

The role of pretreatment in the catalytic valorization of cellulose

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ABSTRACT

The use of fossil resources with the concerning climate change has pushed the development of alternative and sustainable feedstocks for energy, chemicals, and materials production. Lignocellulose is one of the most abundant and promising renewable carbon sources for the transition of a petroleum-based to a bio-based economy. Unlike liquid petroleum oil, the inherent complex polymer structure of the solid lignocellulose makes it recalcitrant for (selective) valorization. Hence, physical and/or chemical pretreatments are usually required to improve the reactivity and/or purity of the feedstock. Promising biorefinery concepts should be able to utilize all components of the lignocellulose. Since cellulose is the most abundant fraction in lignocellulose, this review emphasizes the progress and importance of pretreatment in the conversion of cellulose pulp into chemicals and fuels. The structural and chemical features such as crystallinity, particle size, porosity, and degree of polymerization that influence the reactivity of cellulose are overviewed whenever possible for different reaction types. The advantage and disadvantage of the different approaches for their determination are discussed in detail. The benefits of different pretreatments in bio-chemical and more particularly in chemo-catalytic conversion of cellulose are overviewed. Finally, the future and perspective of (ligno)cellulose pretreatment with regard to cellulose utilization are discussed.

1. Introduction

The utilization of fossil oil for energy and chemicals production is steadily growing as the result of increasing population and industrialization. This causes environmental concerns related to global warming and the depletion of the non-renewable fossil feedstock. Therefore, alternative sources should be identified and used to replace or at least complement fossil oil usage to mitigate greenhouse gas emission. In terms of production of organic chemicals and fuels, biomass represents a promising renewable carbon feedstock because of its abundance in nature and the beneficial presence of functional groups [1–39]. Biofuels such as bioethanol and biodiesel, produced from sugars, starch, and oil from food crops, are well established, but unfortunately, they conflict with the nutritional needs of a growing world population. Therefore, a new generation of biofuels and bio-based chemicals, derived from non-edible plants rich in lignocellulose, offers a preferred alternative. Moreover, integration of biomass conversion in a 'bio' refinery increases the profitability since a wide range of high-valuable chemicals for the pharmaceutical, food and chemical industry can additionally be produced from the lignocellulosic feedstock [2].

Total biomass valorization routes without any pretreatment or separation generally yield complex product mixtures due to the inherent heterogeneity of lignocellulose. For example, bio-oils obtained from pyrolysis without pretreatment consist of a variety of different products including phenolics and sugar degradation products like glyceraldehyde, furfural, and levoglucosan [40]. Upgrading of these complex product mixtures through different approaches such as HDO can yield bio-based fuels and high added value chemicals [41–43]. However, conversion of them faces some challenges due to different thermal stabilities and chemical properties of the different components obtained from biomass pyrolysis. In terms of the conversion towards chemicals with high purity, the necessary purification can not be reached without large separation costs. Therefore, the lignocellulosic biomass is preferably pretreated and fractionated into its main constituents, *viz* cellulose, hemicellulose, and lignin, to reduce the heterogeneity, prior to its conversion. Subsequently, the individual fractions can be selectively converted into a limited set of value-added end-products through biological, chemical, and/or thermal (e.g. pyrolysis) approaches [2].

Hydrolysis of (hemi)cellulose in water constitutes the most commonly used entry point into biorefinery schemes [44], while alcoholysis

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of (hemi)cellulose in alcohols such as methanol and ethanol also shows promising progress in recent year [45]. Pretreatment of lignocellulosic feedstock, whether it proceeds through a physical or chemical method or a combination of the two, appears to improve the reactivity (such as hydrolyzability) of cellulose through changes in, amongst others, cellulose purity, e.g. by removal of e.g. hemicelluloses, lignin and inorganics, particle size, accessible surface area, crystallinity and degree of polymerization [44,46–64]. Therefore, pretreatment is extremely important to promote fast cellulose depolymerization and reduce its structural recalcitrance, in particular when enzymes or solid acids are used as catalysts to enable the hydrolysis. Decades of research has shown and highlighted the pivotal role of lignocellulose pretreatment for an efficient enzymatic depolymerization of cellulose towards glucose, an important platform molecule in biorefinery schemes, but the importance of pretreatment for the chemo-catalytic conversion of cellulose (in water, alcohol, or biphasic solvent) is still scarcely reported, despite some promising advances in the last years.

Hence, this comprehensive review will discuss the impact of several key physicochemical features and pretreatments of (ligno)cellulosic biomass and their importance for chemo-catalytic cellulose valorization processes. The effect of pretreatment on enzymatic cellulose conversion will be briefly discussed as a reference case, while examples of chemo-catalysis will be reviewed in more details. The reader is referred elsewhere for the impact of pretreatment on the bioconversion of cellulose [53–57,59,64,65]. Unconventional pretreatment methods like the usage of plasma, ultrasound, or microwaves are only briefly introduced in this review, and if interested, the reader may consult the recent review works [66–68]. Conversion of isolated lignin and the impact of pretreatment on the physicochemical properties of lignin are also not the subject of this review and the reader is referred elsewhere for this topic [69,70]. Recently developed ‘*lignin first*’ biorefinery approaches are briefly introduced as they work directly on lignocellulose and show excellent results [71]. If appropriate, the consequence of the various treatments are described in terms of the physicochemical changes of cellulose, which are at the origin of its improved reactivity. Note that in contrast to the abundant literatures on the impact of pretreatment on bio-chemical lignocellulose conversion, there are only a few systematic studies concentrating on the impact of pretreatment on chemo-catalytic lignocellulosic conversion. As research on chemo-catalytic lignocellulosic conversion is still in its infancy, many reports dealing with pretreatment issues will be expected in the near future. Hopefully, the reader, for its own creations will be inspired by this review.

2. Lignocellulose

Lignocellulose is a fibrous material that can be found in cell walls of plants such as grasses, trees, and energy crops. It consists of cellulose (25–55 %), hemicellulose (24–50 %), lignin (10–35 %), and minor constituents like acetyl group, pectins, proteins, terpenes, fats, waxes, tannins, and inorganic matter [17,55,72]. Their distributions, which is not uniform in the plant, strongly depend on the plant species, tissues, and maturity of the cell walls. Cellulose is encapsulated in an amorphous, cross-linked hemicellulose/pectin matrix in primary cell walls and a hemicellulose/lignin matrix in secondary cell walls (Fig. 1) [73]. This structural arrangement gives plants their strength and rigidity, and it makes cellulose highly resistant to biological and chemical attack. Remind that cellulose in nature has evolved into a rigid structural function, while it is not meant to be utilized for energy and synthetic purposes.

2.1. Cellulose

Cellulose is a linear polysaccharide of β -1,4 linked glucose units, arranged in cellobiose subunits, and has a reducing and non-reducing end (Fig. 2) [74]. Cellulose polymers generally contain more than 10000 anhydroglucose units, but this is strongly dependent on plant

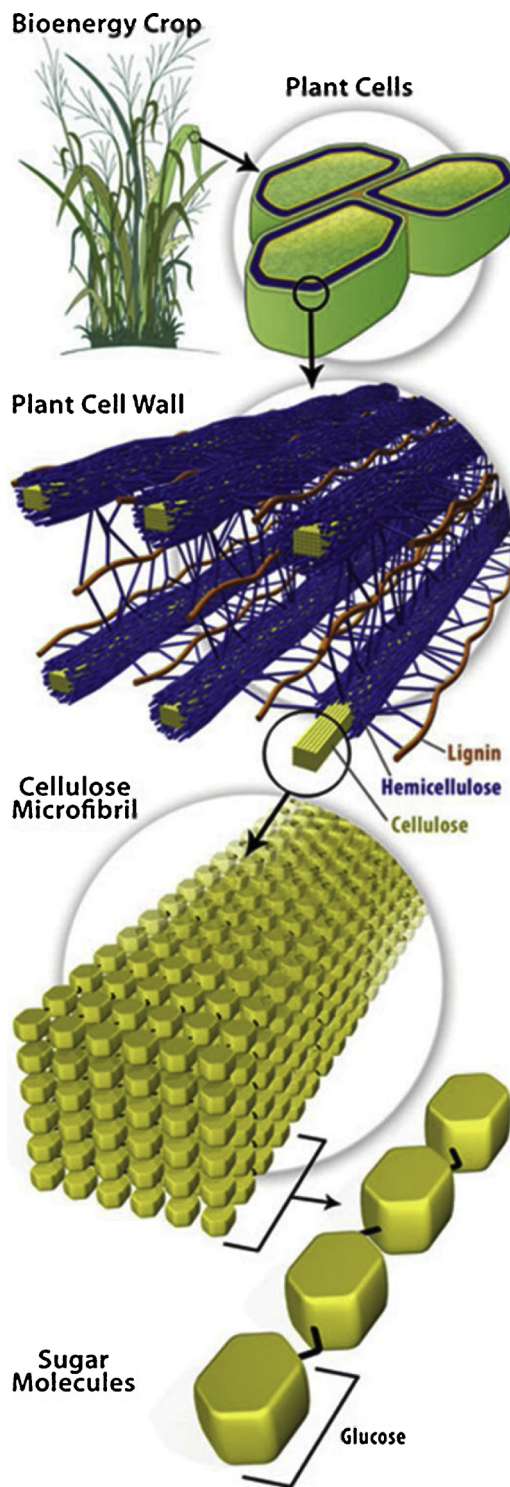


Fig. 1. General structure of lignocellulose in plant cell walls. Based on Ritter [83].

species [75]. These polymers are stacked together in microfibrils consisting of crystalline areas embedded in paracrystalline/amorphous areas [76]. These crystalline regions consist of planar sheets of hydrogen-bonded cellulose chains (Fig. 2), stacked on top of each other by hydrophobic or van der Waals forces and weak C–H \cdots O hydrogen bonds (Fig. 1) [77–80]. Chemical and thermal treatment of native cellulose (cellulose I) can lead to the formation of other cellulose polymorphs (cellulose II, III, and IV), with different crystal unit cells [81,82].

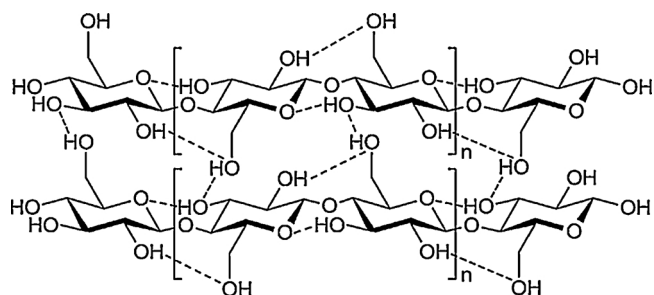


Fig. 2. Molecular structure of cellulose. Adapted from Kobayashi et al. [84].

2.2. Hemicellulose

Unlike cellulose, hemicellulose represents a more heterogeneous group of branched polysaccharides composed of ether-linked pentoses (xylose, arabinose), hexoses (glucose, mannose, galactose, fucose, rhamnose), sugar acids ((4-*O*-methyl-)glucuronic acid), and ester-linked acetyl and feruloyl groups [85]. The structure of hemicellulose varies between different plant species and tissue types. Dicot hemicellulose, for example, contains mostly glucuronoxylan in its secondary cell walls, while conifer hemicellulose mostly exists of galactoglucomannan and glucuronoarabinoxylan, and grass hemicellulose mostly contains glucuronoarabinoxylan [85]. Hemicellulose is not crystalline due to its branched structure and has a lower degree of polymerization than cellulose (mostly about 200) [72,86]. Hemicellulose is associated with cellulose *via* hydrogen bonds and to lignin *via* covalent bonds in lignin-carbohydrate complexes (LCC) [87,88]. Together with cellulose, hemicellulose constitutes the 'holocellulose' fraction of lignocellulosic biomass [89].

2.3. Lignin

Lignin is an amorphous, polyphenolic heterogeneous polymer consisting of multiple C–O or C–C bond-linked *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, assembled from phenylpropane building blocks *p*-coumaryl, coniferyl, and sinapyl alcohol, respectively [87,90]. The relative ratios of these units are dependent on the plant species and tissue. Generally, softwood lignin such as pine or spruce, exclusively contains guaiacyl units (G lignin), while hardwood lignin such as birch and eucalyptus consists of both guaiacyl and syringyl units (G and S lignin) [90]. All three phenylpropanoid units (H, G, and S lignin) are existing in grass. Lignin provides structural rigidity, impermeability and protection against microbial attack and oxidative stress [53]. Delignification without significant cellulose degradation is, therefore, key to an efficient and selective subsequent enhancement of the cellulose reactivity.

3. Impact of (ligno)cellulose properties on cellulose conversion

Depolymerization of cellulose *via* hydrolysis in water is usually the essential step of both chemical and biological valorization process. Conversion in protic solvents like methanol and ethanol, aprotic solvents such as tetrahydrofuran, and water/organic solvent are also studied [45,91–93]. Irrespective of the solvent used, the reactivity of cellulose primarily depends on its (ether bond) accessibility and purity (Fig. 3).

3.1. Cellulose accessibility

The accessibility of cellulose determines the efficiency of cellulose-catalyst interactions and can be divided into two main categories: *i*) macro-accessibility and *ii*) micro-accessibility [94]. Macro-accessibility refers to the outer surface accessibility of cellulose, while micro-accessibility refers more to the accessibility of enzyme-binding sites and

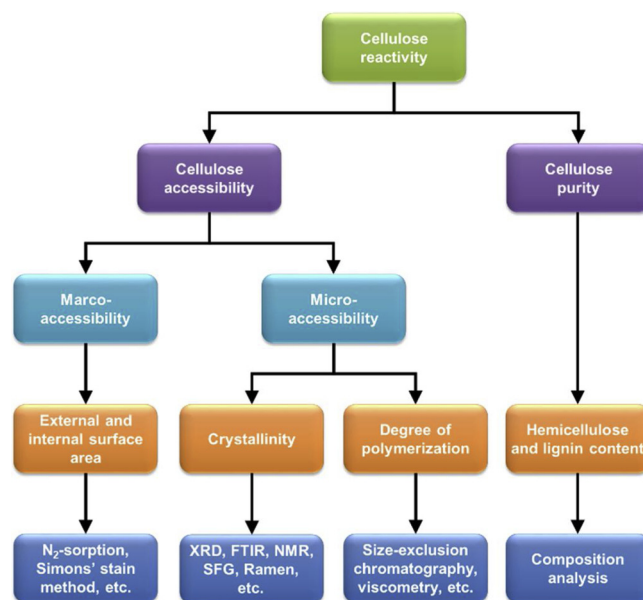


Fig. 3. Factors determine the cellulose reactivity.

β -1,4 glycosidic bonds enclosed within cellulose. Properties influencing the macro-accessibility of cellulose include particle size, porosity, wettability, and hemicellulose/lignin content, while properties determining the micro-accessibility of cellulose include crystallinity and degree of polymerization.

3.1.1. Macro-accessibility

In (ligno)cellulosic biomass, both external and internal (pore) surface areas contribute to the total specific surface area (SSA), commonly expressed in m^2/g . The external SSA depends on particle size, shape, and surface texture. Small particles generally exhibit higher external SSA than larger particles, and consequently, they have larger catalyst interaction surfaces. Catalyst, solvent, and heat are furthermore expected to penetrate more easily to the center of smaller particles. Microcrystalline cellulose powders with well-defined μm -scale particle sizes, like Avicel® PH-101 ($\sim 50 \mu\text{m}$), are commercially available. The particle size distribution (PSD) of biomass samples can be measured through several analysis techniques such as sieving, digital imaging (e.g. scanning electron microscopy), or light scattering (e.g. laser diffraction) [95,96]. With these simple techniques, particle sizes are commonly evaluated in only one dimension (d_p), assuming spherical particles [97]. Since the morphology of biomass particles is generally irregular, fibrous, and non-spherical, particle shapes should be taken into account.

