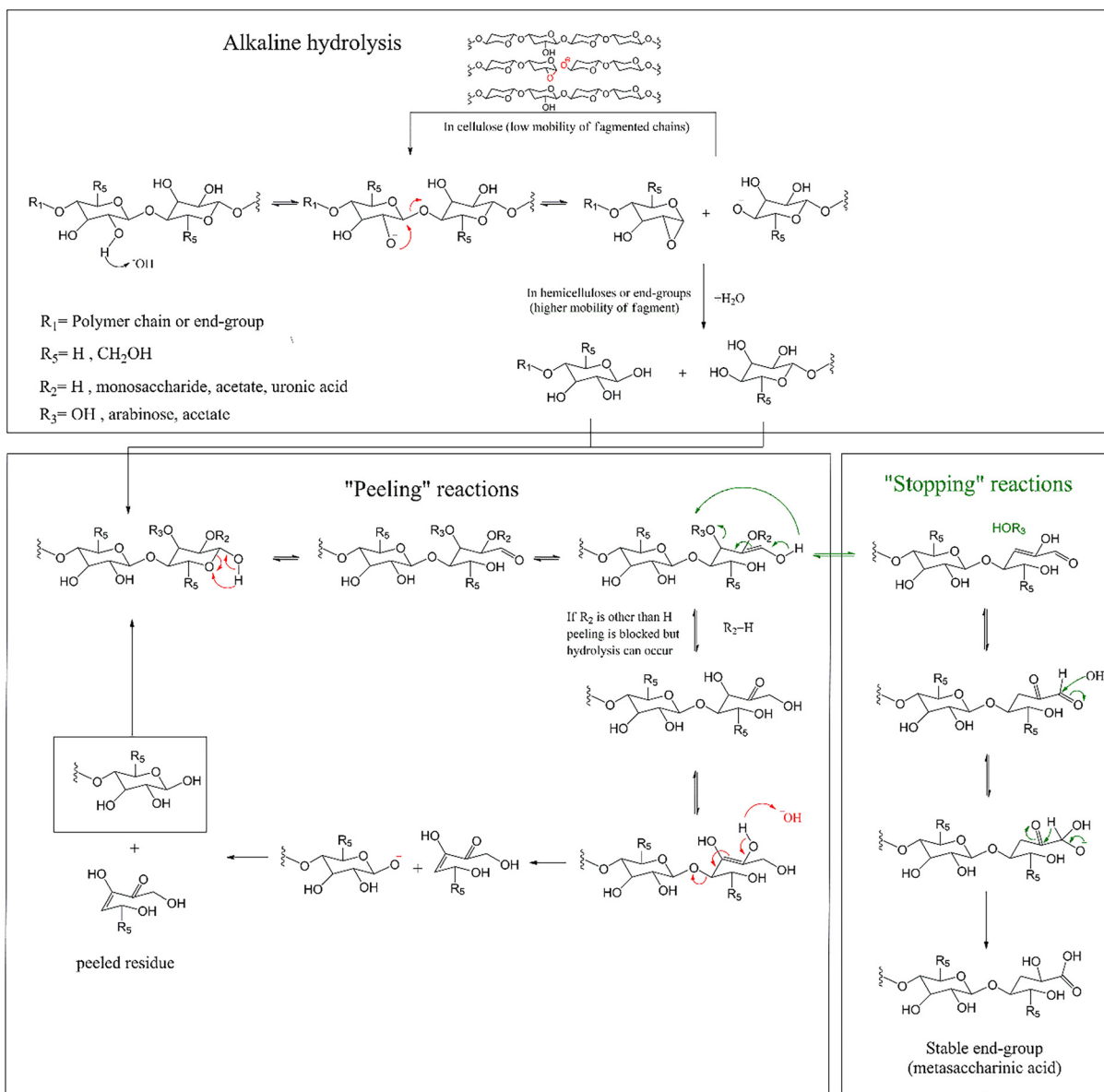


Fig. 1 Carbohydrate reaction mechanisms in alkaline medium (Soda and Kraft).

formation of stable condensables with new C–C bonds, ultimately leading to char precipitates.<sup>68,73</sup> In native wood lignin, these interunit C–C linkages account for approximately 32–35% of total linkages in hardwood and 21–23% in softwood.<sup>74</sup> In acid-catalyzed organosolv systems, such condensation (alkylation) reactions are largely unavoidable, as they proceed more readily than lignin hydrolysis due to their lower activation energy.<sup>75</sup> While lowering reaction temperatures or acid concentrations can help reduce condensation, these adjustments may also hinder efficient  $\beta$ -O-4 ( $\beta$ -aryl ether) bond cleavage. As a result, there is a critical need to develop innovative strategies that suppress lignin condensation while enhancing depolymerization, thereby improving the potential for biomass valorization.

To address the challenges associated with lignin condensation and inefficient biomass fractionation, a new class of technologies known as “lignin-first” approaches has been proposed. The term “lignin-first” refers to fractionation strategies that prioritize the early extraction and stabilization of lignin during biomass processing. These technologies aim to: (i) extract lignin with high purity and maximize its yield from the lignocellulosic matrix, (ii) prevent the formation of new C–C bonds through condensation by stabilizing reactive lignin intermediates, and (iii) depolymerize the extracted lignin into low Mw fragments with high monomer yields.

As illustrated in Fig. 3, several mechanisms have been developed to prevent undesirable condensation reactions. One widely studied example is RCF, which employs selective cata-



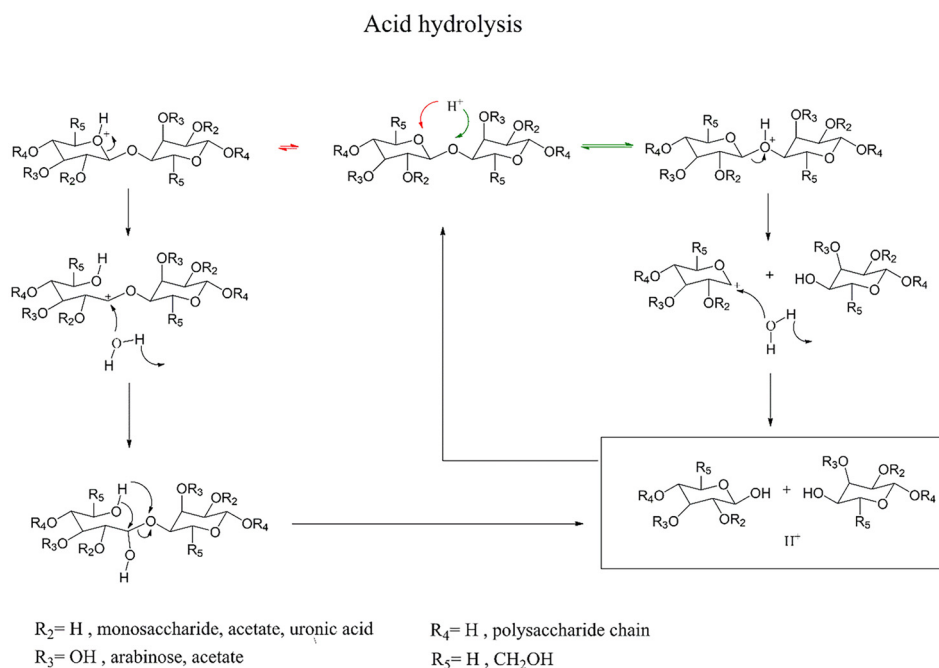
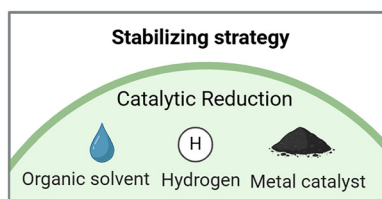


Fig. 2 Carbohydrate reaction mechanisms in acidic medium (Sulfite).

### A. Reductive Catalytic Fractionation (RCF)

#### Reaction Mechanism

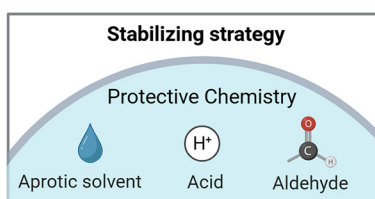
- Solvolysis
- Hydrogenolysis
- Hydrogenation



### B. Aldehyde-assisted Fractionation (AAF)

#### Reaction Mechanism

- Solvolysis
- Acidolysis
- Acetalization



### C. Diol-assisted Fractionation (DAF)

#### Reaction Mechanism

- Solvolysis
- Acidolysis
- Acetalization

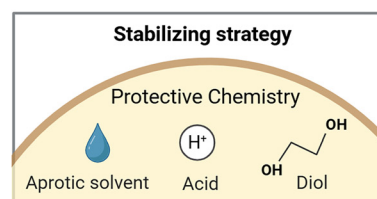


Fig. 3 The types of well-established lignin-first technologies and their stabilizing strategies.

lysts to convert unstable lignin intermediates into more stable derivatives, thus inhibiting further condensation. Similarly, approaches like AAF and DAF use stabilizing agents to protect reactive sites on lignin, effectively preventing the formation of recalcitrant C–C bonds.<sup>76</sup>