A reduction in particle size and concomitant increase in SSA can be achieved using a physical pretreatment such as milling or ultrasound (*vide infra*) and may be accompanied by an improved micro-accessibility through a reduction in crystallinity and/or degree of polymerization. These physical pretreatments can be carried out to render biomass samples more accessible to catalysts or a second pretreatment. Several authors have reported that particle size may even be the determining factor in cellulose hydrolysis efficiency, instead of crystallinity [61,98]. As internal pore volumes may be significant, total SSAs are generally larger than those simply deduced from the particle size. Porosities up to 82 % are reported for microcrystalline cellulose powders [99]. Importantly, pore sizes must be large enough to accommodate enzymes (and other catalysts) for porosity to have an impact on cellulose accessibility and conversion [47,62,63]. While drying lignocellulosic biomass may lead to irreversible pore shrinkage or collapse, swelling with water and polar (protic and non-protic) solvents can significantly increase the internal surface area [54,100]. An

increase in biomass porosity can be achieved using other (physico) chemical pretreatments such as steam explosion, dilute acid, or ammonia fiber expansion (*vide infra*).

Techniques commonly used to determine the accessibility/porosity of (ligno)cellulosic biomass samples include electron microscopy, Simons' stain method, solute exclusion, gas adsorption (e.g. N₂ adsorption), mercury porosimetry, and NMR cryoporometry, relaxometry, and diffusometry [101]. The SSA of microcrystalline cellulose powders has been measured using physical adsorption of N₂ at low temperatures (BET method): SSA values around 1 m²/g are commonly reported [102,103]. Although N₂ physisorption is a robust method for SSA determination, it requires a prior drying of samples (e.g. 105 °C) which might lead to pore collapse and unreliable pore volume determinations. Furthermore, certain areas may be accessible to N₂ but not to catalysts, leading to an overestimation of cellulose accessibility. On the other hand, Simons' stain can be used in the wet state to selectively probe accessible cellulose surfaces [101,104,105]. It consists of direct blue (DB) and direct orange (DO) dyes with different molecular diameters of 1 nm and 5–36 nm, respectively, to selectively probe pores with sizes smaller (DB) or larger (DO) than 1 nm. The ratio of direct orange to direct blue reflects the amount of large to small pores and correlates to cellulose accessibility [105]. Nevertheless, Meng et al. recommend the use of a combination of several analysis methods based on different principles of measurement as the best approach for a complete assessment of biomass accessibility [101]. Various pretreatments have been reported to significantly improve the accessibility of lignocellulosic biomass. For example, Wiman et al. were able to increase the N₂/BET surface area of spruce from 0.4 to 8.2 m²/g through steam pretreatment [106].

The macro-accessibility is influenced by the wettability of the (ligno)cellulosic biomass as well. A thorough fluid impregnation of biomass can increase its accessibility to catalysts, and this fluid impregnation can be improved using microemulsions to overcome the complex capillary structure [107]. Microemulsions are emulsions with unique properties like optical clarity, very low interfacial tension, and the ability to solubilize both polar and non-polar compounds [108,109]. They can ensure a thorough solvent impregnation of even the more constrained spaces of the cell wall, significantly improving biomass accessibility.

The macro-accessibility of cellulose is significantly reduced by the presence of a protective hemicellulose and lignin matrix. This protective matrix also impedes the swelling of cellulose fibers [54]. Although research efforts mostly targeted the influence of this protective matrix on enzyme reactivity [50], there are emerging reports of chemo-catalysts being hindered by lignin as well. Conversion of lignocellulosic biomass to ethylene glycol in the presence of Ni-W₂C/AC was reported to be negatively correlated to the amount of lignin present [32,110–112]. Mineral acids penetrate more easily into the lignocellulosic structure and are therefore used historically for direct biomass saccharification [44]. Various pretreatments like alkaline, organosolv, and ionic liquid pretreatments (*vide infra*) have been reported to remove a large portion of the protective matrix.

3.1.2. Micro-accessibility

3.1.2.1. Crystallinity. In cellulose crystallites, cellulose polymers are firmly held together through intermolecular hydrogen bonds and van der Waals or hydrophobic interactions. This structural arrangement reduces the accessibility and reactivity of the cellulose polymers [75]. This is in sharp contrast to amorphous cellulose, which is more prone to hydrolysis. Mild acid-catalyzed hydrolysis of amorphous regions in cellulose fibers is used to produce microcrystalline cellulose (MCC) for commercial applications (e.g. Avicel®) [113]. However, classifying cellulose as either in crystalline or amorphous phase is an oversimplification, since medium-ordered paracrystalline layers also exist on the outer surface of cellulose crystallites [114,115]. Loelovitch et al. compared the accessibility of various cellulose samples at

deuteration with their average content of amorphous domains and demonstrated that the accessibility was always higher than the amorphous content for all measured samples due to the presence of paracrystalline cellulose: the measured accessibility (0.35) of microcrystalline Avicel PH-301 cellulose was even 52 % higher than its average content of amorphous domains (0.23). Accessible OH groups in both amorphous and paracrystalline domains are converted into OD groups upon exposure to deuterium oxide [115].

Mechanical pretreatment of (ligno)cellulosic biomass or treatment with water, solvents, or intracrystalline swelling agents can greatly reduce internal cohesion and crystallinity, making cellulose more amenable for chemical degradation [6,10,11,16,19,44,53–60]. However, it is important to note that (partial) recrystallization of amorphous cellulose may occur in water due to the high surface tension and hydrogen-bonding capacity of water [116].

Commonly, cellulose crystallinity is characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and solid-state ¹³C cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (¹³C CP MAS NMR). Since crystallinity is one of the key determining factors for catalysis, these analytical techniques will be illustrated in more details. Other techniques like Raman spectroscopy [117] and the recently developed vibrational sum-frequency generation (SFG) spectroscopy technique [118] will be discussed only briefly in this review. The reader is referred to some excellent reviews on cellulose crystallinity determination for more details [119–122].

i) X-ray diffraction (XRD)

The first studies on cellulose crystallinity using X-ray diffraction (XRD) were carried out one century ago [123]. The crystalline fraction of cellulose generates relatively sharp and strong reflections in XRD diffractograms, while the non-crystalline fraction generates broader signals (Fig. 4). The first attempt to determine the crystallinity of cellulose was performed by Hermans and Weidinger [124–126]. This method is based on measuring the integrated intensities of the crystalline signals and that of the diffuse background. The integration was performed by copying the signals on transparent paper of known weight per unit surface, cutting the figures out, weighing them and taking the average value. A crystallinity index was defined as follows:

$$CrI [\%] = \frac{M_{Cr}}{M_{Cr} + M_{Non-Cr}} \times 100$$

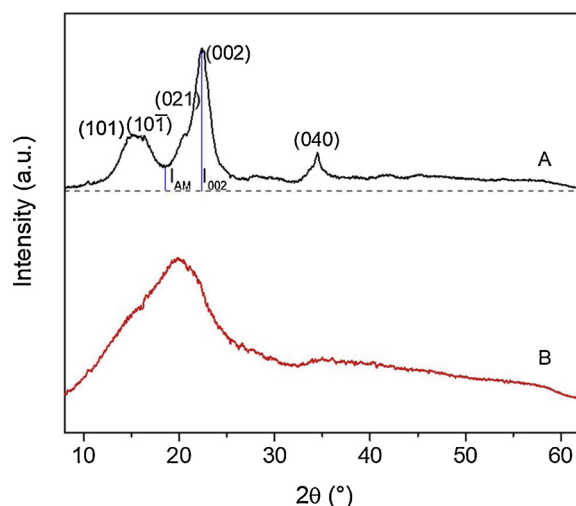


Fig. 4. XRD patterns of (A) Avicel PH-101 cellulose and (B) ball-milled Avicel PH-101 cellulose after baseline subtraction. Intensities are normalized to the highest intensity in each XRD pattern. Annotations in Park et al. [119].

where CrI is the crystallinity index, M_{Cr} is the mass of the crystalline fraction and M_{Non-Cr} is the mass of the non-crystalline fraction. The diffuse background was corrected for radiation scattered by air, thermal scattering, and Compton radiation.

The peak height method was another early attempt to measure the crystallinity of cellulose. With this empirical method, Segal et al. examined the changes in XRD patterns of cotton cellulose, decrystallized with aqueous solutions of ethylamine [127]. The crystallinity index was calculated out of the ratio of the intensity of the crystalline signal ($I_{002}-I_{AM}$) and the total intensity (I_{002}), after subtraction of the background signal, according to the following equation:

$$CrI [\%] = \frac{(I_{002} - I_{AM})}{I_{002}} \times 100$$

In this equation, I_{002} represents the maximum intensity of the signal corresponding to the (002) plane in the cellulose sample at a 2θ angle between 22° and 24° and I_{AM} is the intensity of the amorphous signal at a 2θ angle of about 18° , corresponding to the minimum between the (002) and (101) plane signals (Fig. 4A).

The XRD peak height method is a simple and fast method, but only provides a rough estimation of cellulose crystallinity and has several limitations [119,121,128,129]. First, the method erroneously assumes an equal X-ray sensitivity to amorphous and crystalline phases (in fact all XRD-based methods do and are therefore qualitative or semi-quantitative at best). Second, the minimum intensity between the (002) and (101) plane signals (I_{AM}) does not coincide with the maximum intensity of the amorphous signal, which leads to an underestimation of I_{AM} and a corresponding overestimation of crystallinity. Moreover, only one out of five crystalline reflections in XRD patterns is used in the method. In addition, the method does not take into account the fact that peak shapes are affected by several factors such as crystallite size: small crystallites generate broad reflection signals and only weakly contribute to the measured intensity. As a side note, the fact that I_{AM} does not coincide with the maximum intensity of the amorphous signal might actually be an advantage since the intensity of the amorphous signal at 18° (I_{AM}) appears to correspond to the intensity of the amorphous signal at $22-24^\circ$ (I_{002}). In order to improve the reliability of the Segal method, nanolevel size cellulose crystallites and amorphous cellulose were used to model the substrate to determine the diffraction background. A 2θ range from 10 to 75° is suggested to be more suitable for CrI determination [130].

Another approach to measure crystallinity using all crystalline signals is called the XRD amorphous subtraction method. This method was first described by Ruland [131] and Vonk [132], who determined cellulose crystallinity by subtracting the amorphous contribution from XRD diffractograms, measured by using an amorphous standard. Several different amorphous samples were proposed as amorphous standard: ball-milled cellulose, regenerated cellulose, xylan, or lignin powder. The amorphous signal was scaled by a factor before subtracting it from the sample XRD pattern to avoid negative signals. The crystallinity index was then calculated by dividing the area of the remaining XRD pattern by the area of the original XRD pattern. The main challenge of using this method is to find an appropriate and representative amorphous standard in accordance to the amorphous fraction in the sample.

Fig. 5 presents XRD diffractograms of ball-milled cellulose (B), xylan (C), milled wood lignin (MWL) of poplar wood (D), and poplar wood (E), after a 15 min boiling and 3 h rinsing ethanol/toluene (1:1) extraction in a FOSS Soxtec 2055 extractor to remove extractives) versus microcrystalline Avicel PH-101 cellulose (A). Differences in the diffractograms of ball-milled cellulose, xylan, and lignin are apparent. Hence, amorphous cellulose should be used as an amorphous standard to obtain a more accurate cellulose crystallinity index. Nevertheless, a physical mixture of xylan and lignin has been used to calculate the XRD amorphous subtraction crystallinity of hardwood before and after pre-treatment [133]. The interference of xylan and lignin prevents the

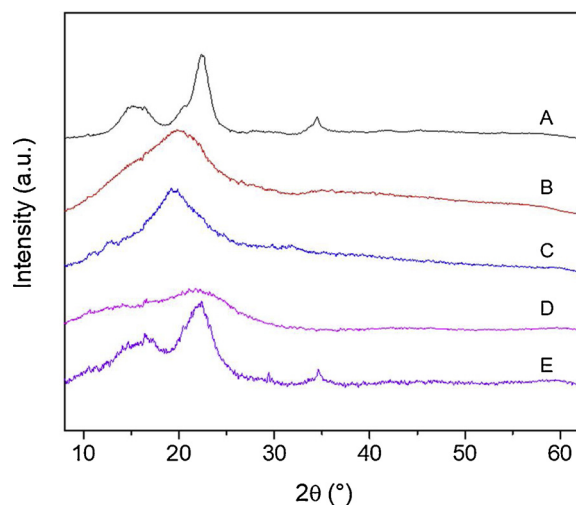


Fig. 5. XRD diffractograms of (A) Avicel PH-101 cellulose, (B) ball-milled Avicel PH-101 cellulose, (C) commercial xylan, (D) milled wood lignin of poplar wood, and (E) poplar wood. Intensities are normalized to the highest intensity in each XRD pattern.

determination of the real crystallinity index of cellulose enclosed within lignocellulosic substrates.

A more elaborate XRD deconvolution method was developed in which the entire XRD pattern, including the amorphous contribution, is fitted with Gaussian [134,135], Lorentzian [136], or Voigt [137] functions [138]. Some assumptions have to be made regarding the shape, width, and number of peaks. The crystallinity index is calculated by dividing the sum of the area of all crystalline signals by the total area of the XRD pattern. Some authors [134,137] used five crystalline peaks (101, 10i, 021, 002, and 040), whereas others [136] proposed only four (101, 10i, 002, and 040). Deconvolution strongly depends on the curve-fitting software and applied parameters (number and position of the signals and the full width at half maximum), making this method less straightforward. It is also possible to determine a crystallinity index based on more sophisticated calculations or refinements of the crystal structure of cellulose like the Debye calculation method [139] or the Rietveld refinement method [140,141].