Beyond improving lignin recovery, lignin-first biorefinery strategies also help suppress the unwanted condensation of carbohydrate-derived intermediates into humins, which are insoluble byproducts that reduce the overall efficiency of biomass valorization. By mitigating both lignin and carbohydrate degradation, lignin-first technologies offer a promising pathway towards more efficient and integrated use of all lignocellulosic biomass components.<sup>77</sup>

## 4. Types of lignin-first technologies

### 4.1 Reductive catalytic fractionation (RCF)

RCF emerged in the early 2010s as a widely adopted lignin-first strategy focused on depolymerizing lignin while suppressing recondensation, with pulp optimization becoming a stronger focus in later works.<sup>78</sup> It operates by integrating three key steps: solvolytic (reactive) extraction of lignin, depolymerization of lignin and catalytic stabilization of reactive intermediates under reductive conditions,<sup>78</sup> Fig. 3. The solvolysis step is responsible for liberating lignin from the biomass matrix and depolymerization, while a reductive metal catalyst, commonly RANEY® Ni, Pd/C, Ni/C, or Ru/C, facilitates the lignin depoly-



merization and stabilization of reactive lignin intermediates.<sup>78</sup> The interplay between solvolysis and catalytic action is critical: solvolysis initiates lignin fragmentation, and subsequent contact with the catalyst surface enables controlled depolymerization (through hydrogenolysis and hydrogenation) and stabilization.<sup>10</sup> This approach results in two main product streams, a crude depolymerized lignin oil and a carbohydrate-rich pulp, primarily composed of holocellulose.<sup>79</sup>

The resulting lignin oil is a high-purity, low- $M_w$  product with broad industrial potential. Applications include biofuels,<sup>80–82</sup> phenolic platform chemicals,<sup>8</sup> epoxy resins,<sup>83–85</sup> and bio-based additives.<sup>9,86</sup> In parallel, the solid pulp fraction retains a high cellulose content, making it suitable for downstream applications such as enzymatic saccharification,<sup>76,87,88</sup> bioethanol production,<sup>87,89,90</sup> naphtha streams,<sup>91,92</sup> or chemicals.<sup>93</sup> RCF thus presents a holistic approach to biomass valorization by maximizing the utility of both lignin and carbohydrate fractions in a sustainable and efficient manner.<sup>94–96</sup>

Besides conventional RCF processes that rely on external  $H_2$ , several catalytic approaches have shown that lignin in raw biomass can also be converted into defined aromatic monomers under hydrogen-free or no-external- $H_2$  conditions. Early examples include tandem organosolv pulping and Pd-catalysed transfer hydrogenolysis directly from wood, using only endogenous hydrogen as the reductant,<sup>64</sup> and the hydrogen-free catalytic fractionation of woody biomass in organosolv media.<sup>97</sup> More recently, hydrogen-free depolymerization of lignin in lignocellulosic feedstocks has been demonstrated in methanol/water without external  $H_2$ ,<sup>98</sup> in microwave-assisted lignin-first depolymerization of birch sawdust,<sup>99</sup> and in self-hydrogen-supplied catalytic fractionation, where structural hydrogens in hemicellulose act as the hydrogen source,<sup>100</sup> as well as in dedicated hydrogen-free RCF studies using alcohol solvents<sup>101</sup> or high-boiling diols.<sup>102</sup> Generally, the use of hydrogen showed most stable lignin oils with lower molecular weight and less unsaturated functionalities next to the aromatic groups.

Recent advancements in RCF technology include the development of hydrogen-free methods, which allow for the direct production of aromatic compounds from biomass without the need for external hydrogen gas.<sup>102</sup> Additionally, the use of unpurified solvents in RCF processes has been proposed as a way to enhance the economic, environmental, and operational efficiency of the technology.<sup>103</sup> The choice of catalyst is particularly critical in determining both the yield and selectivity of aromatic monomers, besides solvent recyclability and scale-up challenges.<sup>104</sup>

#### 4.2 Aldehyde assisted fractionation (AAF)

AAF is an innovative biorefinery approach that uses aldehydes during lignin extraction to prevent condensation and repolymerization reactions by blocking the reactive sites on the lignin aromatic ring.<sup>75</sup> This method results in the formation of stable acetals at the  $\beta$ -O-4 linkages, thereby enhancing the efficiency of lignin fractionation.<sup>105</sup> The AAF process involves using an aprotic solvent (*e.g.*, dioxane) and an acid (*e.g.*, hydro-

chloric acid (HCl)) in the presence of an aldehyde, shown in Fig. 3.<sup>106</sup> Research has demonstrated that AAF significantly improves lignin valorization by achieving high monomer yields, similar to RCF.<sup>107</sup>

The use of aldehydes in lignin fractionation has been shown to enhance the properties of lignin-derived materials, demonstrating the potential of AAF for developing innovative and versatile materials such as gelatin-based hydrogels.<sup>108</sup> In addition to hydrogels, AAF lignin has found applications in a variety of products, including polyurethane bioresins,<sup>109</sup> thermosetting films and coatings,<sup>110</sup> and surfactants.<sup>111</sup> Moreover, AAF can be further optimized by utilizing multifunctional aldehydes, which allow for the simultaneous extraction and functionalization of lignin with non-native functional groups, thereby opening up new avenues for lignin utilization.<sup>106</sup>

AAF offers the advantage of operating without a metal catalyst, thus overcoming issues of catalyst deactivation and recovery. However, there are still challenges associated with this process, including issues related to the recovery and reuse of aldehydes, the use of particular solvents such as dioxane to be most effective, their consumption during the reaction, the use of water-free solvents, and the consumption of HCl. These factors need to be addressed to improve the efficiency and sustainability of the AAF process.

#### 4.3 Diol-assisted fractionation (DAF)

DAF is another lignin-first technology that utilizes protective chemistry, employing diols in an acid-catalyzed organosolv process to stabilize lignin and hemicellulose derivatives.<sup>10,112,113</sup> Typically carried out in organic aprotic solvents with the addition of both an acid and a diol, such as EG, 1,3-propanediol (1,3-PDO) and 1,4-butanediol (1,4-BDO) this process leads to the extraction of stable lignin,<sup>113–115</sup> illustrated in Fig. 3.

During fractionation, solvolysis and acidolysis cleave inter-unit  $\beta$ -O-4 linkages, generating reactive intermediates including Hibbert's ketones and C2-aldehyde-substituted phenolics, which are prone to rapid condensation.<sup>112</sup> Diols mitigate this recondensation by reacting with these intermediates to form stable benzylic acetals, thereby preserving native-like lignin structures.<sup>112</sup> This mechanism has been demonstrated in the work of De Santi *et al.*<sup>116</sup> In 1,4-BDO systems, at low temperatures (120–150 °C), 1,4-BDO pretreatment results in partial delignification but strong preservation of  $\beta$ -O-4 linkages, yielding a lignin stream of high reactivity for downstream catalytic depolymerization.<sup>117</sup> As temperature increases to 160–180 °C, delignification accelerates significantly, corresponding to the progressive disruption of LCCs and increased carbohydrate accessibility.<sup>117</sup>

Beyond classical diols, Cheng *et al.* developed a diol-based deep eutectic solvent (DES) pretreatment that achieves extensive delignification and lignin protection through incorporating the diol hydroxyl functional groups into the  $\alpha$  position of the lignin  $\beta$ -O-4 structure *via* etherification.<sup>118</sup>

Additionally, diols can interact with monosaccharides released from the degradation of hemicellulose in the acidic



environment, resulting in the formation of hydroxyalkylated sugars. These hydroxyalkylated sugars enhance the stability of the system, reducing the formation of pseudolignin (lignin-like condensates from carbohydrate degradation during harsh pretreatment) or humins and improving the quality of the recovered pulp.<sup>119</sup>

Like AAF, DAF overcomes limitations associated with catalyst use. However, the incorporation of diols necessitates additional solvent recovery efforts and/or the introduction of fresh diols, which can increase overall process costs. Despite this, the process's simplicity, low operating pressure, and similarity to organosolv treatment suggest significant potential for scalability.<sup>10</sup>

## 5. Carbohydrate pulp in lignin-first

In softwood and hardwood, the accumulated cellulose and hemicellulose content ranges from 70% to 76% and 55% to 79%, respectively.<sup>120</sup> Recently, driven by the goal of achieving a circular bioeconomy, research into lignin-first technologies has shifted towards improving the quality and expanding the applications of pulp.<sup>87,92,94,121,122</sup> Lignin-first technologies have shown high pulp yields and near-complete preservation of cellulose, opening up numerous opportunities for potential valorization.<sup>87,89,118,123</sup> Reports on RCF have indicated pulp yields – defined as the amount of extracted pulp relative to the initial wood – ranging from 39% to 65%<sup>94,95,123</sup> for birch wood and 43% to 66%<sup>122,124</sup> for poplar, and carbohydrate retention ranging between 48%–95%<sup>87</sup> of the initial carbohydrate in the raw material. In parallel, DAF delivers pulp with (72.5–76.1% cellulose) and (3.9–12.7% hemicellulose) suitable for enzymatic digestion.<sup>121,125</sup> Fig. 4 illustrates a clear trade-off between delignification and carbohydrate retention. High delignification allows more lignin removal, but it simul-

taneously disturbs carbohydrates by partially solubilizing hemicellulose and cellulose. Schutyser *et al.* proposed an empirical descriptor, Lignin-First Delignification Efficiency (LFDE), that defines the process efficiency based on delignification and carbohydrate retention.<sup>123</sup> It should be noted that, although pulp quality is inherently multidimensional, most lignin-first studies do not report parameters such as DP, viscosity, and crystallinity in a systematic and comparable manner. Therefore, Fig. 4 is intentionally limited to illustrating the trade-off between delignification and carbohydrate retention, which forms the basis of the LFDE concept as an empirical descriptor of process performance.