The XRD peak height method remains the most common XRD method to date, despite its evident drawbacks [119]. Crystallinity indices determined with this method are generally higher than those determined with the other two XRD methods. However, it is interesting to consider the nice correlation (adjusted $R^2 = 0.98$) between crystallinity indices determined with the XRD peak height method and those determined with the XRD amorphous subtraction method by Park et al. (Fig. 6) [119]. Since no XRD method enables a quantitative determination of crystallinity, this correlation suggests that the XRD peak height method is as good as the XRD amorphous subtraction method to relatively compare the degree of crystallinity of different cellulose samples. Besides, the XRD peak height method was only meant to be used as a tool to determine relative crystallinity [127].

ii) Fourier-transform Infrared Spectroscopy (FTIR)

O'Connor et al. have studied the FTIR spectra of physically modified cotton cellulose to obtain an infrared-based method for the determination of the crystallinity index of cellulose [142]. It turned out that the absorption band at 1431 cm^{-1} , assigned to a symmetric CH_2 bending vibration at C6 and other vibrations [143], decreased and the absorption band at 898 cm^{-1} , assigned to a C—O—C stretching vibration at the β -1,4-glycosidic linkage [143], increased in intensity during grinding. They defined a crystallinity index as the ratio of the absorbance at these two wavenumbers:

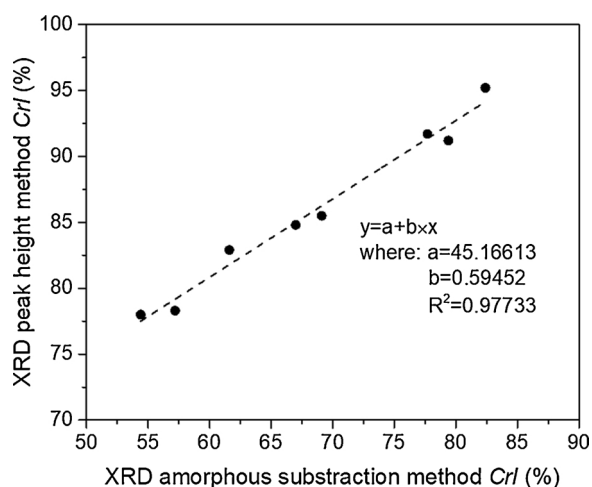


Fig. 6. Correlation between crystallinity indices (CrI) determined using the XRD peak height method and the XRD amorphous subtraction method. Produced according to data from Park et al. [119].

$$CrI = \left(\frac{\alpha_{1431\text{cm}^{-1}}}{\alpha_{898\text{cm}^{-1}}} \right)$$

where α represents the length between a specific baseline and the transmittance minimum, as exemplified in Fig. 7.

Since these adsorption bands are specific to cellulose I, Nelson and O'Connor have defined another, more universal crystallinity ratio that can be applied to both cellulose I and II [144]. They compared FTIR spectra of these two cellulose polymorphs with amorphous cellulose. In this comparison, they saw that several bands in the region between 1200 cm^{-1} and 1400 cm^{-1} were affected by the amorphous content of the sample rather than by the lattice type. The bands at about 1372 , 1335 , and 1315 cm^{-1} showed the strongest changes. The absorption band at 1372 cm^{-1} , assigned to a C-H bending vibration [143], was preferably chosen for crystallinity index determination since it is not affected by differences in the amount of water adsorbed onto the cellulose. To compensate for variations in sample concentration or scattered light intensity the absorbance at 1372 cm^{-1} was divided by an internal standard absorbance at 2900 cm^{-1} (Fig. 7):

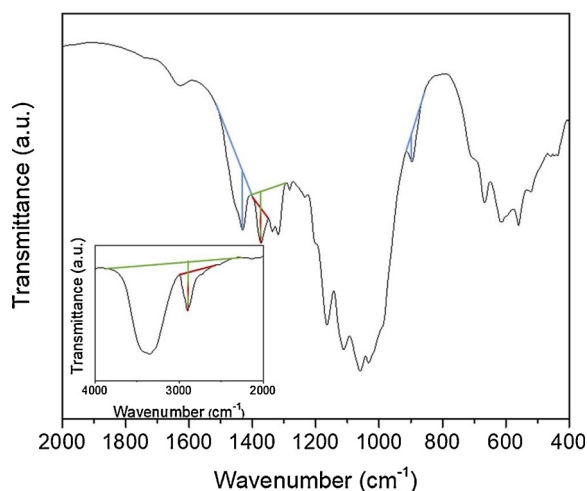


Fig. 7. FTIR spectrum of Avicel PH-101 cellulose indicating the methods of O'Connor et al. (blue), Nelson and O'Connor (green), and Calvini et al. (red). Inset: absorbance at $4000\text{--}2000\text{ cm}^{-1}$ (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

$$CrI = \left(\frac{\alpha_{1372\text{cm}^{-1}}}{\alpha_{2900\text{cm}^{-1}}} \right)$$

The intensity of the internal standard might be influenced by differences in the amount of adsorbed water since the O-H stretch vibration is included in the baseline.

Both FTIR methods mentioned above face the same problem: it is difficult to distinguish the absorption band at 1431 cm^{-1} and 1372 cm^{-1} from adjacent absorption bands. To overcome this problem, Calvini et al. have partly modified the FTIR crystallinity index as proposed by Nelson and O'Connor [145]. They used the same absorption bands, but they proposed another baseline in order to ensure that the absorption band at 1372 cm^{-1} is composed of fewer absorption bands (Fig. 7). The absorption bands and baselines used to calculate the crystallinity index of all above-mentioned methods are compiled in Fig. 7 for comparison. The difficult identification of suitable baselines is a major drawback and compromises the accuracy of these FTIR methods. Therefore, these are less frequently used than the XRD methods.

The accuracy of the FTIR methods is also compromised when lignocellulosic biomass, instead of pure cellulose, is analyzed for cellulose crystallinity index determination. Fig. 8 shows the FTIR spectra of Avicel PH-101 cellulose (A), ball-milled Avicel PH-101 cellulose (B), commercial xylan (C), milled wood lignin of poplar wood (D), and poplar wood (E) between 2000 and 400 cm^{-1} . Several prominent absorbance bands of xylan (e.g., at 1383 cm^{-1} , in Fig. 8C) and lignin (e.g., at 1508 cm^{-1} , aromatic skeletal vibration [146], in Fig. 8D) can be distinguished in the spectrum of poplar wood (Fig. 8E). The visible overlap of cellulose, xylan, and lignin absorption bands in the $1600\text{--}1300\text{ cm}^{-1}$ region and at 898 cm^{-1} makes the determination of the FTIR crystallinity index of cellulose in untreated lignocellulosic biomass impossible.

iii) Raman and vibrational sum-frequency generation (SFG)

Other vibrational methods to evaluate the crystallinity are Raman and vibrational sum-frequency generation (SFG) spectroscopy. Scenzel et al. uses relative intensity ratio of Raman lines of cellulose I at 1462 (amorphous) and 1481 cm^{-1} (crystalline) in conjunction with spectral deconvolution to determine the crystallinity [117]. However, the deconvolution might have band fitting problems due to the low intensities of the selected bands. Therefore, Agarwal et al. used the Raman band intensity ratio of the 380 and 1096 cm^{-1} to determine the cellulose I crystallinity based on univariate regression [147]. Nice correlations

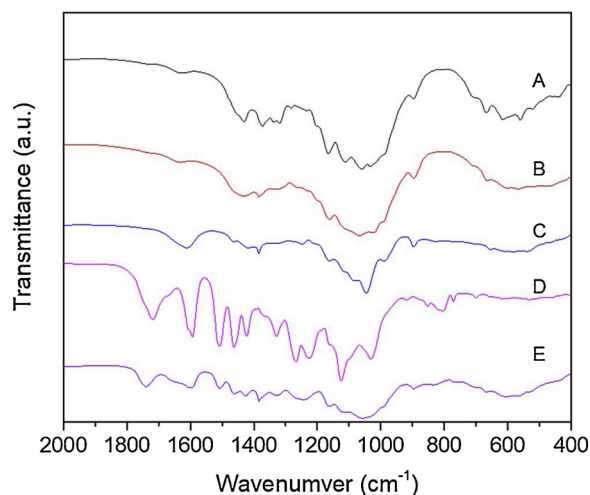


Fig. 8. Normalized FTIR spectra of (A) Avicel PH-101 cellulose, (B) ball milled Avicel PH-101 cellulose, (C) commercial xylan, (D) milled wood lignin of poplar wood, and (E) poplar wood.

with XRD CrI values have been demonstrated. Since hemicellulose shows broad CH_2 features, cellulose crystallinity in real biomass is best approached with the 380 cm^{-1} Raman peak intensity [148].

SFG is an interesting tool to visualize crystalline cellulose in real biomass since amorphous materials from (hemi)cellulose and lignin show no measurable SFG signal [118,149]. SFG can thus be regarded as a crystalline-selective detection method. The $C6H_2$ and intra-chain hydrogen-bonded OH vibrational region reveals rich information with respect to the crystalline cellulose polymorphism [118,150,151]. Therefore, cellulose polymorphs (I_{α} , I_{β} , II, III_I, and III_{II}) can be distinguished by SFG. Crystalline cellulose I has characteristic vibrations at 2944 and 3320 cm^{-1} in the C–H and O–H stretching vibration region, respectively. Shifts of the C–H band show formation of other cellulose crystal packing upon partial decrystallization, while full band disappearance of both O–H and C–H signals is expected after full amorphization. Quantification of crystallinity with SFG is difficult due to the non-linear correlation of its signal with crystallinity.

iv) Solid-state ^{13}C CP MAS NMR

More recent studies showed that the crystallinity index of cellulose samples can also be measured through an evaluation of ^{13}C CP MAS NMR spectra. Using this technique, chemically equivalent carbons can be distinguished if they are present in a different molecular arrangement since the environment of carbon nuclei determines their chemical shift (and line width) in the presence of an external magnetic field. This feature is particularly interesting for measurements on cellulose.

In practice, NMR resonance of the C4 carbon atoms in glucose units of cellulose I shows two distinct signals in NMR: a sharp C4 signal from ordered cellulose and a broader C4 signal from disordered cellulose, at about 89 ppm and 84 ppm chemical shift, respectively (Fig. 9A). This significant difference in chemical shift enables the determination of a crystallinity index. Hence, Newman [152] defined the crystallinity index as follows:

$$CrI (\%) = \frac{A_{Ord}}{A_{Ord} + A_{Disord}} (\times 100)$$

where A_{Ord} (ordered) and A_{Disord} (disordered) represent the signal area obtained by integration from $86\text{--}87$ to $91\text{--}93\text{ ppm}$ and $79\text{--}81$ to $86\text{--}87\text{ ppm}$, respectively (Fig. 10). The applied chemical shift integration boundaries vary between literature sources. However, this definition of the crystallinity index assumes an identical cross-polarization efficiency for the ordered and disordered regions.

This method is referred to as the C4 peak separation NMR method. It

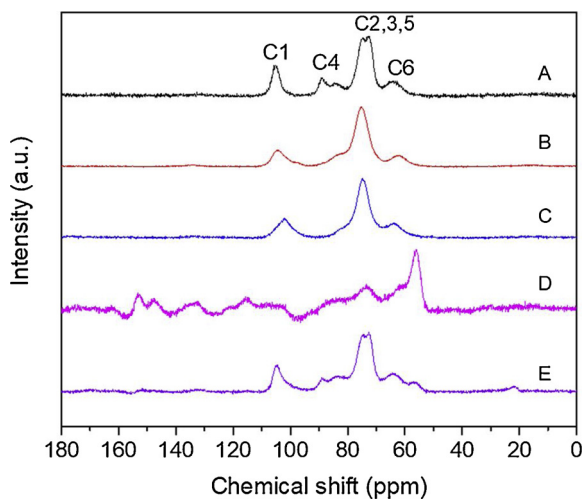


Fig. 9. Normalized solid-state ^{13}C CP MAS NMR spectra of (A) Avicel PH-101 cellulose, (B) ball-milled Avicel PH-101 cellulose, (C) commercial xylan, (D) milled wood lignin of poplar wood, and (E) poplar wood.

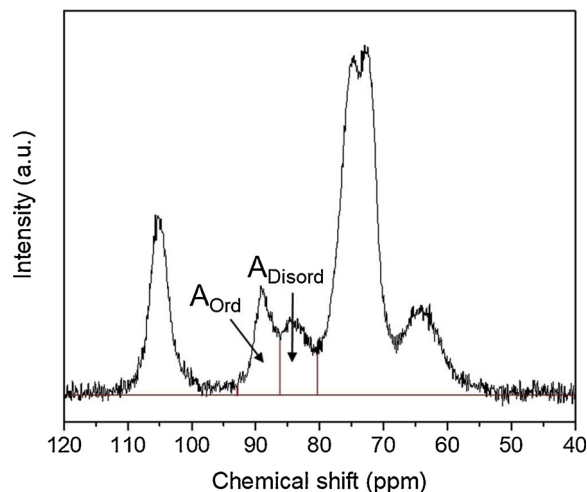


Fig. 10. Solid-state ^{13}C CP MAS NMR spectrum of Avicel PH-101 cellulose indicating C4 region integration intervals.

is relatively simple and easy to perform, but deconvolution and subsequent integration provides a more accurate estimation of cellulose crystallinity. Gaussian [153] and Lorentzian [154] curves with fixed center positions and fixed widths have been used to deconvolute the C4 signal into ordered and disordered C4 signals. However, the ordered and disordered C4 signals do not consist of one signal each but are both an accumulation of several signals. The ordered C4 signal can be deconvoluted into four signals: the I_{α} , I_{β} , $I_{\alpha+\beta}$, and paracrystalline signals (at 89.6 ppm , 88.2 ppm , 88.9 ppm , and 88.7 ppm , respectively) (Fig. 11) [155]. The disordered C4 signal can be deconvoluted into three signals: two signals at 84.6 ppm and 83.6 ppm originate from accessible fibril surfaces, and a broad signal at 84.1 ppm originates from inaccessible fibril surfaces. Gaussian function [154,156,157], Lorentzian [158] function, or a combination [159,160] are used for deconvolution. Paracrystalline cellulose gives rise to signals in the ordered C4 region but can be assumed as either crystalline [153] or non-crystalline [161] in crystallinity index calculations.

Unfortunately, the presence of amorphous xylan and lignin signals in the disordered C4 region still obstructs the determination of the crystallinity index of cellulose within lignocellulosic biomass (Fig. 9A, C, and D). This interference can be eliminated by removing hemicellulose and lignin through chemical pretreatment prior to measurement [162], or by spectroscopically removing these signals using the Newman and Hemmingson's proton spin-relaxation-based spectral edition (PSRE) method [154,163]. The PSRE method enables the spectral separation of cellulosic from non-cellulosic components based on their different proton spin relaxation time constants and is preferred over chemical pretreatment since the crystal structure of the cellulose can be modified during this pretreatment.

Extensive deconvolution is only possible on spectra with high spectral detail. The spectral detail can be improved with stronger static magnetic fields or magnetic fields with better homogeneity. However, a proper determination of the crystallinity index of less-ordered cellulose samples still remains quite difficult. Furthermore, this method is based on assumptions regarding the shape and number of signals.

Park et al. suggested a new NMR technique to measure cellulose crystallinity [164]. Analogous to the XRD subtraction method, the NMR subtraction method is based on the subtraction of an amorphous cellulose spectrum from the original spectrum. In this study, amorphous cellulose produced by the method of Atalla and Schroeder [165] was used as an amorphous standard. To avoid negative signals, the authors applied a scale factor to the spectrum of the amorphous standard. The main advantage of this method comprises the relative simplicity of implementation compared to the aforementioned fitting methods with

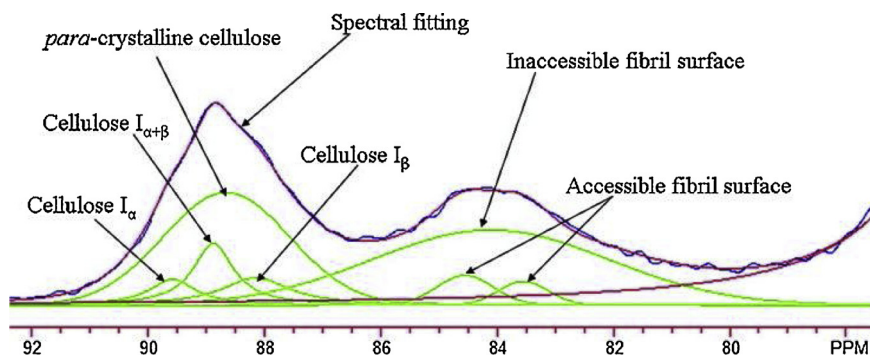


Fig. 11. A typical spectral fitting for the C4-region of the ^{13}C CP MAS NMR spectrum of native *Buddleja davidii* cellulose. Adapted from Hallac et al. [155].

deconvolution. Moreover, the NMR subtraction method evaluates the crystallinity index with respect to the entire spectrum instead of only the C4-region and can be applied to cellulose with any level of crystallinity.