While cellulose is largely retained in the pulp, hemicellulose and part of the cellulose are typically solubilized, ending up in the aqueous phase as monomers/oligomers. The fate of the solubilized sugars is often reported as (i) methylated sugar (methylated xylose) in methanol RCF system,<sup>126</sup> (ii) conversion to sugar alcohol *e.g.*, xylitol for xylose and sorbitol for glucose, usually with a high water to alcohol ratio and sufficient heterogenous catalytic activity, (iii) sugars and sugar alcohols can undergo hydrogenolysis to polyols such as EG and propylene glycol under limiting heterogenous catalytic activity.<sup>127,128</sup> Integrating the water fraction with pulp *via* a separate hydrolysis and fermentation (SHF) to bioethanol is a promising path to valorize it.<sup>87</sup> In DAF system, hemicellulose is converted to hydroxylated sugars,<sup>119</sup> and in diol-based DES the solubilized hemicellulose led to both stabilized sugars and dehydration products such as furfural-type compounds.<sup>118</sup> In conventional pulping, a fraction of the hemicelluloses remains associated with the fibers due to the nature of the cooking chemistry, resulting in higher pulp yield and contributing to paper strength, whereas the dissolved carbohydrates end up in the black liquor together with technical lignin and are burned for energy.<sup>129,130</sup>

The following section of the review summarizes recent progress in lignin-first technologies with a focus on pulp production and its quality (composition and key physicochemical properties), examines current research and applications, identifies knowledge gaps, and outlines future directions. While the properties of pulp can go beyond the sections discussed here, the categorization of pulp properties in the following section, *viz.* 5.1 Chemical and 5.2 Structural and 5.3 Morphological properties, reflects the availability of data in literature.

### 5.1 Chemical properties

The chemical properties of pulp are crucial factors that determine its quality and its suitability for different applications, directly influencing the market value of the isolated pulp. Lignin-first biorefineries have been shown to produce pulp with a wide range of yields and chemical compositions, depending on the solvent and reaction parameters, as illustrated by the data in Table 1.

The selection of solvent is a pivotal factor in the solubilization of lignin. In organosolv processes, the degree of delignification is primarily influenced by the solvent's ability to solubilize lignin and cleave its linkages through solvoly-

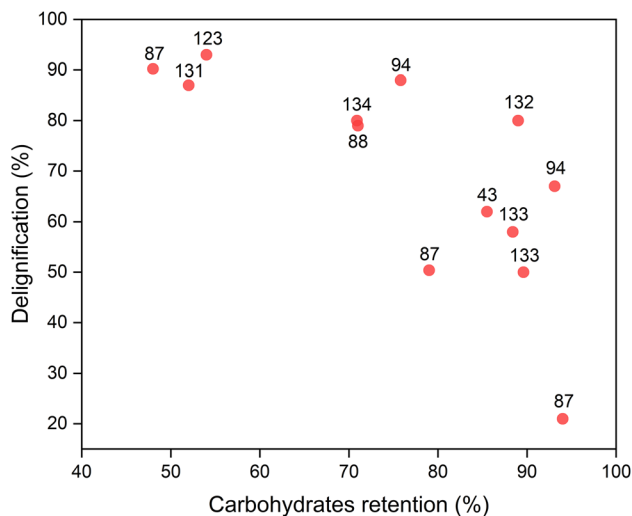


Fig. 4 Relationship between carbohydrate retention (%) and delignification (%) in pulp from RCF. Numbers above the dots represent the reference number.<sup>43,87,88,94,123,131–134</sup>



**Table 1** An overview of pulp from lignin-first biorefineries, (SR): sugar retention, (DD): degree of depolymerization, isopropyl alcohol/water (iPrOH/H<sub>2</sub>O)

Tech	Biomass	Conditions					Properties					Ref.	
		Solvent	Catalyst	Temperature (°C)	Additives	Time (h)	Pulp yield (%)	Hemicellulose (%)	Cellulose (%)	SR (%)	Lignin (%)		DD (%)
RCF	Birch	MeOH	5 wt% Ru/C	235		3	65	19	60		10		95
RCF	Poplar	MeOH	5 wt% Pd/C, 5–10 wt% ZnCl <sub>2</sub>	225		12	66.2			73.7			124
RCF	Poplar	2-Propanol/ water (7 : 3 v/v)	RANEY® Ni	220		3	52	7	84	52	4	87	131
RCF	Poplar	2-Propanol/ water (7 : 3 v/v)	RANEY® Ni	200		3	55	9	80	89	6	80	134
RCF	Poplar	2-Propanol/ water (7 : 3 v/v)	RANEY® Ni	200	1.1 mmol g <sup>-1</sup> wood of NaOH	3	58	15	75	Xylose = 56%	5	90	141
RCF	Birch	MeOH	Ni-Al <sub>2</sub> O <sub>3</sub>	250		3			55.6			84	91
RCF	Birch	MeOH	Ni-Al <sub>2</sub> O <sub>3</sub>	250		3		29.3					89
RCF	Birch	MeOH	Pd/C	250		3	39						123
RCF	Pine	EG	Pd/C	250		3	39			54		93	123
RCF	Triplolid poplar	MeOH	Ru/C	220	4 wt% Cs <sub>2</sub> CO <sub>3</sub>	4		17.8	72.3	71		79	88
RCF	Poplar	EtOH-H <sub>2</sub> O 65 : 35 v/v	2.5 wt% Pd/C	175	HCl 0.36 N	3	43		90		3.3		122
RCF	Birch	MeOH	Ni-Al <sub>2</sub> O <sub>3</sub>	200		3	83	26.1	49.6	94	24.4	21	87
RCF	Birch	MeOH	Ni-Al <sub>2</sub> O <sub>3</sub>	235		3	65	27.9	52.5	79	19.4	50.4	87
RCF	Birch	MeOH : H <sub>2</sub> O, 80 : 20 (v/v)	Ni-Al <sub>2</sub> O <sub>3</sub>	250		3	35	4.1	88.8	48	7.2	90.2	87
RCF	Eucalyptus	MeOH	MoOx /SBA-15	260		4				95		93	164
RCF	Bagasse	iPrOH/ H <sub>2</sub> O, 70% v/v	RANEY® Ni	180		3				85.5		62	43
RCF	Hybrid poplar	1 : 1 w/w methanol- water	Ru/C	200		3						83	142
AAF	Beech	1,4 dioxane	(37 wt%) HCL	80					71		15		165
AAF	Beech	GVL	(37 wt%) HCl	80				9	88				166
AAF	Birch	1,4 dioxane	HCl	85	Propionaldehyde formaldehyde	3	39.1	6	78.1		2.8		167
AAF	Birch	1,4 dioxane	HCl	85		3	35.3	2.6	79.4		4		167
DAF	Poplar	EG and 1,4- butanediol	0.5 M HCl	80		3	41.4	3.9	77.7			80.4	125
DAF	Bagasse	Ethylene carbonate	1.2% H <sub>2</sub> SO <sub>4</sub>	90	EG	0.5		12.7	72.5		10.3		121
DAF	Bagasse	Propylene carbonate	1.2% H <sub>2</sub> SO <sub>4</sub>	90	Propylene glycol	0.5		9.6	76.1		9.9		121



sis.<sup>135</sup> In contrast, the RCF process relies less on the solvent's lignin solubility, as high delignification rates have been achieved with solvents like methanol and EG, which exhibit relatively low lignin solubility.<sup>91,123</sup> Instead, solvent polarity plays a critical role in delignification, with more polar solvents facilitating deeper penetration into the lignocellulosic matrix, enabling more efficient fragmentation of the *in planta* lignin.<sup>123,136</sup> Polar solvents like EG, methanol, and ethanol have been shown to exhibit high delignification efficiency while preserving holocellulose (*i.e.*, cellulose and hemicellulose) integrity.<sup>88,93,95,122,136</sup>

Schutyser *et al.* conducted a comparative study on EG and methanol pulping of birch sawdust, revealing that both solvents effectively removed lignin, although EG resulted in lower xylan retention under similar processing conditions.<sup>123</sup> In methanol, hemicellulose acetate groups are converted to alkyl acetates, while in the presence of EG, EG mono-acetates are formed, which can subsequently undergo hydrolysis to yield EG and acetic acid.

Although water is a highly polar solvent that leads to significant delignification, it is generally not ideal for RCF due to its tendency to cause extensive removal of pentose sugars and up to 20% of the hexose fraction, converting them into a diverse range of polyols. Nonetheless, the incorporation of water into an organic solvent as a delignification agent can enhance the process by increasing the overall polarity, improving the transport of the liquor into the wood matrix, and thereby facilitating lignin extraction and solvolysis.<sup>134</sup>

In addition to water, the utilization of acids like (HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) or bases like (NaOH and Cs<sub>2</sub>CO<sub>3</sub>) as additives/co-catalyst can promote delignification by helping bond breaking or lignin solubilization. Acids are known for their ability to catalyze hydrolysis of glycosidic bonds in the hemicellulose, whereas alkaline environment promotes lignin fragmentation and dissolution by breaking the ether bond between lignin and carbohydrate,<sup>137,138</sup> and by generating phenolate functions. Major carbohydrate reactions such as peeling, and hydrolysis in acid or alkaline environments are discussed in sections 1.1 and 1.2. Renders *et al.* for instance, compared the effect of adding H<sub>3</sub>PO<sub>4</sub> and NaOH during RCF of pine sawdust in the presence of MeOH and Pd/C at 200 °C. Their results indicated that delignification increased from 56% to 96% and 85% with the addition of 5 g L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> and 5 g L<sup>-1</sup> NaOH, respectively.<sup>138</sup> Acidic conditions typically lead to low hemicellulose retention in the pulp due to the hydrolysis of hemicellulose.<sup>138</sup> In contrast, cellulose is preferentially retained in the solid pulp fraction under acidic environments, owing to its higher crystallinity and lower susceptibility to solubilization compared to hemicelluloses,<sup>138,139</sup> although partial depolymerization and a reduction in degree of polymerization of the pulp may still occur.<sup>140</sup> Under alkaline conditions, hemicellulose retention is generally enhanced, whereas cellulose retention may decrease due to cellulose swelling and partial amorphization, which weakens the structural integrity of the cellulose. The addition of low concentrations (1–2%) of inorganic bases, such as NaHCO<sub>3</sub> or NaOH, can enhance hemicellulose

retention from 47% to 60% due to pH neutralization without significantly affecting cellulose content.<sup>141</sup> Acid pre-hydrolysis or hemicellulose acidolysis is a pretreatment method where biomass is soaked in acidic solutions at specific temperatures prior to RCF.<sup>139</sup> This step facilitates hemicellulose removal by catalyzing hydrolysis, resulting in pulp with a higher cellulose purity. Cheng *et al.* reported that acidolysis with FeCl<sub>3</sub> at 170 °C for 10 minutes on moso bamboo yielded pulp with only 3.5% hemicellulose retention and 18.9 wt% lignin.<sup>139</sup> Subsequent RCF treatment (MeOH, 5 wt% Pd/C at 160 °C for 2 h) completely removed the remaining hemicellulose. FTIR analysis revealed that acidolysis alters the chemical properties of the pulp, with key changes including: (i) the generation of more methyl and methylene groups, (ii) destabilization of carbonyl groups, and (iii) removal of aliphatic ethers.

In a recent study by our group, it was demonstrated that using a recycled solvent mixture including methanol, methyl acetate, water, acetic acid, and crude oil can facilitate the lignin extraction and hemicellulose removal.<sup>103</sup> For example, incorporating 80% of the recycled solvent mixture into the RCF system (5% Pd/C, 220 °C, 30 bar H<sub>2</sub> for 2 h) led to 93% delignification while most of the cellulose was retained in the pulp.<sup>103</sup> Supporting this approach, Jang *et al.* showed that recycling the lignin-oil product itself as a cosolvent (up to 80 wt% in MeOH/H<sub>2</sub>O, or even 100 wt% oil alone) provided high delignification levels (83–93%) and maintained aromatic monomer selectivity, lignin-oil quality, and cellulose retention across ten recycle runs, thereby reducing the need for fresh solvent and alleviating downstream recovery requirements.<sup>142</sup>

Under typical RCF conditions, glucan (cellulose) is largely preserved, often exceeding ~85–95% retention depending on severity, whereas hemicellulose retention (and amorphous cellulose) is more variable and sensitive to process conditions (*e.g.*, pH, temperature, solvent) (Table 1).<sup>43,89,100,142</sup> The carbohydrate profile of the residual RCF pulp is dependent on the initial feedstock; while glucan retention remains consistently high across species, the hemicellulose fraction reflects the native composition, with hardwood-derived pulps being xylan-rich (5–15%)<sup>141,143</sup> and softwood-derived pulps retaining significant glucomannan (8–12%).<sup>143,144</sup> In contrast, herbaceous feedstocks like wheat straw yield pulps with higher hemicellulose retention (up to 20%), primarily as arabinoxylans, alongside higher residual ash content.<sup>101,144</sup> The residual hemicellulose in RCF pulps is rarely fully intact. Instead, it exists as a mixture of partially preserved polymers, oligomeric fragments, and soluble degradation products.<sup>43,87</sup> The fate of the solubilized sugar is usually reported as methylated sugar, sugar alcohol, and (smaller) polyols depending on the process conditions and solvent type (more details in section 5).

In addition to the solvent, the process conditions in the RCF method play a significant role in shaping the chemical properties of the isolated carbohydrate pulp. Therefore, understanding the impact of these factors is essential for optimizing the RCF process to achieve the desired chemical characteristics. A summary of the effects of these parameters is provided in Fig. 5.





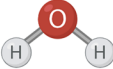
Additives		
<p><b>a</b> Base </p> <ul style="list-style-type: none"> <li>Promote lignin fragmentation and dissolution</li> <li>Enhances hemicellulose retention while reducing cellulose retention</li> </ul>	<p><b>b</b> Acid </p> <ul style="list-style-type: none"> <li>Increase delignification</li> <li>Promote hemicellulose hydrolysis</li> <li>Enhances cellulose retention while reducing hemicellulose retention</li> </ul>	<p><b>c</b> Water </p> <ul style="list-style-type: none"> <li>Increase delignification</li> <li>Promote hemicellulose hydrolysis</li> </ul>
Reaction conditions		
<p>Temperature</p>	<ul style="list-style-type: none"> <li>Higher temperature improves lignin removal but lower pulp yield</li> <li>Higher temperature degrade carbohydrates and lower DP</li> </ul>	
<p>Solvent</p>	<ul style="list-style-type: none"> <li>Polar solvents show high delignification efficiency</li> <li>Ethylene glycol fragments fiber aggregates without damaging them</li> <li>Water is unsuitable as a sole solvent due to excessive removal of pentose and hexose sugars</li> </ul>	
<p>Time</p>	<ul style="list-style-type: none"> <li>Delignification typically proceeds through an initial rapid stage followed by a slower regime</li> <li>Longer time allows sugar degradation and reduce pulp yield</li> </ul>	

Fig. 5 Summary of the impact of RCF parameters on the pulp chemical and structural properties.

Temperature is a key factor in solvolytic extraction, as it promotes the cleavage of lignin intermonomer linkages. An increase in temperature enhances the degree of delignification, resulting in pulp with lower lignin content.<sup>87,131,136,145</sup> However, higher temperatures also reduce carbohydrate retention due to the promotion of hydrolysis of hemicellulose.<sup>146</sup> For instance, increasing the temperature from 180 °C to 220 °C for poplar wood in 2-PrOH/H<sub>2</sub>O (7 : 3, v/v) in the presence of a nickel catalyst increased the degree of delignification from 53% to 87%, while hemicellulose retention decreased from 82% to 41%.<sup>131</sup> Similarly, another study reported that raising the temperature from 180 °C to 260 °C significantly reduced cellulose retention from 36.5% to 23.4% and hemicellulose retention from 62.8% to 61.9%, indicating damage to the polysaccharide structure.<sup>145</sup>

Reaction time influences the extent of delignification by controlling the progression of lignin removal across distinct kinetic regimes. Delignification typically proceeds through an initial rapid stage, dominated by the cleavage of more labile LCCs linkages, followed by a slower regime associated with the removal of more recalcitrant lignin structures and stronger LCCs bonds.<sup>147–149</sup> Consequently, most lignin removal (up to ~70%) typically occurs during the early stages of the reaction,<sup>149</sup> while prolonged reaction times contribute little additional delignification and instead promote carbohydrate

loss, leading to reduced pulp yield and carbohydrate retention.<sup>68,88</sup>

Although the presence of hydrogen gas is critical for the reductive catalytic stabilization of lignin, it does not significantly affect the carbohydrate retention (*i.e.* similar pulp yield and cellulose and hemicellulose content with or without hydrogen gas).<sup>88,150</sup> However, the presence of hydrogen during RCF reaction prevents sugar dehydration and the formation of furfural or HMF – and therefore solid humins – that are important inhibitors for fermentation applications,<sup>87</sup> and instead forms several C2 to C6 polyols as soluble sugar derivatives.