A short, tentative summary of the performance of the discussed methods regarding several key crystallinity index determination parameters is provided in Table 1. Good performances are indicated with a (+), bad performances with a (-). (-/+) is used in the case of uncertainty as to whether the parameter is applicable to the method and for methods which are of intermediate proficiency compared to other methods. For all NMR methods, efficient separation of cellulose from non-cellulosic components in lignocellulosic biomass using the PSRE method was assumed. Although the XRD peak height method appears to be the least interesting method for the determination of the crystallinity index of cellulose, it is still very practical and can be used for relatively comparing cellulose samples with different crystallinities.

Generally, it can be concluded that the ^{13}C CP MAS NMR subtraction method overshadows the other methods due to its practicability, applicability and accuracy.

3.1.2.2. Degree of polymerization. Together with the crystallinity, cellulose degree of polymerization (often denoted as DP, *i.e.* the average amount of β -1,4 linked anhydroglucose units in a polymer) defines the micro-accessibility of cellulose to enzymes (*viz.* exoglucanases) [94]. Exoglucanases – cellulose enzymes (cellulases) which release cellobiose units – work at the (non)reducing ends of cellulose chains [166]. Cellulose degree of polymerization also determines the solubility: cellulose oligomers with DP of 2–6 are soluble in water, while cellulose oligomers with DP of 7–13 are merely partially soluble in hot water [167]. Cellulose oligomers with a DP larger than 30 already exhibit structural similarities with cellulose and are insoluble in water [168]. Cellulose hydrolysis in dissolved conditions is known to be more straightforward than in undissolved conditions [44]. Finally, the amount of glucosidic bonds that have to be broken to fully convert the polymer into its individual glucose units equals the DP minus one. Hence, cellulose samples with a high average DP are expected to be hydrolyzed more slowly to glucose than cellulose with a low average DP. At least, this statement holds true for the hydrolysis of (crystalline) cellulose using enzymes, which sequentially ‘digest’ the chain. However, not per se for non-selective catalysts: they can cut the polymers randomly, such as in the middle of the chain. This non-selective effect will be more pronounced when starting from amorphous cellulose and/or using solubilized acids. However, within the class of soluble acids, heteropoly acids such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ seem to mimic the progressive hydrolysis, since high selectivity to glucose was obtained already at low cellulose conversions, while mineral acids like H_2SO_4 initially form high contents of solubilized cellulose oligomers, which are subsequently gradually converted to glucose [19]. Although the origin of this biomimicry was not explained, the role of the heteropolyanion is

probably a decisive factor. Such unexpected observations are worthwhile to investigate in more details.

Cellulose degree of polymerization can be defined in terms of weight average (DP_w), number average (DP_n), or viscosity average (DP_v) [166,169]. Generally, determination of DP faces some difficulties as, depending on the used method, cellulose needs to be isolated since hemicelluloses and lignin interfere with the DP determination [169]. Furthermore, cellulose is insoluble in all common solvents and should, therefore, be dissolved in metal complex solutions (*e.g.* cuprammonium hydroxide or Cuoxam), dipolar aprotic solvents/lithium chloride (*e.g.* *N,N*-dimethylacetamide/lithium chloride), ionic liquids (*e.g.* 1-butylmethylimidazolium chloride) [44], or derivatized, *e.g.* by tricarbanilation, to increase its solubility [170,171]. The right choice of purification and/or dissolution methods is important as these pretreatments should not alter the chain length of cellulose, either by degradation or aggregation, prior to DP analysis [167,171–173]. Viscometry and size-exclusion chromatography (SEC), in the form of gel-permeation chromatography, are the most commonly used methods. Viscometry is a rapid and convenient method, but this technique only provides a viscosity average DP (DP_v) [174]. Furthermore, it provides no absolute molar weight, as the method is solvent and temperature-dependent [169,175]. SEC, on the other hand, provides information concerning the molar mass distribution, and both molecular weight average DP (DP_w) and number average DP (DP_n) can be determined [169]. Accuracy of DP data obtained with SEC will depend on the used detection method and standards [176]. Detection of cellulose compounds is often done using a refractive index (RI), ultraviolet (UV), or light scattering (*e.g.* multi-angle laser light scattering) detector. A combination of light scattering detectors with RI or UV detectors makes it possible to determine the actual molar mass distribution [175,176]. Commercially available pullulan standards are the most commonly used standards for DP and molar mass distribution of cellulose. Pullulan is a polymer consisting of α -1,6-linked maltotriose units [172]. Although pullulan shows some structural similarities with cellulose, corrections should be made to determine the actual DP and molar mass distribution based on calibration with pullulan [176]. An alternative way to determine the DP_n of cellulose is by analyzing the total monomer glucose and reducing end glucose content of cellulose [177].

As mentioned before, cellulose polymers in native cellulose can have a DP of more than 10000 anhydroglucose units. Some examples of encountered values in literature: flax DP 8000, aspen (DP 2500), fir (DP 2500), α -cellulose isolated from wood fibers DP 800–1100, raw cotton (DP 7000), and microcrystalline cellulose ($\text{DP} \leq 350$) [178,179].

3.2. Cellulose purity

Cellulose purity, defined by the presence of hemicellulose, lignin, and other minor constituents, is known to be very important for cellulose macro-accessibility, catalyst activity/stability, and product selectivity. The composition of lignocellulosic biomass samples can be

Table 1 Summary of the performance of the discussed methods to determine the crystallinity index of cellulose.

| | XRD | | | FTIR | | | ¹³ C CP MAS NMR | | | |
|---|----------------|-----------------------|---------------|-----------------|---------------------|----------------|----------------------------|---------------------------------------|------------------|-----------------------|
| | Peak height | Amorphous subtraction | Deconvolution | O'Connor et al. | Nelson and O'Connor | Calvini et al. | C4 peak separation | C4 peak separation and deconvolution. | C4 deconvolution | Amorphous subtraction |
| | Lignocellulose | - | - | - | - | - | - | + | + | + |
| Cellulose | - | + | + | - | - | - | - | + | + | + |
| Lignin/hemicellulose interference | - | - | - | - | - | - | - | - | - | - |
| Differentiation between amorphous and crystalline signals | - | + | -/+ | + | + | + | - | -/+ | -/+ | + |
| Applicability to low levels of crystallinity | - | + | + | - | + | + | + | -/+ | + | + |
| Applicability to lattice types other than cellulose I | - | + | + | - | + | + | + | -/+ | - | + |
| Practicability | + | -/+ | - | + | + | + | + | -/+ | - | + |
| Accuracy | - | -/+ | -/+ | - | - | - | - | -/+ | + | + |

accurately determined through validated methods issued by the Technical Association of the Pulp & Paper Industry (TAPPI) [180] or the US National Renewable Energy Laboratory (NREL) [181].

Next to physical hindrance, cellulose impurities may cause a decrease in cellulose conversion due to catalyst neutralization, fouling, or active site poisoning. For instance, wood can neutralize small amounts of mineral acid catalysts due to an ion-exchange between the inorganic cations associated with the bound and free anions in wood and the protons in the reaction mixture [182]. This acid neutralization capacity depends on the nature of the feedstock [183]. Cellulases are inhibited by non-productive binding with lignin [184], but also by pretreatment-released biomass degradation products such as xylose, xylose oligomers, and phenolics [185]. Micro-organisms can be inhibited by pretreatment-released biomass degradation products like 5-hydroxymethylfurfural (HMF), furfural, and phenolics [53]. In chemo-catalytic conversion routes, poisoning or contamination of metal catalysts by waxes, fatty acids, proteins, tannins, pectins, and inorganic impurities (e.g. Cl⁻, S, Ca, Fe) might occur [186–190].

In contrast to cellulases, which are cellulose specific, absence of cellulose specificity in chemo-catalytic conversion routes might lead to a decrease in product selectivity and purity due to simultaneous conversion of (hemi)cellulose and lignin. Partial solubilization of cellulose, hemicellulose, and lignin from biomass is already possible under hydrothermal conditions at temperatures above 473 K [191]. Such conditions are typically applied in chemo-catalytic reactions like hydrolytic hydrogenation or hydrogenolysis of cellulose. Several authors confirmed lignin degradation during these type of biomass reactions due to the hydrothermal conditions or non-selective action of the used catalyst [110,111,188,192]. Soluble lignin fractions and insoluble condensation products might inactivate catalysts through the covering or poisoning of active sites, leading to low product yields [110,188].

In conclusion, an increased cellulose purity and macro-accessibility in combination with a decreased crystallinity and degree of polymerization are expected to accelerate cellulose conversion in both chemical and biological valorization processes. Pretreatments of the (ligno)cellulose will consequently play a key role in future biorefinery schemes, next to its original fractionation purpose. In addition, pretreatment of lignocellulosic biomass as a tool to improve cellulose reactivity might be considered as long as the economics of the process allows the extra costs.

4. Pretreatments to improve cellulose conversion

(Ligno)cellulosic biomass can be subjected to a wide range of physical, chemical, physicochemical, and biological treatments in order to enhance the purity and accessibility of cellulose through a disruption of the (ligno)cellulosic structure (Fig. 12) [53–60]. Physical pretreatments typically increase the accessibility of cellulose, while chemical and biological pretreatments can increase both the accessibility and purity of cellulose. Contacting (ligno)cellulosic biomass with water, swelling agents, or solvents can lead to swelling or dissolution of cellulose fibers, resulting in a reduced internal cohesion and an increase in glycosidic bond accessibility. Physicochemical pretreatments combine both physical and chemical pretreatment methods. The pros and cons of a wide range of pretreatment methods are discussed in more details in the following section, especially with regard to the subsequent chemo-catalytic valorization of cellulose. These methods can be used either separately or together to improve the reactivity of cellulose *via* altering the accessibility and/or purity (*vide infra*).

4.1. Physical milling

Mechanical wood pulping is probably the oldest pretreatment method and it has been used since the 1840s for the production of high-quality cellulose fibers for paper manufacturing. Nowadays, there is a worldwide annual production of around 35 million tons of mechanical

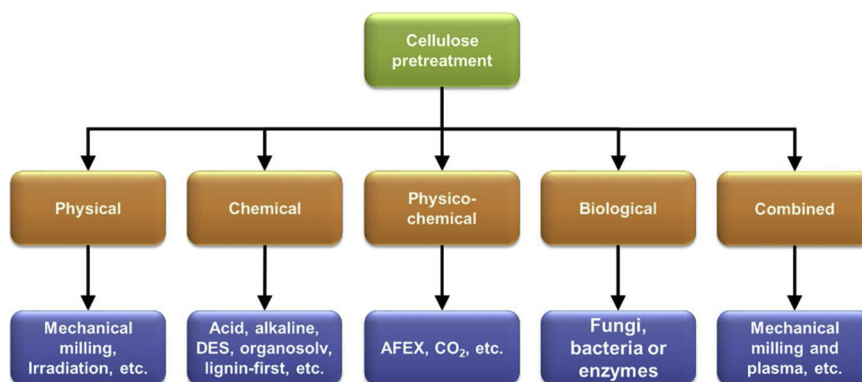


Fig. 12. Overview of the approaches used for cellulose pretreatment.

pulp [193,194]. However, for chemical production in biorefineries, the main purpose of milling is rather a reduction in particle size and crystallinity. In addition, a disruption of the lignocellulose structure and a decrease in the degree of polymerization is targeted as well. A reduction in particle size entails an increase in specific surface area and improves mass and heat transfer processes. Compared to mechanical pulping, where the intention is to preserve the quality of cellulose fibers as much as possible, more intense milling can be expected in biorefineries for chemicals. All the changes in (ligno)cellulosic structure induced by milling lead to more efficient subsequent (ligno)cellulose pretreatments and/or cellulose conversions.

Milling pretreatment (wet or dry) includes compression, ball, two-roll, knife, attrition, hammer, colloid, vibro energy, disk, and freeze-milling [54,195,196]. Ball milling is often used in research – especially prior to chemo-catalytic processes with a solid catalyst – and leads to profound improvements in cellulose reactivity. Dry ball milling prior to chemo-catalytic processes is mostly performed until complete cellulose amorphization is accomplished and demonstrated with analytical techniques such as XRD and ^{13}C -CP/MAS NMR. Wet ball milling can induce a transformation of native cellulose I to the thermodynamically more favorable cellulose II polymorph [197]. There is some disagreement in literature whether cellulose II is less or more reactive than cellulose I. This issue is addressed in more details in the alkaline pretreatment section.

As an example of the effect of ball milling on enzymatic cellulose conversion, Sipponen et al. reported an increase in the enzymatic conversion of maize cellulose to glucose from 33 % up to 89 % after only 3 h of ball milling at 600 rpm [198]. They attributed this improvement to a combination of cell wall disruption, cellulose crystallinity reduction, and hemicellulose depolymerization. Significant improvements were also reported for the solid acid-catalyzed hydrolysis of cellulose to glucose: After a 48 h ball milling pretreatment of microcrystalline cellulose, Benoit et al. observed a significant increase in glucose yield from < 1 % to 13 % after 1 h of hydrolysis at 423 K with ion-exchange resin Amberlyst 35 as solid acid catalyst [199]. Van de Vyver et al. obtained 50 % glucose yield from 24 h ball milled microcrystalline Avicel PH-101 cellulose after 24 h of hydrolysis at 423 K with sulfonated silica/carbon nanocomposites [16,200]. Similarly, Pang et al. reported 94 % conversion of ball-milled cellulose (48 h) after 24 h of reaction at 423 K with a sulfonated CMK-3 solid acid catalyst yielding 74.5 % glucose [201]. Fukuoka et al. demonstrated that mix-milling microcrystalline cellulose with a solid acid catalyst, *viz.* activated carbon K26, could drastically improve the otherwise limited downstream cellulose-catalyst interaction, enabling glucose yields up to 88 % with only 0.012 % of HCl [202]. Grisel and Smit reported the beneficial impact of ball milling and mix-milling Avicel PH-101 cellulose: after a 48 h ball milling pretreatment, cellulose conversion increased from 11 % to 40 % (glucose yield: 5% to 22%) and from 23 % to 43 % (glucose yield: 8% to 28%) after 4 h of reaction at 453 K in the

presence of H-mordenite and Norit CAP Super (NCS) solid acid catalysts, respectively. The highest glucose selectivity (95 %) was obtained after mix-milling Avicel PH-101 cellulose with NCS, which the authors attributed to the scavenging of by-products (such as HMF, levulinic acid, and formic acid) by NCS, thus preventing the formation of humins and reducing glucose losses [203].