It is worth noting that most of the data published about chemical properties of pulp is coming from RCF studies, highlighting the need for more investigation from other lignin-first technologies. However, although RCF has explored the effects of individual reaction conditions on pulp quality, the synergistic interactions between multiple factors remain limited and are often system-dependent.<sup>151–154</sup> As a result, the use of a mathematical model based on a design of experiments (DOE) approach with more focus on pulp and its chemical nature may be strongly recommended. DOE not only enables the analysis of individual parameters but also supports the development of models to investigate the combined effects of multiple variables. In conventional pulping, process intensity is often expressed through the severity factor, a numerical factor that



combines reaction temperature, time, and, in some cases, pH.<sup>31,155</sup> Applying this concept to lignin-first processes is feasible; however, the formula should be adapted to account for solvent effects (e.g., solvent polarity), as the classical expression was initially developed for hydrothermal water-based systems and neglects the influence of solvents. For instance, the severity factor has been implemented in some organosolv-based studies,<sup>156,157</sup> where mostly acid is added as some type of catalyst. On top of using different types of alcoholic solvents (i.e., ethanol or methanol), even different ratios of ethanol/water resulted in an offset of the results, where no clear correlation could be obtained between the severity factor and delignification.<sup>158–160</sup> Next to the solvent, the composition of the substrate also plays a significant role. Substrates that consist of a higher holocellulose:lignin ratio, such as sorghum derived waste<sup>161</sup> are generally more susceptible to dissolution of the carbohydrates and thus resulting in lower pulp yields in comparison to those with a lower ratio. Also, the lignin and its interunit linkages and interactions with the carbohydrate matrix will determine if more lignin is extracted, and their correlation to the severity factor used. Accordingly, softwoods generally require harsher conditions than hardwoods, mainly due to the higher abundance and stability of LCCs arising from their distinct hemicellulose composition, together with a higher proportion of recalcitrant C–C interunit linkages in the lignin structure.<sup>162</sup> Last but not least, RCF also adds the complexity of a heterogeneous catalyst, which not only helps the stabilization of the dissolved lignin to ultimately obtain a lignin oil with a high content of monomeric lignin molecules, but also the rate of the stabilization becomes increasingly important when wanting to incorporate this factor into a simple equation. Integrating these parameters into a common factor would enable more consistent comparison of process conditions and help predict key outputs such as lignin content, yield, and carbohydrate retention. It could also support the empirical descriptor LFDE, which compares processes based on delignification and carbohydrate retention as mentioned above.<sup>123</sup>

Furthermore, integrating advanced artificial intelligence (AI) tools can significantly enhance the understanding of these complex interactions. Such tools can process large datasets, identify patterns, and predict outcomes with high precision, assisting researchers in optimizing experimental conditions more efficiently. Additionally, the role of various catalysts in shaping the chemical properties of pulp remains an underexplored area in the literature. Although the use of AI and machine learning (ML) in the pulping industry is still in its early stages, recent work by Chrzastowska *et al.* demonstrated their potential by applying ML-assisted NIR and Raman spectroscopy for the non-destructive quantification of extractives in pulping matrices, marking a promising step toward the integration of AI and ML in the field.<sup>163</sup>

## 5.2 Structural properties

In addition to its chemical composition, the structural properties of pulp, such as degree of polymerization (DP), vis-

cosity, and crystallinity, are crucial factors in determining its suitability for a wide range of applications.

DP, representing the average number of glucose units within a cellulose chain, plays a pivotal role in determining pulp quality and mechanical strength. Pulp produced through lignin-first technologies has been reported to exhibit a generally higher DP compared to that obtained *via* organosolv process. This difference is largely attributed to the degradation effects induced by organic acids inherent in the lignocellulosic matrix during organosolv treatment.<sup>12,134</sup> In organosolv pulping, acids from the lignocellulose remain in the mixture and lower the pH, promoting cellulose depolymerization. For instance, pulp produced *via* RCF from poplar wood (2-PrOH/water mixture, RANEY® Ni catalyst) at 220 °C for 3 hours demonstrated a threefold increase in DP compared to organosolv.<sup>134</sup>

Viscosity, a crucial parameter, functions as an indirect indicator of DP, offering valuable insights into the molecular weight ( $M_w$ ) and solubility of cellulose. This property is especially significant for applications such as dissolving pulp (high-purity cellulose pulp for dissolution into regenerated cellulose) and the production of cellulose derivatives. Maintaining an optimal viscosity (400–600 mL g<sup>-1</sup>) ensures efficient processing and uniform dissolution, and optimal reactivity of dissolved pulp.<sup>168</sup> While viscosity has been reported for RCF pulps, especially in dissolving pulp studies, systematic evaluation of the effects of RCF process variables on viscosity is still limited.<sup>122,169,170</sup> In contrast to RCF, the impact of organosolv fractionation on DP and viscosity has been investigated.<sup>171</sup> Acid-catalyzed organosolv systems show a strong dependence of viscosity on process severity, solvent composition, and acid concentration.<sup>171</sup>

The carbohydrate fraction of pulp is composed of both amorphous regions, primarily constituted by hemicellulose and portions of less-ordered cellulose, and crystalline domains, which are predominantly formed by highly structured cellulose chains. The crystallinity of cellulose serves as a critical indicator of the extent of molecular ordering within the fiber matrix, significantly influencing the material's susceptibility to chemical modification and enzymatic hydrolysis. In lignin-first biorefining technologies, the crystallinity of the resulting pulp is frequently altered as a consequence of the selective removal of amorphous components, such as hemicellulose and lignin. This structural reorganization often reveals a linear correlation with the degree of delignification, underscoring the intricate relationship between biomass fractionation and cellulose morphology.<sup>12,90,125</sup> For example, Pan *et al.* compared the crystallinity index (CI) of poplar wood before and after DAF treatment, reporting a CI of 51.8% for treated pulp compared to 34.4% for untreated wood.<sup>125</sup> Similarly, the crystallinity of RCF pulp showed 3–9% higher amounts of crystalline cellulose compared to organosolv treated with the same solvent (2-PrOH/H<sub>2</sub>O 7/3 v/v) and temperature (200–220 °C).<sup>134</sup> Liu *et al.* also reported an increase of CI from 41.8% of birch to 50.9% in carbohydrate pulp obtained by RCF (10 wt% RuN/ZnO/C, MeOH, 240 °C, 4 h).<sup>172</sup>



In the context of RCF (Pd/C, 250 °C, 3 h), both methanol and EG result in a comparable CI (63%), although EG facilitates more liberation of individual fiber cells.<sup>123</sup>

As lignin-first technologies have primarily centered on lignin valorization and its downstream applications, the structural characteristics of the pulp have received comparatively limited attention. While the effects of reaction parameters in organosolv processes have been extensively studied, the specific impact of the catalytic environment in RCF system remains less well understood. It is therefore recommended that future research systematically investigate the influence of catalytic environments on key structural properties of the pulp, such as DP, intrinsic viscosity, and crystallinity.

### 5.3 Morphological properties

The morphological properties of the pulp, including fiber surface structure, length, width, shape, and coarseness, play a critical role in determining its performance for paper applications. These properties directly impact the mechanical strength, flexibility, and bonding ability of the pulp fibers, which are essential for paper production, fiber reinforcement, and composite materials.<sup>173,174</sup> For example, longer fibers are known to enhance tensile strength and tear resistance, while finer fibers contribute to smoother surface finishes and better fiber bonding.<sup>175,176</sup> Traditional pulping techniques, widely used in industry, are effective at defibrillating wood, yielding long individual fibers that are ideal for paper production.

Emerging lignin-first technologies have demonstrated significant morphological changes in raw materials during processing.<sup>12,90,121,123,134</sup> The choice of solvent plays a critical role in both delignification and defibrillation. Schutyser *et al.* found that pulp produced from birch using RCF with methanol at 250 °C exhibited fiber aggregates with diameters of 100–200 μm and lengths around 1 mm. In contrast, RCF with EG produced fluffier, well-separated fibers with diameters of 10–20 μm while maintaining fiber length.<sup>123</sup> Similarly, Zhang *et al.* reported that adding EG to a DAF system facilitated defibrillation while preserving fiber length, resulting in fibers of 100–1000 μm, compared to 250–500 μm without EG.<sup>121</sup> This highlights the suitability of glycols like EG for defibrillation, making them promising solvents for paper applications and material upgrades.

Moreover, there is a correlation between hemicellulose removal and pulp fluffiness.<sup>123,134</sup> Low hemicellulose content leads to a more fibrous structure, as removing xylan fractions in the cellulose matrix allows for greater fiber separation. Ferrini *et al.* observed that organosolv pulp from poplar with lower hemicellulose content exhibited a more porous and fibrous surface compared to RCF pulp, which retained higher hemicellulose levels.<sup>134</sup> Additionally, temperature plays a role in pulp morphology: lower temperatures (160–180 °C) produce individual thin fibers and agglomerates of finer fibers, while higher temperatures (200–220 °C) result in thicker fibers with smoother surfaces.<sup>134</sup>

Traditional pulping techniques, such as kraft or sulfite processes, have been extensively optimized over decades to yield

fibers with properties finely tuned for paper manufacturing, including strength, flexibility, and durability.<sup>177–179</sup> In contrast, the fiber characteristics of lignin-first pulps remain underexplored and poorly understood, particularly in terms of their suitability for high-performance material applications.

To address this critical shortfall, future research must prioritize several key areas. First, a systematic investigation into how varying reaction parameters such as temperature, solvent composition, catalyst presence, and residence time influence pulp morphology is essential. Second, studies should move beyond laboratory-scale biomass to incorporate industrially relevant wood chip sizes, thereby enabling a more accurate assessment of fiber dimensions and their implications for papermaking potential. Third, the scope of fiber property evaluation must be broadened to include comprehensive mechanical and structural metrics, such as tensile strength, degree of fibrillation, fines content, coarseness, and bulk density, missing in today's research. Addressing these challenges is crucial for bridging the gap between lignin valorization and carbohydrate utilization, and for establishing a holistic understanding of lignin-first pulps.

## 6. Pulp applications

Pulp from conventional pulping is primarily used by the paper and packaging industry to make a variety of paper products, such as specialty papers, tissues, and boards. It is also used as dissolving pulp, which enables regenerated fibers (viscose, Lyocell) and derivatives (cellulose acetate; ethers such as CMC/HEC; and microcrystalline cellulose). By contrast, lignin-first technologies are still emerging and are being explored as pathways for the isolated carbohydrate, aiming to valorize lignocellulosic constituents beyond lignin. This section provides an overview of current and potential applications of pulp produced from lignin-first processing and outlines areas for further research.