Hydrolytic hydrogenation of cellulose to hexitols (sorbitol, mannitol, and sorbitan) improves also significantly after ball milling pretreatment. In this respect, Geboers et al. reported a quantitative one-pot conversion of ball-milled Avicel PH-101 cellulose (24 h) to hexitols in only one hour of reaction using soluble heteropoly acids for cellulose-to-glucose hydrolysis and commercial Ru on carbon for subsequent glucose-to-sorbitol hydrogenation at 463 K [19]. Conversion of unpretreated microcrystalline cellulose only yielded 56 % hexitols at 77 % cellulose conversion in five hours of reaction, emphasizing the strong impact of ball milling pretreatment. Van de Vyver et al. used an insoluble bifunctional 3 wt.% Ni/CNF catalyst for the hydrolytic hydrogenation of cellulose and observed a significant improvement in sorbitol/mannitol yield from 35 to 57 % (cellulose conversion from 87 to 92 %) obtained at 483 and 463 K, respectively, after a ball milling pretreatment of 24 h [204]. Fukuoka et al. observed improvement from 43 to 58 % in sorbitol/mannitol yield and from 66 to 82 % in cellulose conversion using a bifunctional 2 wt% Pt/BP2000 catalyst at 463 K after ball milling cellulose for 48 h [205]. Similarly, Ma et al. reported that the sugar alcohol productivity is significantly improved by using ball-milled cellulose compared to microcrystalline cellulose by hydrolytic hydrogenation over zirconium phosphate and Ru/C [206]. Ribeiro et al. reported enhanced direct production of sorbitol after mix-milling cellulose together with a Ru/AC catalyst in a laboratory ball mill for 4 h at 20 Hz: after 5 h of reaction, cellulose conversion increased from 36 to 89 %, while the sorbitol yield increased from 15 to 69 %. These authors also determined the crystallinity, degree of polymerization, and particle size of microcrystalline cellulose in function of milling time and frequency. Remarkably, while the crystallinity and degree of polymerization steadily decreased with milling time and frequency, no further reduction in particle size could be observed after 4 h of milling at 10 Hz. This observation possibly indicates aggregation of cellulose particles during ball milling. Sels et al. comprehensively investigated the impact of cellulose crystallinity, particle size, and degree of polymerization on the conversion rate of cellulose and sugar alcohols selectivity over Ru/USY and a trace amount of HCl [207]. It is revealed that the degree of polymerization has a large influence on the conversion rate and selectivity when the average DP is higher than 200. After that, the particle size and crystallinity play a dominant role. Moreover, other crucial factors are lignin content and acid buffer capacity of cellulose. Higher delignification efficiency and purification are therefore required to obtain higher conversion rate and selectivity.

Besides, ball milling facilitates the conversion of lignocellulose to ethylene glycol. The ethylene glycol yield from ball-milled Miscanthus

(450 rpm, 3–6 h) achieves 52 %, which is comparable to the result of pure cellulose [208]. Liu et al. demonstrated that the reactivity of cellulose can be significantly improved by ball milling of 2 h in the conversion of cellulose to *n*-hexane [209].

Ball milling has long been considered not likely to be industrially feasible because of its high energy demands and requirement for large unit dimensions [210,211]. Meine et al. described the existence of large-scale industrial ball mills (volume of 112 m³, Cemtec, Austria) in the cement industry [212]. The authors foresee a possible use of such mills in lignocellulosic biomass pretreatment, entailing moderate energy requirements (± 10 % of the energy content of bioethanol that could be produced from this pretreated lignocellulosic biomass) and costs (85 € per ton of bioethanol), provided that milling time can be confined to two hours. It is interesting to validate the intensity of milling power of large facilities and its impact on the structure of cellulose. The type of milling and efficient transfer of forces is indeed very important. Many authors therefore prefer to use a planetary ball mill, which can significantly reduce milling time due to its exceptional interplay between frictional and impact forces in this type of ball mill. Nevertheless, planetary ball mills are limited to laboratory size [213].

Interestingly, several research groups have tried to improve the ball milling pretreatment efficiency by adding acids in a so-called reactive milling set-up (Fig. 13, I) [214]. Hick et al. were the first to report acidic clays as efficient catalysts in solvent-free mechanocatalytic depolymerization of cellulose to water-soluble products in a shaker ball mill [215]. The authors obtained 84 % solubilization of microcrystalline cellulose in only 3 h of milling in the presence of acidic delaminated kaolinite. Later, Meine et al. discovered that ball milling microcrystalline cellulose after impregnation with mineral acids reduces its degree of polymerization profoundly, even to the extent that the cellulose powder becomes completely soluble in water [212]. This extensive decrease in the degree of polymerization and solubilization enables a faster downstream cellulose-to-glucose hydrolysis at lower temperatures, which is interesting from an energetic point of view. The authors obtained complete α -cellulose (which is purified wood holo-cellulose) solubilization after H₂SO₄-impregnation and two hours of planetary ball milling pretreatment, enabling a near-quantitative conversion to glucose (91 %) and xylose (96 %) at 403 K in only one hour of reaction [212]. Lignocellulosic substrates like sugarcane bagasse and beech wood could also be solubilized completely after H₂SO₄ or HCl impregnation and two hours of ball milling pretreatment [212,216,217]. This ‘water-soluble lignocellulose’ can be selectively converted into sugars at 140 °C for 1 h, while lignin was precipitated as sulfur-free lignin [218]. Combined with a hydrogenation catalyst, Ru on carbon, this mechanocatalytic reactive ball milling technique enabled

the conversion of microcrystalline cellulose to 94 % hexitols at 423 K in four hours of reaction [219]. Similarly, Shrotri et al. obtained a ~90 % hexitol yield during hydrolytic hydrogenation of mechanically depolymerized acidulated microcrystalline cellulose using a bimetallic Ni-Pt/alumina catalyst at 473 K for one hour [220]. The authors used 0.25 mmol g⁻¹ H₂SO₄ and a planetary ball milling pretreatment of 10 h to produce a fully water-soluble cellulose powder. Dehydration of sorbitol to sorbitan during hydrolytic hydrogenation was avoided through the introduction of a preliminary H₂SO₄-neutralization step. The soluble cellulose oligomers were found to have an average DP_N of about 7 and interestingly, milling induced the formation of α -1,6 bonds. This α -1,6 branching of cellulose oligomers increases the water-solubility above DP of 6. Besides, Carrasquillo-Flores et al. demonstrated for the conversion of α -cellulose, beech wood, and sugar cane bagasse polysaccharides to high yields of HMF (up to 79 %) and furfural (up to 87 %) at low temperatures (443 K) and remarkable short reaction times (3–15 min) after reactive milling [221]. The ‘water-soluble lignocellulose’ can be obtained with milling of 1–3 h after H₂SO₄ impregnation even for 1 kg scale [222]. Thus, the energy consumption significantly decreases with upscaling of the experiments from 1 g to 1 kg. Tomishige et al. reported that production of hexanols from cellulose is benefited from mechanocatalytic depolymerization of cellulose by adding H₂SO₄ or HCl during the ball milling [223]. Ball milling H₂SO₄ impregnated barley straw shows high saccharification efficiency. It is revealed that not only the mechanical parameters such as grinding time and pausing time but also the internal temperature as well as acid concentration influence the conversion rate [224]. Higher internal temperature and acid concentration facilitate the yield of reducing sugars.

Depolymerization of the solid cellulose over solid acids is restricted to the weak interaction by collision between cellulose and catalysts. In order to address this issue, Fukuoka et al. investigated mix ball-milling cellulose with carbon materials to improve the interaction (Fig. 13, II) [202,225–228]. Since the carbon materials contain low acidity, mechanocatalysis was not observed. The crystallinity indices determined from ¹³C-CP/MAS NMR and XRD (via peak height method) are almost the same for mix ball-milled cellulose and singularly milled ones. The mix ball-milling gives 13 times higher rate constant of cellulose than that of milling without catalysts as a result of enhanced interaction [229]. This approach can also be applied to lignocellulosic biomass such as Eucalyptus [230,231]. Although solid residue including lignin after conversion of (hemi)cellulose inhibits the recycling of the carbon materials, the carbon materials together with insoluble residue are easily converted back to fresh carbon materials [231]. This mix-milling mainly improves the solid-solid reaction to obtain soluble oligomers

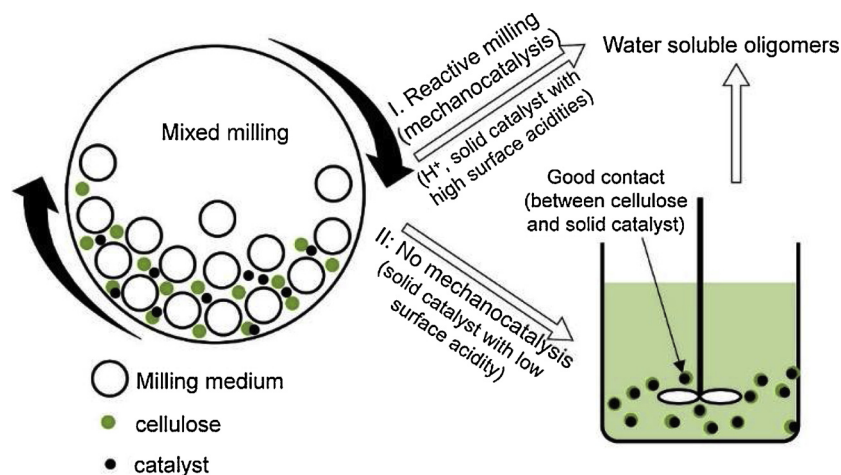


Fig. 13. Mechanical milling of cellulose with (homogeneous and heterogeneous) acid catalyst. For homogeneous acid, the cellulose is first impregnated with acid solution and dry it before mechanical milling.

from cellulose since soluble oligomers are major products (> 70 %). While the main product is glucose when adding a trace amount of homogeneous acid such as HCl [202]. Compared to milled cellulose (milling time of 2 h), hydrolytic hydrogenation over commercial Ru/C after mix-milling cellulose with a solid acid zirconium phosphate improved the cellulose conversion from 77.6 % to 100 % and sugar alcohols yield from 65.1 % to 90.3 % at 463 K [232].

Although ball milling can reduce the crystallinity of cellulose, heating the ball-milled cellulose in water can cause recrystallization of cellulose. However, the recrystallization of ball-milled cellulose is much lower if the heating is conducted in an organic solvent such as butanol [233,234]. Hence, depolymerization of (ball-milled) cellulose could be facilitated in alcohols comparable to hydrolysis [233]. Feng et al. reported that cellulose properties like the crystallinity, degree of polymerization, and particle size have no significant influence on the conversion of cellulose in alcohols with the presence of sulfonated hyperbranched poly(arylene oxindole)s catalyst [235].

In summary, intense milling improves the reactivity of cellulose and the concept of reactive milling and/or mix milling is a step forward in the use of milling in cellulose conversion. Despite the fast, low energy cellulose conversions and good product yields, ball milling on itself remains energy-intensive and the first economic assessment has yet to be validated on a larger scale. In addition, while milling is especially beneficial for the activation of microcrystalline cellulose, the conversion of cellulose in milled lignocellulosic materials is hindered in some catalytic processes, since no lignin is removed upon milling [54]. Additional delignification steps may, therefore, be required. It remains questionable whether milling cellulose pulps after delignification pretreatment is really necessary.

4.2. Irradiation

Irradiation pretreatment includes gamma ray, electron beam, microwave (electromagnetic), and ultrasound (acoustic) irradiation, applied either alone or in combination with other pretreatment techniques, and hydrolysis of biomass (Fig. 14). Electromagnetic radiation can be subdivided in high-energy, ionizing (gamma and electron) and lower-energy, non-ionizing (microwave) radiation. Ionizing radiation ionizes atoms through the removal of electrons and induces profound chemical changes, while non-ionizing radiation only excites molecular rotational and vibrational modes [236].

Gamma rays [237] and electron beams [238] are reported to depolymerize and decompose lignocellulosic biomass, thus improving the

reactivity of cellulose. Betiku et al. reported a more than threefold increase in enzymatic softwood and hardwood cellulose digestibility after an irradiation pretreatment with gamma rays at a dose of 40 kGy and 90 kGy, respectively [239]. Electron beam irradiation (EBI) of bagasse, a by-product of the sugar cane industry, at a dose of 100 MR can lead to a twofold or fourfold increase of the glucose yield during enzymatic or hydrochloric acid hydrolysis, respectively [240]. Bak reported that water soaking-based electron beam irradiation (WEBI) of rice straw at a dose of 80 kGy prior to enzymatic hydrolysis could increase glucose yields from 30 % to 70 % [241]. Without water soaking, EBI only afforded a glucose yield of 52 %. It is believed that swelling of rice straw increases the interaction surface between electrons and the substrate.

With microwave irradiation, an efficient *in situ* generation of heat throughout (ligno)cellulosic substrates and reaction media can be accomplished, leading to increased reaction rates compared to conventional heating with an external source [242]. This irradiation technique is therefore frequently used to assist other pretreatment techniques and hydrolysis itself [243]. Lu et al. applied a microwave-assisted dilute sulfuric acid pretreatment to rape straw prior to enzymatic conversion. A glucose yield increase from 12 % to 58 % was achieved after 3 min of microwave pretreatment at 900 W in 2% (v/v) H₂SO₄ [244]. The authors suggest that microwave irradiation partially disrupts the lignin structure, leading to increased cellulose accessibility. Microwave pretreatment (1300 W, 5 min) of sugarcane bagasse in glycerol removes more hemicellulose and lignin than treatment in water [245]. This leads to a much higher glucose concentration from enzymatic hydrolysis of a sample from microwave pretreatment in glycerol (237.5 mg/g) than that of pretreatment in water (22.6 mg/g). Hydrolysis of microcrystalline cellulose to glucose with heterogeneous biomass char sulfonic acid catalysts (BC-SO₃H) was efficiently accelerated under microwave irradiation at 350 W, enabling a significant glucose yield increase from 3% to 17 % after 1 h of reaction at 363 K [246]. Fan et al. reported the mechanism behind the direct microwave-assisted hydrothermal depolymerization of microcrystalline cellulose to glucose at elevated temperatures (453–493 K). It was suggested that above 453 K, a weakening of the hydrogen bond network in amorphous cellulose regions enables the microwave-induced rotation of free CH₂OH groups and the concomitant formation of levoglucosan, which is subsequently hydrolyzed to glucose (Fig. 15) [247]. The ability to hydrolyze cellulose in water-inaccessible regions makes microwave heating more efficient than conventional heating. Microwave-assisted hydrothermal pretreatment can selectively dissolve hemicellulose from lignocellulose without adding any chemicals [248,249]. The dissolved hemicellulose has many

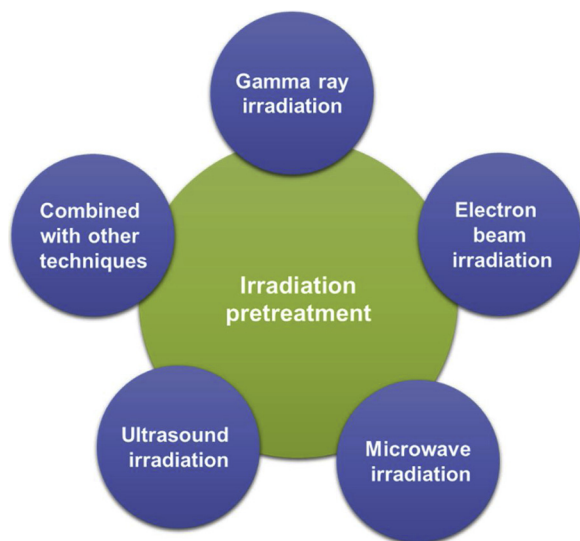


Fig. 14. Typical type of irradiation pretreatment.