### 6.1 Enzymatic hydrolysis and biochemical applications

The effective utilization of carbohydrates in pretreated lignocellulosic biomass for biochemical conversion hinges on their hydrolysis into fermentable sugar monomers. While bioethanol has traditionally been the most studied end product, a diverse range of alternative bio-based platform chemicals, such as lactic acid, succinic acid, and 1,4-butanediol can also be produced through microbial fermentation.<sup>180</sup> These compounds hold significant promise in supporting the global transition toward a more sustainable, circular bioeconomy. Although the scientific literature is rich with examples of such bioconversions, only a limited number have advanced to commercial scale. This underscores the ongoing challenge of achieving efficient and cost-effective carbohydrate conversion, which requires not only robust pretreatment and hydrolysis processes – enzymatic or chemical – but also the development and deployment of highly optimized microbial strains capable of high-yield fermentation under industrial conditions.<sup>181</sup>



Pretreatment of lignocellulose biomass is essential for enzymatic hydrolysis by disrupting its recalcitrance structure, creating low-crystalline regions and removal of lignin.<sup>182</sup>

The structural complexity of lignocellulose adds to this challenge. Cellulose is a  $\beta$ -1,4-linked glucose homopolymer with high crystallinity, while hemicellulose is a heterogeneous branched polymer of sugars like xylose, mannose, and glucose, along with various acidic groups and substitutions.<sup>183</sup> Hydrolyzing cellulose requires endoglucanases, exoglucanases, and  $\beta$ -glucosidases,<sup>184</sup> while hemicellulose breakdown necessitates a range of enzymes such as xylanases,  $\beta$ -xylosidases, and accessory enzymes (*e.g.*, arabinofuranosidase, acetyl xylan esterase) to remove side chains and breakdown of the backbone.<sup>185</sup> Advancements like lytic polysaccharide monoxygenase (LPMO), copper-containing enzymes catalyzing oxidative cleavage of glycosidic bonds, have further improved enzymatic hydrolysis and even reduced enzyme loading requirements.<sup>186</sup> In addition, non-catalytic proteins like swollenin and expansin increase enzyme-susceptible surface area and loosen fiber structure without breaking any bonds.<sup>187</sup> Commercial enzyme cocktails are formulated with carefully balanced ratios of various cellulolytic and hemicellulolytic enzymes, streamlining their application in biomass hydrolysis. Notable examples include Cellic® CTec2/3 from Novonosis, Allerase® Trio™ from DuPont Genencor, enzyme blends from DSM, and AlternaFuel® CMAX™ from Dyadic. While these advanced formulations have significantly improved the efficiency of lignocellulosic biomass conversion, enzyme requirements are not uniform. They vary depending not only on the type of feedstock but also on the specific biorefinery process employed, particularly due to the presence of inhibitory side-products and varying substrate compositions. As a result, enzyme cocktails often require customization or supplementation to achieve optimal hydrolytic performance across different processing conditions.<sup>188</sup>

Two important factors that should be maximized during pretreatment to improve enzymatic hydrolysis of pretreated biomass are disrupting native structures to lower crystallinity and lowering lignin content. Various studies have shown the benefit of lower crystallinity and increasing its susceptibility to enzymatic hydrolysis<sup>189</sup> which is a direct effect of the enzyme's accessibility to cellulose stands. Residual lignin poses a dual challenge to enzymatic hydrolysis by sterically hindering enzyme access and causing non-productive enzyme binding *via* hydrogen bonding, electrostatic, and hydrophobic interactions,<sup>190</sup> as extensively reviewed by Yuan and colleagues.<sup>191</sup> This is especially evident when comparing lignin-first technologies where the extracted lignin-monomers are stabilized (*e.g.*, through reductive hydrogenation during RCF) or not (*e.g.*, organosolv). During organosolv, recondensation of lignin on the pulp occurs and causes barriers, resulting in lower susceptibility to enzymatic hydrolysis.<sup>134</sup> Additives such as polyethylene glycol (PEG), Tween, and Triton-X can mitigate part of the enzyme-lignin interactions, enhancing enzyme availability and improving sugar yields.<sup>192</sup> Similarly, water-soluble lignin derivatives like lignosulfonate have shown additive-like benefits<sup>193</sup> but this effect remains dependent on the pretreat-

ment conditions and phenolic profiles, which can also introduce inhibitory effects,<sup>194</sup> making it a complex matter.

Table 2 shows enzymatic hydrolysis or fermentation yields of different lignin-first technologies, varying between 50 and 100% of the theoretical yields. A one-to-one comparison between studies to rank or find the optimal lignin-first technology is unfortunately not possible due to the varying process conditions used in the reported technologies. For instance, contact time, pH, temperature, additives (*e.g.*, alkaline or acid), water concentration and solvent type all have an effect on the efficiency of delignification and the resulting pulp composition, with direct consequences on enzymatic hydrolysis efficiency. The introduction of the severity factor offsets the use of extremes by trading off temperature against time with integration of pH to describe the overall delignification and hemicellulose loss.<sup>195</sup> Indeed, with altering processing conditions, near full hemicellulose removal can be achieved and is not taken into account when reporting the enzymatic hydrolysis of the remaining solid pulp after pretreatment (carbohydrate retention in Table 2 takes into account both cellulose and hemicellulose). Both delignification and carbohydrate retention must be balanced carefully to avoid negating the benefits of enhanced enzymatic hydrolysis. We recently highlighted this trade-off in a study on birch wood processed *via* RCF under different conditions with subsequent SHF. Although the lowest lignin-content pulp (7.2 wt%) achieved the highest ethanol titer, it only retained 48% of the initial carbohydrates. In contrast, a pulp with 19.4 wt% lignin content retained 79% carbohydrates and achieved the highest overall calculated ethanol yield, based on the initial carbohydrates in the biomass, but delivered a lower lignin oil yield.<sup>87</sup>

Next to the varying processing conditions, the solid and enzyme type/loading differ between studies, and both affect the efficiency of the reported enzymatic hydrolysis as well, making direct comparison even more cumbersome.

Solid loading describes the amount of solids used as a weight percent of the total volume in the reaction. Studies showing the valorization potential of the pulp obtained after various types of pretreatment often utilize low solid loadings ( $\leq 5$  wt%, Table 2), as it shows high conversion of holocellulose to monomeric sugars, Table 2. However, using higher solids loadings ( $> 15$  wt%) improves economics by resulting in higher sugar and product concentrations, smaller reaction sizes for equivalent output, and reducing downstream costs of water usage.<sup>196</sup> Often, high solid loading is a necessity. Bioethanol production, for example, has to achieve at least 4 wt% ethanol for the distillation process, by which ethanol is extracted from the fermentation broth post fermentation, to be economically feasible: distillation requires a tremendous amount of energy and is more cumbersome at lower ethanol concentrations.<sup>197</sup> To achieve these ethanol concentrations, a minimum amount of 8 wt% sugars is required (maximum theoretical ethanol yield is 0.51 g ethanol/g glucose/xylose) and typically translates into a lignocellulose loading for hydrolysis of  $> 20$  wt%.<sup>198</sup> However, the reduced amount of free water at high-solid conditions causes challenges like poor mixing,



Table 2 Enzymatic applications of lignin-first pulp

Substrate	Type of enzymatic application					Enzyme		Yield (%)		Ref.	
	Tech	Pulp yield (%)	Sugar retention (%)	Saccharification	Fermentation	Pulp loading (%)	Type	loading	Saccharification		Fermentation
Birch	RCF	65	78.6	—	SHF	15	Ctec2	18 FPU g <sup>-1</sup>	—	60	95
Poplar	RCF	66.2	73.7	×	—	1	CtecX	60 FPU g <sup>-1</sup>	95	—	124
Beechwood	AAF	—	88	×	—	8.3	Ctec2	30 FPU g <sup>-1</sup>	78	—	166
Poplar	RCF	52	67.6	×	—	1	Celluclast	350 U g <sup>-1</sup>	50	—	131
Poplar	RCF	55	71	×	—	1	Celluclast	350 U g <sup>-1</sup>	81	—	134
Poplar	DAF	44	NED	×	—	2	Ctec2	15 FPU g <sup>-1</sup>	85	—	125
Birch	RCF	56	88	×	SHF	10	Accelerase trio	10 FPU g <sup>-1</sup>	—	73	89
Poplar	RCF	NED	71	×	—	1.5	Ctec3	333 FPU g <sup>-1</sup>	92	—	88
Baggasse	DAF	54.9	73.7	×	—	2.6	Accelerase trio	20 FPU g <sup>-1</sup> glucan	90	—	121
Birch	RCF	83	94	—	SHF	10	Ctec2	35 FPU g <sup>-1</sup>	—	49	87
Birch	RCF	65	79	—	SHF	10	Ctec2	35 FPU g <sup>-1</sup>	—	75	87
Birch	RCF	35	48	—	SHF	10	Ctec2	35 FPU g <sup>-1</sup>	—	90	87
Apple Wood	RCF	—	NED	×	—	2	Ctec2	15 FPU g <sup>-1</sup>	75	—	90
Birch	RCF	39.1	NED	×	—	2.5	Cellulase	33,33 FPU g <sup>-1</sup>	104	—	210
Moso Bamboo	RCF	61.8	87.3	×	—	5	Ctec2	15 FPU g <sup>-1</sup>	64.9	—	139
Poplar	RCF	88.7	60.4	—	SHF	5	Ctec3	100 FPU g <sup>-1</sup>	—	95	96
Poplar	RCF	81.9	65.6	—	SHF	5	Ctec3	100 FPU g <sup>-1</sup>	—	73	96
Poplar	RCF	85.6	67.1	—	SHF	5	Ctec3	100 FPU g <sup>-1</sup>	—	71	96