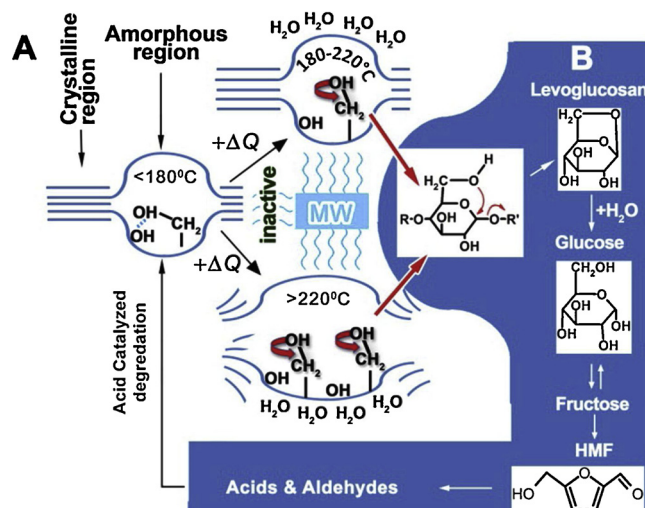


Fig. 15. Scheme of the cellulose-microwave interaction as a function of temperature: (A) mechanism of CH₂OH group activation; (B) route of cellulose degradation toward acids and aldehydes. Adapted from Fan et al. [247].

industrial applications such as food-applicable prebiotics or packing.

Ultrasound irradiation creates pressure differences in reaction media and improves the accessibility of (ligno)cellulosic biomass through microjet erosion, cell wall collapse, and enhanced mass transfer/mixing processes [68]. Ultrasound can also enhance delignification through the creation of radicals. Zhang et al. reported improved hydrolysis of microcrystalline cellulose with a sulfonated carbon solid catalyst (AC-SO₃H) after sonication pretreatment [98]. This improvement was mainly attributed to a decrease in particle size, since no significant decrease in crystallinity, as determined by the XRD peak height method, or DP was observed. Glucose yields up to 42 % are at par with those obtained after ball milling pretreatment, emphasizing that particle size and accessible surface area can be more critical for an efficient hydrolysis than cellulose crystallinity in some cases. The quantity of alkali metals such as potassium, calcium, and magnesium in eucalyptus can be reduced by ultrasound (300 W and 28 kHz) pretreatment [250]. Meanwhile, the crystallinity (XRD peak height method) of cellulose increased from 31.8 % for the untreated sample to 35.5 % for the pretreated sample as a result of removal of hemicellulose, lignin, and amorphous cellulose.

Although irradiation pretreatment constitutes a promising and growing research area, they are generally considered energy-demanding, expensive, and difficult to apply on an industrial scale [54]. Nevertheless, microwave pretreatment is already being used on an industrial level, albeit limited [242].

4.3. (Physico-)Chemical hydrothermal pretreatment

During hydrothermal pretreatment, lignocellulose is contacted with hot water or steam to enable the degradation and redistribution of hemicellulose and lignin [251]. Water-soluble metal catalyst inhibitors like minerals can also be removed through hydrothermal pretreatment [187,252].

The severity of hydrothermal pretreatment can be expressed by the severity factor $\log(R_0)$ as follows [253]:

$$\log(R_0) = \log \left[t \exp \left(\frac{T(t) - 100}{14.75} \right) \right] + |pH - 7|$$

where t is the time in minutes (mins) and $T(t)$ is the temperature in degrees Celsius (°C). This factor can be used to compare the severities of different hydrothermal pretreatments. The equation implies that high temperatures, long pretreatment times and extreme pH values increase the severity of hydrothermal pretreatments. At high temperatures, increased self-ionization of water lowers its pH and improves its acid-base catalytic properties [254,255]. Nevertheless, acids or bases can be added for enhancement of the severity [256–259]. During hydrothermal pretreatment, degradation of hemicellulose liberates organic acids like acetic acid, which in turn assist in further hydrolysis reactions [49]. Although lignin can be degraded and solubilized a well, it is known to repolymerize e.g., through the formation of carbonium ions after cleavage of lignin β-O-4 ether bonds (Fig. 16) [71,260]. Melting of hydrophobic lignin can also occur during hydrothermal pretreatment and leads to droplet formation and lignin redistribution upon cooling [261]. Removal and redistribution of hemicellulose and lignin lead to an increase in pore volume and improves the accessibility of cellulose [56]. Furthermore, cellulose accessibility can be improved through amorphization of crystalline cellulose in water at high temperatures and pressures (> 593 K, 25 MPa) in addition to a reduction in DP [260,262,263]. However, cellulose aggregation might occur under the hydrothermal pretreatment conditions to increase the lateral size of crystallites [264].

Hydrothermal pretreatment includes liquid hot water (LHW) and steam (explosion) pretreatment. LHW pretreatment at 473–503 K solubilizes up to 60 % of the lignocellulose, including 35–60 % of the lignin and almost all of the hemicellulose [191]. Flow-through LHW

pretreatment systems are known to remove more lignin (up to 50 % of the original lignin) than batch systems due to reduced lignin repolymerization reactions [256]. Pseudo-lignin was not observed by time-of-flight secondary ion mass spectrometry imaging after hydrothermal flow-through pretreatment, while it was present after a hydrothermal pretreatment in a batch reactor [266]. The lignin movement was mainly observed at the cell corner of the lignocellulose during the flow-through hydrothermal pretreatment. Mosier et al. reported that LHW pretreatment of corn stover leads to complete enzymatic hydrolysis of the remaining polysaccharides [267,268]. On the other hand, Pang et al. reported no distinct improvement in glycol yield (3%–5%, calculated as mol% carbon of total feedstock carbon) and a lower conversion of corn stalk (83 % to 63 %) using a solid Ni-W₂C/AC catalyst after LHW pretreatment at 393 K (Fig. 17a; G) [110]. In this study, the LHW removed practically all solubles, 25 % of hemicellulose and only a negligible amount of lignin (1%), leading to increased hemicellulose and lignin contents and a decreased hemicellulose to lignin ratio in the pretreated corn stalk (Fig. 17b; G). The removal of soluble compounds during pretreatment leads to the observed lower conversion. Since both cellulose and hemicellulose yield glycols, no distinct improvement in glycol yield can be expected when hemicellulose is removed instead of lignin, which is the inhibitory. Hence, LHW pretreatments might lead to lignin redistribution and an increased (hemi) cellulose accessibility, but also entail extensive (hemi)cellulose removal. The substrate amount is hence lowered sometimes, while the expected poisoning effect of lignin on the hydrogenation sites of the Ni-W₂C/AC catalyst can still limit the glycol yield and selectivity as well.

Since many catalytic reactions are performed in more or less the same conditions as hydrothermal pretreatment processes, the same chemistry and processes are expected to occur during these catalytic reactions. Fukuoka et al. applied a hot water pretreatment (3 h at 373 K) to raw silver grass prior to its catalytic conversion to sugar alcohols in the presence of a supported platinum catalyst at 463 K [252]. This pretreatment reduced the amounts of metal cations (and their counter anions), P, and S in silver grass, leading to an increase of the pentitol yield from 51 % to 72 % (based on hemicellulose content) and decrease of glycol byproducts from 6.0 % to 3.4 %. While P and S are known poisons for metal catalysts, certain anions in the mineral fraction of silver grass could decelerate the conversion of cellulose (e.g. SO₄²⁻, CO₃²⁻ and HCO₃⁻) or even perform base-catalyzed side-reactions, leading to the formation of glycol byproducts and reduced sugar alcohol yields (e.g. CO₃²⁻, and HCO₃⁻). The negligible increase in sorbitol yield (7.4%–8.6%) after this pretreatment is ascribed to the presence of lignin, which should be removed to increase the accessibility of cellulose.

During steam explosion, lignocellulose is contacted with steam at high temperature (433–533 K) and pressure (0.69–4.83 MPa) for a short contact time, followed by a sudden explosive decompression [55,56]. Water inside biomass expands and disrupts the lignocellulosic structure upon depressurization, thus increasing the accessibility of cellulose to reactants and catalysts. Wyman et al. reported 83.7 % xylose and 100 % glucose yield after acidic steam pretreatment (3% SO₂/463 K/5 min) of poplar wood and subsequent enzymatic hydrolysis [269]. Sun et al. applied a combination of steam pretreatment and alkali on corn stalk to improve its conversion to ethylene glycol and glycerol in the presence of a Ni-W₂C/CSAC (coconut shell activated carbon) heterogeneous catalyst at 518 K [270]. After a steam explosion pretreatment for 1 h at 0.4 MPa and a subsequent 5% NaOH pretreatment for 24 h at 333 K, corn stalk hemicellulose and lignin were efficiently removed up to 84 % and 72 %, respectively, affording an ethylene glycol yield of 20 wt.% and a glycerol yield of 52 wt.%. It was suggested that the initial steam explosion step accomplishes hemicellulose hydrolysis, lignin decomposition, and a disruption of the lignocellulosic structure, thus significantly increasing the accessibility of cellulose to the catalyst.

Drawbacks of hydrothermal pretreatment are the possible formation

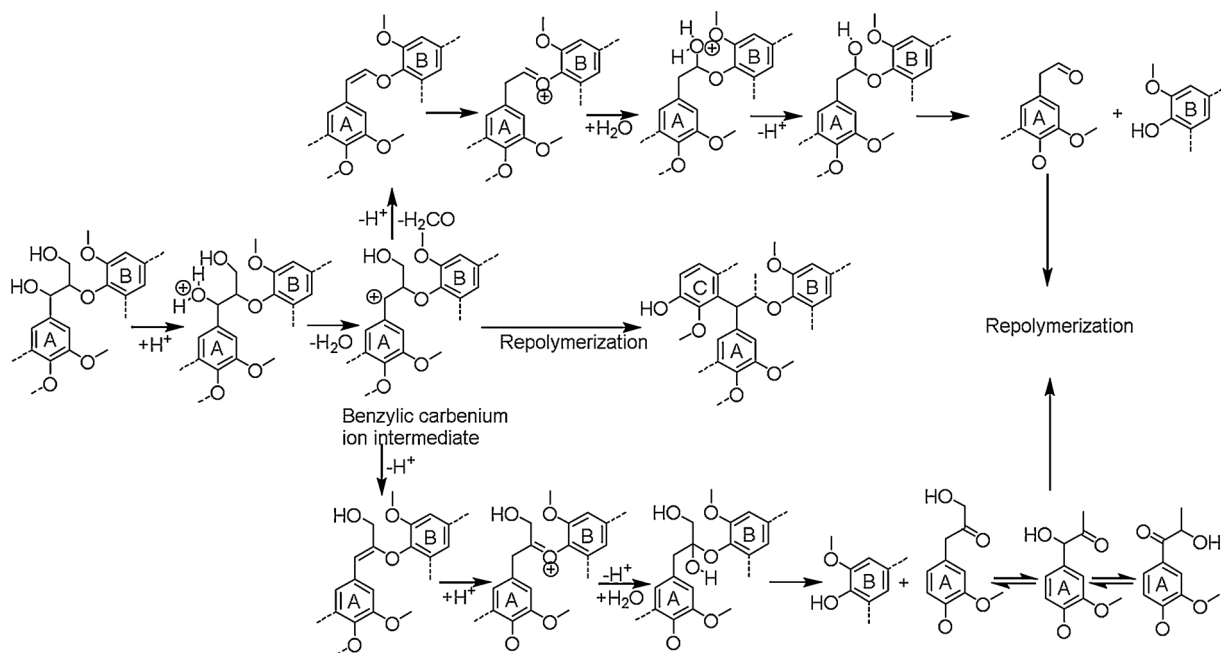


Fig. 16. Lignin depolymerization and repolymerization reactions in water in acidic conditions. Based on Beckham and Sels et al. [71,265].

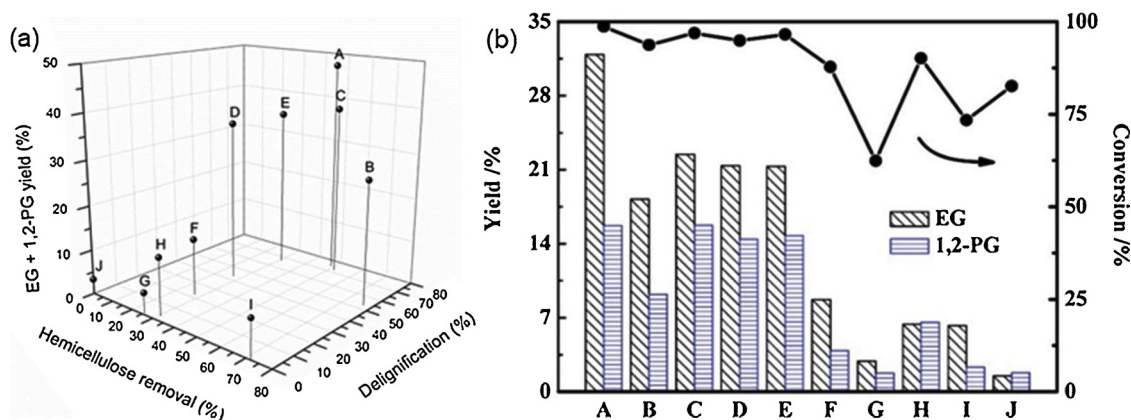


Fig. 17. (a) Plot of the combined EG and 1,2-PG yield in function of the amount of hemicellulose removal and delignification during various pretreatments. (b) Corn stalk conversion, ethylene glycol (EG) and 1,2-propyleneglycol (1,2-PG) yields after various pretreatments. (A) ammonia and H_2O_2 , (B) butanediol, (C) NaOH, (D) H_2O_2 , (E) ammonia, (F) 50 % ethanol, (G) hot water, (H) hot limewater, (I) SCO_2 , (J) raw corn stalk. Reaction conditions: 2% Ni-30 % W_2C/AC , 518 K, 150 min. Based on and reproduced from Pang et al. [110].

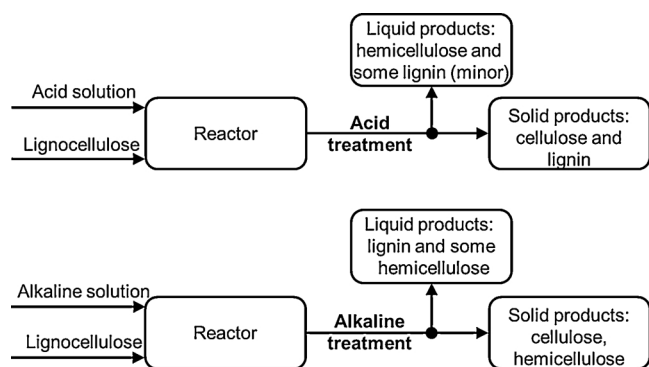


Fig. 18. Process flow scheme of acid and alkaline treatment.

of furfural, HMF, and phenolics, which might inhibit downstream conversion processes. However, a high industrial potential of steam and LHW pretreatments in enzymatic biomass valorization has been suggested on account of their adequate performance and economic

effectiveness [53]. Besides, the transformation of native lignin into more recalcitrant lignin makes its further valorisation difficult. The degradation of hemicellulose also reduces its value.