NED – not enough data.

improper mixing, lower heat/mass transfer and increased viscosity, all of which reduce hydrolysis efficiency.<sup>199</sup> Examples to overcome these limitations are alternative feeding strategies<sup>200</sup> and reactor designs.<sup>201</sup>

Enzyme dosage – commonly expressed in Filter Paper Units per gram of biomass (FPU g<sup>-1</sup>) or as total protein per gram – plays a critical role in determining the efficiency of enzymatic hydrolysis, yet it remains one of the most significant cost factors in biomass processing. It is important to note that the FPU is an arbitrary and somewhat outdated metric. Originally defined in 1987,<sup>202</sup> it measures the amount of enzyme protein required to solubilize 4% of a 50 mg strip of Whatman No. 1 filter paper within one hour. Despite its continued use in scientific literature, this metric fails to account for the activity of essential auxiliary enzymes and hemicellulases, which also contribute substantially to biomass deconstruction. As such, relying solely on FPU can provide an incomplete and potentially misleading assessment of enzyme performance in complex lignocellulosic systems.

Dosages typically range between 10 to 60 FPU g<sup>-1</sup> biomass, with higher efficiencies often requiring prolonged hydrolysis time at low enzyme dosages.<sup>203</sup> On-site enzyme production can severely lower the cost,<sup>204</sup> yet still remains expensive, ranging from \$ 4.24<sup>205</sup> to \$ 56.78 per kg protein<sup>206</sup> depending on the assumptions and constraints used within the model. The relative cost of the enzyme can also be expressed per kg of ethanol produced and has been shown to differ immensely in different publications, ranging from \$ 0.07 to \$ 0.194, depending on different factors within configurations and between models<sup>207</sup> while others claim that these are still underrepresented with reported values up to \$ 0.492.<sup>208</sup> Various integration methodologies are possible that link saccharification and fermentation together, each with its (dis)advantages, with SHF being the most commonly reported.<sup>209</sup>

## 6.2 Chemical applications

The chemical conversion of carbohydrates refers to the transformation of carbohydrate molecules, such as monosaccharides, disaccharides, and polysaccharides, into valuable chemicals, fuels, and materials through a variety of chemical reactions. Carbohydrate pulp can be converted into a variety of platform chemicals such as xylitol, sorbitol, furfural, HMF, and levulinic acid, through catalytic or non-catalytic methods.<sup>211,212</sup> These intermediates find applications in diverse industries, such as biofuels, petrochemicals, textiles, cosmetics, and pharmaceuticals.<sup>213,214</sup> For instance, HMF can serve as a precursor to a variety of high-value products, including 2,5-bis(hydroxymethyl)furan, used in polyurethane synthesis, and 2,5-dimethylfuran, which is under investigation as a fuel blend component and high-performance solvent.<sup>215,216</sup>

Recent studies have expanded the use of pulp beyond enzymatic hydrolysis, focusing on its chemical conversion into valuable products. For example, using EG as a solvent in RCF yields pulp with lower crystallinity and enhanced reactivity for catalytic conversion.<sup>123</sup> This RCF-derived pulp can be transformed into EG with a 26 wt% yield.<sup>123</sup> Lie *et al.* proposed a



one-pot catalytic process in dimethyl carbonate (DMC) for the depolymerization of RCF-derived pulp, leading to the production of furfural (FF), HMF, and 5-methoxymethylfurfural (MMF), with yields of 47.7% for FF and MMF.<sup>93</sup> In this process, cellulose is first depolymerized into glucose, followed by isomerization to fructose and subsequent dehydration to HMF. Under acidic conditions in DMC, methanol is generated, which reacts with HMF to produce its etherified derivative, MMF. A decrease in yield is attributed to sugar degradation into humins during the reaction. The structure of the humin was not investigated.

In addition to platform molecules and glycols, the chemo-catalytic conversion of carbohydrates can also yield alkanes. Over the past few decades, numerous strategies have been developed to enable this transformation, most of which use biphasic catalytic systems to address the complexity of the sequential reaction steps involved.<sup>91,217–225</sup> A notable example is the conversion of cellulose to naphtha, a mixture of C5–C6 alkanes, using  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and Ru/C in an *n*-decane/water biphasic system, achieving yields up to 82% within just 6 h.<sup>219</sup> This process involves cellulose hydrolysis, glucose dehydration, and subsequent hydrodeoxygenation *via* HMF, while effectively bypassing stable intermediates such as isosorbide. The biphasic system plays a dual role: it physically separates the acid and metal catalysts to suppress glucose hydrogenation to sorbitol, an isosorbide precursor, and it extracts reactive intermediates like HMF from the acidic aqueous phase, thereby minimizing humin formation.<sup>219</sup> More recently, an integrated wood-to-naphtha process has been demonstrated, combining lignocellulose fractionation with carbohydrate-derived alkane synthesis. RCF was used to selectively solubilize lignin, yielding a carbohydrate-rich pulp that was subsequently converted to naphtha using an optimized biphasic catalytic system, achieving yields comparable to those obtained from pure cellulose.<sup>92</sup> The resulting naphtha-range alkanes are suitable as drop-in fuels or as feedstock for steam crackers, enabling the production of ethylene and propylene for further upgrading into polymers and other value-added chemicals.<sup>91</sup>

One significant challenge in the chemical conversion of carbohydrates is sugar degradation, which results from sugar instability and leads to unwanted byproducts, reducing overall yields. The use of protection group chemistry during biomass depolymerization has been shown to stabilize carbohydrates, preventing dehydration and degradation.<sup>165</sup> For instance, Questell-Santiago *et al.* demonstrated that formaldehyde in AAF pretreatment stabilizes xylose as diformylxylose during biomass pretreatment, and glucose as diformylglucose during cellulose depolymerization.<sup>165</sup> This stabilization strategy enhanced carbohydrate yields by threefold compared to reactions without formaldehyde. The diformylxylose formed can operate as a sustainable apolar aprotic solvent with performance comparable to DMSO and DMF in alkylation and hydrogenation.<sup>226,227</sup>

### 6.3 Potential applications

The potential applications of pulp derived from lignin-first technologies are gaining increasing attention as industries

shift toward more sustainable solutions. As discussed above, lignin-first pulp has mainly been utilized as a raw material for enzymatic hydrolysis and chemical conversion. However, its potential as a fiber-based material remains limited, presenting an opportunity to develop new application directions with significant market potential.

In recent estimates, the global pulp and paper market was valued at approximately 379 billion USD in 2024, with an anticipation to grow up to 551 billion USD by 2034.<sup>228</sup> Notably, pulp from lignin-first biorefineries remains underexplored as a raw material for paper manufacturing, which presents an opportunity for a profitable new application. RCF may represent a promising pathway to paper-pulp production, especially when conducted in alkaline environments. Generally, RCF achieves high delignification, yielding pulp with low lignin content suitable for mild bleaching, yet sufficient defibrillation should be achieved to ensure the generation of suitable fibers. Additionally, the RCF process using EG can fragment fiber aggregates without damaging individual fibers, thereby preserving fiber length, which is a critical property in papermaking.<sup>123</sup> The fiber length correlates directly with tensile strength, the most important mechanical property in paper production.

Most previous studies have focused on lignocellulosic sawdust. While the usage of wood beyond sawdust has been explored in RCF system,<sup>131,134,229</sup> the understanding of the effect of wood size on pulp properties remains relatively limited, this is particularly the case for fiber and mechanical characteristics required for high-quality paper products. This understanding is essential for considering RCF as a viable method for large-scale fiber applications.