4.4. Acid

Sulfite pulping was already practised in the 19th century [271]. During this pulping process, mixtures of sulfurous acid and/or its alkali salts are employed to cleave and sulfonate lignin to water-soluble lignosulfonates. During acid sulfite pulping, formed lignin carbonium ions (Fig. 16) are sulfonated [193], preventing cleavage of β -aryl ether bonds and lignin recondensation.

Acid pretreatment can be applied for hemicellulose removal prior to enzymatic hydrolysis as well as for direct production of monomeric sugars from both cellulose and hemicellulose depending on the severity of the process (see process scheme in Fig. 18) [272,273]. This severity may also be expressed by the severity factor R_0 (vide supra) of the pretreatment. Shorter reaction times and lower temperatures can be applied to obtain the same severity factor compared to aqueous

pretreatment due to the lower pH values in acid pretreatment [254]. Acid pretreatment of (ligno)cellulose is generally performed with dilute or concentrated acid solutions at elevated and low temperatures, respectively [54]. HCl [274] and H₂SO₄ [275] are historically used, but there are several reports on the use of other acids like HF [276], HNO₃ [277], H₃PO₄ [278], SO₂ (in combination with steam pretreatment, *vide supra*) [272], organic acids (e.g. maleic acid [279], fumaric acid [280], oxalic acid [281], formic acid [282], and acetic acid [283]), and heteropoly acids [284]. Dicarboxylic acids, like oxalic acid, are known to hydrolyze β-1,4 glycosidic bonds more selectively than H₂SO₄ [285,286]. In the case of oxalic acid, this might be attributed to the lower acid dissociation constant (pK_a = 1.25, 4.14 vs. -3, 1.99 for H₂SO₄), which leads to less severe dehydration reactions. Furthermore, oxalic acid with its two distinct carboxylic acid groups shows similarities with the efficient and selective acid-base active site of (hemi)cellulolytic enzymes, which involves two carboxylic acid groups as well [281]. Concentrated acid solutions can swell or dissolve cellulose and can be used at low temperatures, which is energetically more favourable than using dilute acids at elevated temperatures. However, soluble acids (especially at higher concentrations) are hard to recycle, very corrosive, and they lead to the production of large amounts of neutralization waste. Some concentrated organic acids, like formic acid and acetic acid, even dissolve lignin [57]. In case of heteropoly acids, especially the partial Cs salts can be removed upon precipitation [34].

Severe acid treatments (low pH, high temperatures and/or long residence times) lead to the degradation of liberated sugars to furans (like HMF and furfural), carboxylic acids (such as levulinic and formic acid), and insoluble humic substances [272,287,288]. Although sugar degradation products imply sugar losses and can be inhibitory to microorganisms, furans and levulinic acid are interesting platform molecules for the production of fuels, chemicals, and polymers [289–291]. The large scale acid-catalyzed conversion of (ligno)cellulose to levulinic acid (up to 70 % yield) is established in the Biofine Process, which proceeds in two stages [292]. Less severe acid treatments prevent sugar degradation but they are less efficient in (hemi)cellulose hydrolysis. Many different acid types, both soluble and insoluble, have been used to directly convert various cellulose sources into chemicals, with levulinic acid, HMF, and lactic acid being the most favourable ones [12,291,293]. The use of biphasic conditions enables high HMF yields through the extraction of this reactive chemical from the aqueous phase into an organic phase, which avoids further converting to levulinic or formic acid [93]. There is a vast literature now studying the best circumstances of kinetics (true conditions and catalysis) and extraction ability (through solvent choices and additives) to improve HMF yields [93,294–296].

Acid conversion of (hemi)cellulose is also performed in alcohols instead of water since it can yield alkylglucosides, xylosides, and alkyl levulinate [45,297–300]. Compared to hydrolysis in water, conversion of (hemi)cellulose in alcohols has some advantages, such as improvement of reaction rate and product yield, inhibition of humins and chars. For instance, conversion of cellulose to alkyl levulinate in alcohol gives a higher yield than levulinic acid obtained in water [235,301]. The presence of Brønsted acid sites promotes the formation of alkyl levulinate, while the strong Lewis acid sites facilitate the formation of levulinic acid in water [301–303]. Similarly, conversion of cellulose in alcohol gives higher yield to alkylglucosides than that to produce glucose in water at similar conditions [304]. In addition to methyl levulinate, Sn^{II}-triflate can transform cellulose to a mixture of useful-hydroxyesters such as methyl lactate, methyl vinyl glycolate, and methyl-4-methoxy-2-hydroxybutanoate in methanol [305].

Another way to stabilize products is foreseen in the bifunctional approach. For example, hydrolytic hydrogenation at elevated temperatures constitutes an interesting option for cellulose valorization [6,10,11,19,34,35,187,204,306–312]. In hydrolytic hydrogenation, liberated monomeric sugars are immediately hydrogenated to more thermo-stable sugar alcohols (mainly sorbitol) using metal catalysts.

Similarly to sugars, further acid-catalyzed dehydration of these sugar alcohols can occur, forming polyols like sorbitan and isosorbide, but other degradation stays limited [6,10,28]. Sugar alcohols and their dehydration products are key molecules for the production of fuels (such as H₂ and alkanes), chemicals, and polymers [28,313–315]. The hydrolytic hydrogenation of cellulose to hexitols (mainly sorbitol, sorbitan, and isosorbide) has been the subject of research for decades. In this respect, Sharkov emphasized the importance of lignocellulose pretreatment for the chemo-catalytic conversion of lignocellulose polysaccharides to polyols: impurities like proteins, tannins, pectins, and minerals were found to deactivate hydrogenation catalysts quite rapidly [187]. In addition to sugar alcohol production, cellulose can be converted to other alcohols such as ethylene glycol, acetol, or propylene glycol [112,316–320]. One-pot conversion of cellulose to gasoline also follows a bifunctional approach. It can be achieved by hydrogenation of sugar obtained from hydrolysis of cellulose *via* acid to sugar alcohols, followed by hydrodeoxygenation of sugar alcohols to gasoline in the aqueous phase [209,321,322]. It was found that the presence of biogenic impurities such as amino acids with sulfur deactivates the Ru/C catalysts [321]. Gasoline precursors from cellulose can also be realized directly, combining bifunctional catalysis with biphasic conditions. Mechanistically, it involves dehydration of sugars to HMF in the aqueous phase, followed by hydrodeoxygenation of HMF to gasoline in an organic phase [323–325]. In this biphasic system, the hydrodeoxygenation catalyst is kept in the organic phase to avoid the hydrogenation of sugars to sugar alcohols in the aqueous phase, and allow HMF to diffuse in the organic phase where it is converted into alkanes, using modified Ru/C catalyst. Since HMF and sugar are unstable under acidic condition at high temperature, lower concentration of sugar and HMF is preferred to avoid their side reactions. Therefore, cellulose with large particles or low surface area can give higher gasoline yield due to its low conversion rate [325].

4.5. Alkaline

Kraft pulping is the dominant wood pulping process since the 1940s [271]. In the Kraft process, high-quality cellulose fibers for the paper industry are produced from wood, using a combination of NaOH and Na₂S for delignification. Alkaline pretreatment removes lignin through cleavage of lignin ether bonds and solubilizes hemicellulose through saponification of the intermolecular ester bonds between hemicellulose and lignin, increasing porosity and overall cellulose accessibility (see process scheme in Fig. 18) [55,326]. Alkaline pretreatment chemicals include NaOH [327], Ca(OH)₂ (lime) [328], and ammonia [329] and they can be used in combination with oxidative agents like O₂ and H₂O₂ for delignification improvement [326].

Degradation of cellulose under alkaline conditions may also occur, but cellulose is much more resistant to basic attack compared to hemicellulose [326]. Nevertheless, alkaline solutions can increase the accessibility of cellulose to exoglucanases through its depolymerization. For example, Bali et al. reported a reduction of poplar cellulose DP_n from 342 to 77 after 1 h of pretreatment in a 2% NaOH solution at 393 K [330]. Alkaline cellulose degradation takes place through peeling of reducing end-groups or random scission of cellulose chains, ultimately resulting in the formation of organic acids such as lactic acid (through retro-aldol reactions and H-shifts) and concomitant neutralization of the alkaline solution [293,331].

Due to the substantial amount of delignification during alkaline pretreatment, higher cellulose conversions are often reported after an alkaline pretreatment compared to acid pretreatment [327,332]. Silverstein et al. reported enzymatic cotton stalk glucan conversions of 61 % and 24 % after NaOH pretreatment and H₂SO₄ pretreatment, respectively [327]. Zhao et al. reported enzymatic Crofton weed stem cellulose conversion ratios of 7.40 % and 2.61 % (w/w, based on the cellulose in the pretreated samples) after NaOH pretreatment and H₂SO₄ pretreatment, respectively [332].

More concentrated aqueous solutions of NaOH (> 8%) are reported to induce swelling and dissolving of the native cellulose I. Recrystallization to the thermodynamically more favorable cellulose II polymorph occurs after neutralization of NaOH or washing [81,333–335]. This transformation is called ‘mercerization’. Disruption of hydrogen bonds during fiber swelling decreases the crystallinity of cellulose and increases its accessibility and reactivity, despite the partial recrystallization to cellulose II [336,337]. There is some disagreement in literature about the reactivity of cellulose II. Some authors report a decreased reactivity compared to cellulose I [75,338], while others report an increased reactivity [339,340]. Wada et al. tentatively suggested that an increase in reactivity is ascribed to the difference of hydrophobic forces between the cellulose sheets in cellulose I and II, with cellulose I displaying the strongest hydrophobic interaction [340]. Nevertheless, a beneficial influence of the lower crystallinity of cellulose II after mercerization on its reactivity cannot be ruled out.

Liquid ammonia is able to swell cellulose I and II fibers through the disruption of cellulosic hydrogen bonds and the formation of a cellulose-ammonia complex [341–343]. Recrystallization to polymorphs cellulose III_I and III_{II} occurs after evaporation of ammonia, depending on the extent of recrystallization proportional to the temperature applied during pretreatment (Table 2) [337,343,344]. Cellulose III_I is believed to be more readily degradable than cellulose I due to its larger unit cell dimensions [345]. Igarashi et al. discovered that ammonia treatment of cellulose I to obtain cellulose III_I also results in an increased number of cellulase-accessible lanes on the cellulose surface, which avoids the occurrence of cellulase traffic jams and hence significantly enhances the number of moving cellulase molecules and enzymatic hydrolysis rates [346].

Mittal et al. reported a significant decrease and alteration of crystallinity and a concomitant increase in enzymatic digestibility of Avicel PH-101 (Table 2), α -cellulose, cotton linters, and corn stover cellulose after pretreatment with aqueous NaOH and liquid ammonia [337]. These cellulose pretreatment methods could also be interesting for chemo-catalytic cellulose conversion.

Alkaline pretreatment has been applied to improve chemo-catalytic biomass conversions suffering from lignin inhibition. Pang et al. reported significant increases in corn stalk conversion and glycol yield with a solid Ni-W₂C/AC catalyst after pretreatment with hot limewater (Ca(OH)₂), NaOH, ammonia, or a subsequent combination of ammonia and H₂O₂ pretreatment (Fig. 17a; A, C, E, and H) [110]. During FTIR analysis, a reduction was observed in absorbance at 3348 cm⁻¹ attributed to the OH stretching vibration of cellulose after some of these pretreatments, which they attributed to a disruption of cellulose hydrogen bonds. This reduction probably partially compensates the low level of delignification (3%) during hot limewater pretreatment (Fig. 17b; H). The most extensive delignification was achieved with ammonia and H₂O₂ (75 %), leading to a distinct increase in glycol yield

Table 2
Crystallinity and enzymatic conversion data of Avicel PH-101 cellulose before and after selected NaOH and ammonia pretreatments. Data from Mittal et al. [337].

| | | Treatment conditions | | | |
|--|------------------|----------------------|--------------|-------------------------|-------------------------|
| | | None | NaOH (298 K) | NH ₃ (298 K) | NH ₃ (403 K) |
| Amorphous content (%) | | 26 | 47 | 46 | 26 |
| Crystalline cellulose content (CrI, %) | I | 74 | – | – | – |
| | II | – | 53 | – | – |
| | III _I | – | – | 54 | 74 |
| Crystallite size (Å) | | 46 | 37 | 38 | 55 |
| Cellulose conversion (%) | 16 h | 39 | 66 | 49 | 36 |
| | 24 h | 46 | 76 | 59 | 49 |

CrI: crystallinity index, determined using the XRD amorphous subtraction method.

(from 3 % to 48 %) and cellulose conversion (from 83 % to 99 %). Besides, pretreatment of miscanthus with ammonia improves its conversion to ethylene glycol in the presence of tungstic acid and Raney Ni [188]. The ammonia pretreatment afforded a thorough delignification and removal of epidermal tissue components, such as waxes, pectins, and fatty acids, which led to a significant ethylene glycol yield increase from ± 13 % to ± 40 % after 2 h of reaction at 518 K at 10 wt% feedstock concentration. The low ethylene glycol yield from raw miscanthus at these high feedstock concentrations is attributed to the profound deactivation of Raney Ni by compounds originating from both epidermal tissues and lignin. Fukuoka et al. applied an alkali-explosion and neutralization pretreatment (1.4 % NaOH, 24 h at 298 K and 2 min at 463 K, followed by explosion and neutralization with HCl) to silver grass to improve its conversion into sugar alcohols in the presence of a supported Pt catalyst through the removal of lignin, salts, and metal catalyst poisons like P and S [252]. Similar to the hydrothermal pretreatment of silver grass (*vide supra*), the removal of salts and metal catalyst poisons enabled an increased pentitol yield and reduced glycol byproduct yield. A significant hexitol yield increase from < 1 % to 20 % (based on cellulose content) was obtained after 24 h of reaction at 463 K as a result of the extensive delignification (the Klason lignin content decreased from 21 % to 11 %) during pretreatment. This pretreatment was also successfully applied to Amur silver grass (29 % hexitol yield) and wheat straw (23 % hexitol yield). Goswami et al. also used an alkaline pretreatment (4% NaOH, 393 K, 1 h) to improve sugar yields from rice straw. The pretreatment removed up to 50 % of the original lignin, enabling sugar yields as high as 26 % after 4 h of reaction at 410 K in the presence of a glycerol-based solid carbon acid catalyst [347]. Recently, chemo-catalytic conversion of cellulose into ethanol has been demonstrated with high yield over Ru-WO_x/HZSM-5 [348], Mo/Pt/WO_x [349], H₂WO₄-Pt/ZrO₂ combination catalyst [350], and H₃PO₄ and Ni@C combination catalyst [351]. Ethylene glycol is an intermediate of cellulose to ethanol in this chemo-catalytic pathway [348–350]. The yield of ethanol reaches 26.3 % (carbon yield based on the input carbon in the lignocellulose) in conversion of raw miscanthus over Mo/Pt/WO_x. After alkaline pretreatment to remove lignin, the ethanol yield is improved to 43.1 %, which is similar to that obtained from pure cellulose [349].

4.6. Ammonia fiber expansion (AFEX) and extractive ammonia (EA)

Ammonia fiber expansion (AFEX), sometimes referred to as ammonia fiber explosion, is based on the same concept as steam explosion, except that liquid ammonia is used instead of steam and no mass loss occurs during the pretreatment (dry-to-dry process) [55,64,352].