Dissolving pulp holds significant promise for various applications, particularly in the production of regenerated cellulose fibers like viscose and lyocell. These fibers are gaining popularity in the textile industry as eco-friendly alternatives to synthetic fibers, offering a more sustainable solution without compromising on quality or performance.<sup>230</sup> Global production of dissolving pulp was estimated at approximately 10.5 million metric tons in 2020, with the potential to reach 217 million metric tons by 2050.<sup>231,232</sup>

Organosolv fractionation under acidic conditions shares mechanistic features with sulfite pulping, particularly in the acid-catalyzed hydrolysis of hemicelluloses.<sup>233</sup> As a result, organosolv pulps often resemble sulfite pulps more than kraft pulps, not only in terms of cellulose purity<sup>233</sup> but also in mechanical properties.<sup>234</sup> In this context, RCF systems operating under acidic conditions have indeed been reported to yield pulps with characteristics approaching those of dissolving-grade cellulose, such as reduced hemicellulose content and lower lignin residues.<sup>122,169</sup> For example, a study by Witthayolankowit *et al.* demonstrated the viability of producing dissolving pulp with desirable properties, including controlled lignin and hemicellulose content, as well as optimal viscosity, from spruce wood. This was achieved using RCF system that employed an ethanol–water solvent mixture (65 : 35%v/v), HCl, and Pd/C catalysts at 200 °C, showcasing the potential of this



approach for efficient dissolving pulp production.<sup>169</sup> Another study emphasized that RCF notably reduces water consumption when compared to cotton production, while also lowering both global warming potential and cumulative energy demand in relation to traditional viscose production methods.<sup>122</sup>

A critical challenge in the development of RCF-derived pulps, particularly for dissolving pulp applications, is the potential transfer of metals from heterogeneous catalysts to the pulp, which can influence both product purity and process economics. Various strategies have been investigated to limit catalyst contamination, including solvent-based recovery of Ru/C and Pd/C catalysts,<sup>126,128</sup> magnetic separation of RANEY® Ni,<sup>131</sup> the use of catalyst pellets placed in physically separated baskets,<sup>89</sup> and the design of magnetically recoverable catalyst supports.<sup>235</sup> These approaches highlight ongoing efforts to improve catalyst handling and recycling while maintaining effective lignin depolymerization. Nevertheless, experimental studies indicate that metal leaching, catalyst attrition, or partial loss may still occur under certain operating conditions, even in systems designed to minimize direct catalyst-fiber contact.<sup>235,236</sup> For high-purity applications such as dissolving pulp, where strict specifications apply, systematic assessment of metal leaching, catalyst recovery efficiency, and reactor configuration becomes particularly important.

The production cost of fiber applications within lignin-first biorefineries is an important consideration for assessing industrial relevance. Several techno-economic analyses (TEA) of RCF have been reported,<sup>103,237,238</sup> primarily focusing on process scale-up and the minimum selling price of lignin oil, and consistently identifying capital expenditure (CAPEX) as the dominant cost contributor, largely due to the high-pressure reactor. These costs can be reduced through shorter residence times, lower reaction temperatures, and solvent recycling.<sup>103</sup> Reported minimum selling prices for RCF-derived lignin oil range from approximately 1500 to 2870 € per ton,<sup>103,238</sup> while the carbohydrate pulp stream – typically evaluated for enzymatic saccharification for bioethanol production – was kept at 400 € per ton in these calculations, for typical wood feedstock prices around 150–200 € per ton.<sup>95</sup> In comparison, conventional kraft pulp prices in Europe range from about 800 to 1200 € per ton,<sup>239</sup> whereas technical kraft lignin is commonly valued at 220–430 € per ton.<sup>240</sup> To date, there are quite a few techno-economical studies on RCF,<sup>103,241,242</sup> but no dedicated TEA has evaluated for fiber applications from RCF; however, the substantially higher value of RCF lignin oil relative to technical lignin suggests that lignin valorization may partially offset the higher processing costs, emphasizing the importance of integrated biorefinery economics rather than pulp production alone.

Future research should further explore how RCF systems can be tuned toward specific fiber applications, such as packaging and papermaking, while also assessing the overall economic viability of the process when lignin oil valorization is integrated. In addition, building on existing studies on dissolving pulp production, more attention should be given to catalyst contamination and metal leaching into the pulp, as these

factors are critical for high-purity cellulose applications. Furthermore, integrating lignin oil valorization alongside RCF pulp production presents a compelling opportunity to boost the overall sustainability of the process, maximizing the value of all biomass components and contributing to a more circular and eco-friendly biorefining approach.

## 7. Conclusion and perspectives

This review comprehensively discusses lignin-first ligno-cellulose biorefinery technologies from pulp perspectives, providing a definition of lignin-first concept and highlighting the different technologies involved with a focus on RCF. It explores pulp properties, such as chemical, structural, and morphological properties, demonstrating their influence in different applications. Unlike lignin, pulp derived from lignin-first processes remains underexplored and underutilized across all fields. To address this, we have provided an overview of its current applications and potential opportunities.

Lignin-first technology represents an innovative approach to biorefineries, aiming to maximize the utilization of raw material components and contribute significantly to a circular bioeconomy. The literature introduces various lignin-first strategies that differ in their stabilizing mechanisms, with RCF being the most extensively studied. RCF employs metal catalysts in a reductive environment to stabilize lignin derivatives, producing pulp with high yields, high carbohydrate retention, and low lignin content. These favorable chemical properties make the pulp suitable for a variety of applications, like biofuel and chemicals. Additionally, changes in structural properties, such as degree of polymerization, viscosity, and crystallinity, have been observed. Morphological properties are also promising, especially when specific solvents like glycol are used during RCF, as they preserve fiber integrity during fractionation. This property is highly important for the paper industry, which creates an opportunity for a profitable application. Currently, the applications of lignin-first driven pulp are still limited to enzymatic hydrolysis, biofuel, and chemical conversions. Since the demand for sustainable materials keeps growing, research and development for lignin-first biorefineries will be necessary to enable the full potential of these renewable resources.

Future research should consider the following gaps and opportunities:

(i) While substantial insights into pulp chemistry and structure have been established through organosolv and lignin-first studies, a unified and systematic understanding of how reaction parameters such as temperature, solvent system, catalyst type, and reaction time collectively influence the chemical functionality and structural features of lignin-first pulps remains limited. In particular, differences in how these parameters affect functional group distribution, carbohydrate accessibility, and pulp reactivity across distinct lignin-first technologies are not yet consistently evaluated under comparable frameworks. This lack of clarity limits our ability to tailor



pulps for specific downstream applications, particularly where chemical reactivity and surface functionality are critical. Advanced analytical techniques such as Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, when applied in a systematic and comparative manner across different lignin-first processes, have the potential to shed light on these chemical nuances. Such studies would not only deepen our fundamental knowledge but also enable the rational design and optimization of pulps with targeted properties for high-value applications.

(ii) Although the effects of individual reaction parameters on pulp quality have been extensively studied, the complex, synergistic interactions between multiple variables remain largely unexplored. These interdependencies can significantly influence key pulp characteristics, such as fiber morphology, chemical composition, and mechanical performance, yet they are often overlooked in single-variable studies. To address this, the development of robust mathematical models using advanced Design of Experiments (DoE) methodologies is essential. DoE enables systematic exploration of multivariable relationships, providing deeper insights into how combined reaction conditions, such as temperature, pressure, solvent composition, and catalyst type, collectively shape pulp properties. In addition, introducing a severity factor for lignin-first with considering solvent and catalyst effect, can assist in comparing different process conditions and predicting outputs. In parallel, the integration of AI and ML tools offers powerful new avenues for predictive modeling and process optimization. By training algorithms on large, multidimensional experimental datasets, ML can uncover hidden patterns and nonlinear correlations that traditional statistical methods may miss. These data-driven approaches can accelerate the identification of optimal process conditions for producing pulp tailored to specific applications, such as high-strength fibers, dissolving pulp, or bio-based composites. Together, DoE and AI-driven modeling form a complementary toolkit that will be instrumental in advancing lignin-first technologies toward greater efficiency, scalability, and product versatility.

(iii) Although lignin-first fractionation has already been demonstrated on larger wood sizes, more systematic optimization is still required to ensure efficient and uniform delignification under industrially relevant conditions. Optimizing lignin-first systems for larger biomass particles would open the door for more advanced and realistic investigations into critical fiber properties. These include tensile index, degree of fibrillation, fiber length and width, fines content, and coarseness, all of which play a pivotal role in determining the mechanical performance and suitability of the pulp for high-value material applications such as paper, textiles, and bio-composites. Understanding how these properties are influenced by process conditions at scale is key to tailoring pulps for specific end uses.

(iv) The unique properties of pulp derived from RCF present a compelling opportunity for its integration into a wide range of material applications, particularly in papermaking and the production of regenerated cellulose fibers such as viscose and lyocell. RCF pulp typically exhibits favorable

characteristics, such as high cellulose purity, tailored fiber morphology, and adjustable crystallinity, which are critical for achieving the performance standards required in these industries. These qualities not only make RCF pulp a technically viable substitute for conventionally produced pulps but also position it as a sustainable alternative aligned with the increasing demand for environmentally responsible materials.

Moreover, the dual benefit of RCF, simultaneously valorizing both lignin and carbohydrates, enhances the overall economic viability of the process, contributing to a more circular and resource-efficient biorefinery model. By leveraging both the structural integrity of cellulose fibers and the potential for lignin-derived chemicals, RCF offers an integrated approach to biomass utilization that reduces waste and maximizes value. As such, advancing RCF pulp for applications in fiber-based materials could play a pivotal role in reducing reliance on fossil-based resources and supporting the global shift toward sustainable, bio-based manufacturing.

Ongoing research efforts, coupled with strong collaboration between academia and industry, will be critical to realizing the full potential of RCF-derived materials and facilitating their successful integration into mainstream commercial markets. This partnership is key to overcoming technical barriers, scaling up processes, and aligning product performance with industrial requirements.

## Author contributions

Khaled W. Al-Shwafy: writing – original draft, visualization, methodology, investigation, formal analysis, data curation. Thomas Nicolaï & Hannes Latine: writing – review & editing, validation. Duarte M. Neiva: writing – review & editing, visualization. Elien Lemmens & Nikolaus Schwaiger: editing, supervision, project administration, funding acquisition, conceptualization. Bert F. Sels: review & editing, supervision, project administration, funding acquisition, conceptualization, corresponding author.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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