AFEX pretreatment is typically performed by contacting liquid ammonia (0.3–2.0 g NH₃/g dry biomass) with moist biomass (0.1–2 g H₂O/g dry biomass) and heating (313–453 K) for 5–60 min before depressurization (see process scheme in Fig. 19) [352]. Ammonolytic and hydrolytic cleavage of intermolecular ester bonds between hemicellulose and lignin occurs during the AFEX process due to the action of ammonia [64,353]. Fermentation inhibitory compounds like furans found after acid pretreatment are hardly formed here [64]. After depressurization, migration of solubilized hemicellulose, lignin, and cell-wall extracts to the outer cell wall surfaces and corners creates pores with diameters ranging from 10 to 1000 nm, enhancing the cellulose accessibility to cellulases [354]. In contrast to liquid anhydrous ammonia, conventional AFEX pretreatment does not significantly alter cellulose crystallinity due to the high concentration of water in the employed ammonia solution [354]. Presence of water prevents the insertion of ammonia in the cellulose crystal structure.

Holtzappple et al. reported nearly quantitative sugar yields in the enzymatic hydrolysis of AFEX pretreated Bermuda grass and bagasse using very low enzyme loadings (5 IU/g) [355]. Disadvantages of AFEX pretreatment include its poor performance on high lignin content samples and the need for ammonia recycling [55]. Also, pore diameters

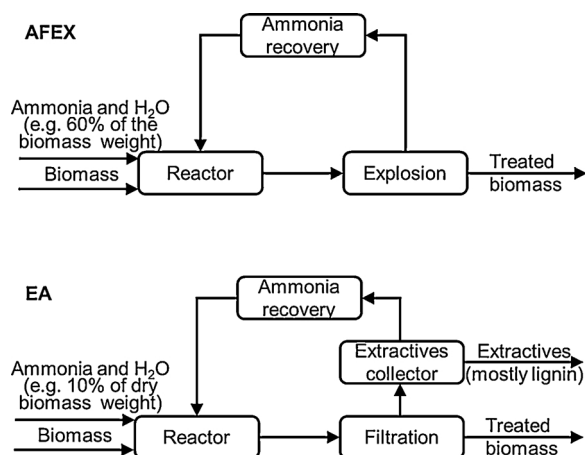


Fig. 19. Process flow scheme of AFEX and EA pretreatment.

in the nm range are expected to be insufficient for many conventional solid chemo-catalysts. For instance, solid hydrotalcite nanoparticles, used for cellulose hydrolysis, already have particle diameters in the μm range [356]. However, hydrolysis in hot (acidic) water, often the rate-determining step to produce valuable chemicals from cellulose, will undoubtedly benefit from the improved cellulose accessibility. We therefore expect AFEX pretreatment to be a promising tool to activate cellulose for chemical processing.

Transformation of cellulose I to cellulose III through liquid ammonia can increase the enzymatic hydrolysis rate up to 5 folds [357,358]. Therefore, a pretreatment method termed 'Extractive Ammonia (EA)' was developed to simultaneously extract lignin and transform cellulose I to highly digestible cellulose III via liquid ammonia (around 10 % water) at 393 K (see process scheme in Fig. 19) [359,360]. In the case of AFEX, the moisture is higher (ca. 60 %), which impedes the formation of cellulose III. Nearly all polysaccharides can be maintained through EA with lignin removal of 45 %. Although AFEX also keeps most of the sugars, the dissolved lignin is deposited on the pretreated cell wall after the evaporation of ammonia. Therefore, EA pretreated corn stover generates a higher sugar yield compared to the traditional AFEX with using 60 % less enzyme. Besides, the EA consumes much less ammonia (0.022 g per 100 g biomass) than AFEX (0.02 g per g biomass). The disadvantage of EA is the high operation pressure, which will increase the capital cost of the pretreatment unit. It should be noted as well that the incorporation of nitrogen into biomass through ammonia pretreatment could lead to the generation of NO_x during incineration of related compounds or an additional hydrodenitrogenation before burning [361]. In addition, the presence of nitrogen might deactivate the catalysts of a chemo-catalytic process. In summary, although ammonia-based pretreatment technology has shown advantages for biochemical process [362], the impact on chemo-chemical process is uncharted terrain.

4.7. Oxidative pretreatment

Oxidizing agents are since long used to bleach paper pulps for the production of white paper, which can serve as a value-added end product in biorefineries. Oxidizing agents like H_2O_2 [363], O_3 [364], O_2 [365], air [365], peracids [366], hypochlorite [367], and chlorite [368] can be used for biomass delignification to improve the accessibility of cellulose. However, the formation of inhibitory phenolic compounds can compromise further downstream processing by enzymes and microorganisms [53]. Oxygen and H_2O_2 act as highly reactive free radicals in alkaline solutions and they are therefore frequently used to improve delignification during alkaline pretreatment [326]. In addition, wet oxidation pretreatments are known to open the crystalline structure of cellulose [369]. Degradation of hemicellulose and cellulose can also

occur during oxidative pretreatment due to the mostly unselective action of the oxidizing agents [53,370]. In this respect, peracetic acid is reported to selectively degrade lignin [366]. Teixeira et al. reported an impressive increase in enzymatic cellulose hydrolysis from 6.8 % to 98 % after hybrid poplar and sugar cane bagasse delignification with 21 % peracetic acid at ambient temperatures [366]. An enzyme mix of xylanase/ β -glucosidase was proven more effective than cellulase preparations due to the presence of undegraded xylan in pretreated samples. In addition, Xu et al. reported that part of the hydroxymethyl groups on glucose units could be oxidized to carboxyl groups during the oxidation pretreatment [371]. These acid sites can act as the active sites for the catalytic depolymerization of cellulose. The yield of glucose is significantly enhanced after oxidation pretreatment compared to non-pretreated or ball-milled α -cellulose.

Successful application of oxidative pretreatment for chemo-catalytic conversion of lignocellulose has been reported very recently. Pang et al. have shown significant increases in corn stalk to glycol conversion in the presence of a solid $\text{Ni-W}_2\text{C}/\text{AC}$ catalyst after delignification with H_2O_2 (43 % lignin removal). Thanks to this pretreatment, the glycol yield and conversion increased from 3% to 36 % and from 83 % to 95 %, respectively (Fig. 17a and b; D). The authors also tested a combination of ammonia and H_2O_2 pretreatment, removing 75 % of lignin showing a glycol yield increase from 3 % to 48 % and a conversion increase from 83 % to 99 % (Fig. 17a and b; A) [110]. Interestingly, the glycol yield correlates well with the amount of delignification and corn stalk conversion was near complete after both pretreatments.

4.8. Organosolv fractionation

Organosolv pretreatment of lignocellulosic biomass relies on degradation and solubilization of hemicellulose and lignin in non-aqueous or aqueous organic solvents, improving cellulose purity, accessibility and degradability (Fig. 20) [57,166]. Water and organic solvents can also induce significant swelling of cellulose through a disruption of the internal cohesion, mainly in the intercrystalline, amorphous regions [372–376].

Different organic solvents have been used in organosolv pretreatment [57,166], including alcohols (e.g. ethanol) [377], ketones (e.g. acetone [378] and methyl isobutyl ketone) [379], organic acids (e.g. formic acid [380] and acetic acid) [381], organic peracids (e.g. performic acid) [382], and esters (e.g. γ -valerolactone, GVL) [383]. The ability of organic solvents to solubilize lignin depends on the Hildebrand solubility parameter or δ -value of the solvent, which is ideally $\pm 11 \text{ cal}^{1/2}/\text{cm}^{3/2}$ for adequate lignin solubility [384]. Examples of good lignin solvents are acetic acid ($\delta = 10.1 \text{ cal}^{1/2}/\text{cm}^{3/2}$), formic acid ($\delta = 12.1 \text{ cal}^{1/2}/\text{cm}^{3/2}$), ethanol ($\delta = 12.9 \text{ cal}^{1/2}/\text{cm}^{3/2}$), acetone ($\delta = 9.7 \text{ cal}^{1/2}/\text{cm}^{3/2}$), and γ -valerolactone ($\delta = 11.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$) [166,385].

Most organosolv pretreatments are carried out auto-catalytically at high process temperature (458 – 483 K), but acid catalysts can be added to increase process severity and hence the rate of delignification and hemicellulose degradation [57,166]. Additionally, acid catalysts are able to lower the degree of polymerization of cellulose during organosolv pretreatment, making cellulose more amenable for subsequent degradation by e.g., exoglucanase enzymes [166]. Other agents like NaOH are added as well to improve the delignification.

The organic solvent induced cellulose swelling is attributed to the amount of hydrogen bonding interactions between cellulose and the solvent, correlated to acid-base/dispersive interactions and solvent molar volume [374]. These hydrogen bonding interactions induce solvent uptake in the amorphous cellulose structure, resulting in a reduced cohesion within cellulose fibers. The swelling rate increases excessively with temperature [373]. Boluk has emphasized the importance of high electron-pair donor/acceptor number ratios (DN/AN) and high electron-pair donor/acceptor number differences (DN-AN) for the good swelling behavior of organic solvents [374]. Hydrogen atoms in the

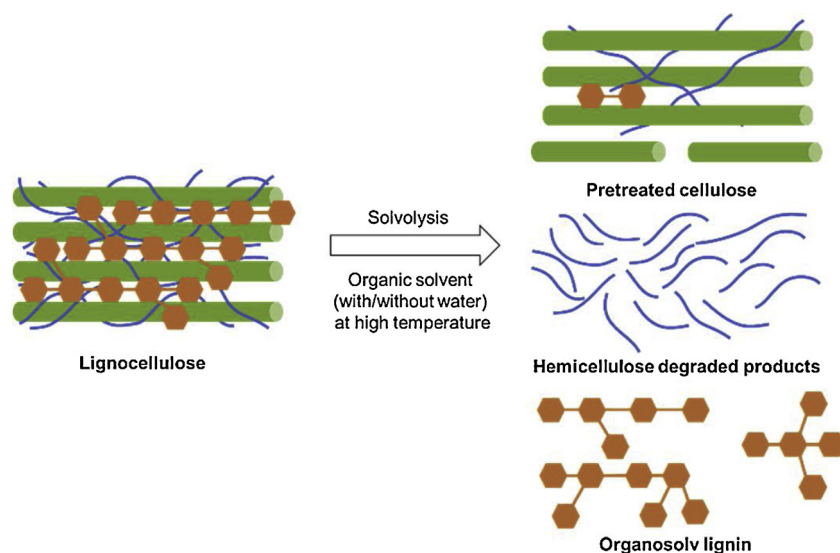


Fig. 20. Scheme of organosolve pretreatment of lignocellulose.

hydroxyl groups of cellulose act as electron acceptors (acid), implying that the organic solvent should possess a distinct electron donor (base) capability for improved hydrogen bonding interactions with cellulose. Note that the base strength should be stronger than that of the oxygen atoms, contributing to the same hydrogen bonds. Basicity of the oxygen and how it probably protects cellulose from acid-catalyzed degradation has been recently investigated in a theoretical study by Loerbroks et al. [386].

Organosolv treatment has been studied extensively for both paper manufacturing, for which high cellulose purity, high fiber strength, and crystallinity are essential, and as a pretreatment prior to (enzymatic) hydrolysis, for which a high cellulose reactivity is important [57,377,387–390]. Thorough removal of residual solvents from the cellulose pulp is necessary for subsequent biochemical processing due to their possible inhibitory effect on enzymatic hydrolysis and/or fermentation [57]. Chemo-catalytic processes probably doesn't require that high purity. Organosolv pretreatments are especially of interest for use in biorefineries on account of their ability to fractionate lignocellulosic biomass into three separate, high-quality process streams: a solid cellulose-enriched pulp, a solid, high-purity lignin precipitate, an aqueous mixture of hemicellulose products (such as sugars, sugar derivatives like furfural and organic acids), and extractives (such as minerals and proteins) [57,166]. In such an approach, the lignin stream can be used as well for a wide variety of applications like adhesives, resins, and the production of fuels and chemicals [69]. Several organosolv pretreatment processes have proven their efficiency and have been up-scaled, such as the Organocell [391] (methanol/water/NaOH), Alcell [392] (ethanol/water), and CIMV (Compagnie Industrielle de la Matière Végétale) [387] ((per)acetic acid/(per)formic acid/water) processes. Particularly, ethanol as a solvent is of interest due to its low price, low boiling point, good lignin solubility, and excellent compatibility with bioethanol production, but the other processes have proven their viability and efficiency as well [57,166].

Although organosolv processes are classically evaluated in terms of enzymatic hydrolysis efficiency, they are also investigated for enhanced chemo-catalytic conversion. Pang et al. demonstrated the efficiency of organosolv pretreatment in the chemo-catalytic conversion of corn stalk [110] and miscanthus [188]. An increase in corn stalk conversion and glycol yield was reported using a solid Ni-W₂C/AC catalyst after organosolv pretreatment with 1,4-butanediol at 473 K. This pretreatment, removing 53 % of the lignin, enabled a yield increase from 3% to 28 % and a conversion increase from 83 % to 94 %. Pretreatment with ethanol/water (50:50) at 393 K removes less lignin (22 %), and this is

reflected in the smaller yield (from 3% to 13 %) and conversion (from 83 % to 88 %) increase (Fig. 17a and b; B and F) [110]. The modest delignification obtained by the ethanol organosolv pretreatment thus explains the minor improvement in glycol yield. Miscanthus was pretreated in methanol, ethanol, acetone, and ammonia for 2 h at 423 K to improve its conversion to ethylene glycol through delignification and removal of inhibitory epidermal tissue components. Ethanol pretreatment was also carried out with the addition of ammonia or NaOH to improve delignification. The largest extent of delignification was achieved with alkali-based organosolv pretreatments (ethanol/ammonia, ethanol/NaOH, and ammonia), resulting in an ethylene glycol yield increase from ± 13 % for raw miscanthus to ± 40 % for all three pretreated samples after 2 h of reaction at 518 K in the presence of tungstic acid and Raney Ni at 10 % feedstock concentration.

Recently, there are some new and interesting approaches for biomass fractionation. In the OrganoCat process, lignocellulosic biomass such as beech wood, mate tea, and reed can be fractionated into cellulose, hemicellulose, and lignin using a biphasic system consisting of an aqueous phase oxalic acid catalyst and an organic 2-methyltetrahydrofuran (2-MeTHF) phase [393–396]. Mild processing at 413 K induces an effective fractionation and prevents the degradation of liberated sugars to by-products like furfural. Lignin fragments are extracted with 2-MeTHF, hemicellulose sugars accumulate in the aqueous phase, and cellulose is obtained as a solid pulp. After recovery of the cellulose pulp through filtration, the system can be reused several times in repetitive-batch mode, which significantly improves process economics and enables processing of up to 400 g L⁻¹ of beech wood [393]. This pretreatment can cause a significant enhancement in enzymatic hydrolysis rate of the cellulosic phase (such as 6.7 fold for bamboo) compared to unpretreated lignocellulose [394,396]. Since oxalic acid can be crystallized from the aqueous phase, an aqueous solution of hemicellulose sugars can be obtained as well, while lignin can be recovered through the distillation of 2-MeTHF from the organic phase. Although oxalic acid can be crystallized from the aqueous stream, several hurdles appear, such as the removal of water and the thermal degradation of oxalic acid. Therefore, another biogenic catalyst, 2,5-furandicarboxylic acid (FDCA), was evaluated in the OrganoCat process [397]. FDCA can efficiently fractionate the three main components of lignocellulose. Moreover, more than 97 % of FDCA can be recovered by using a simple precipitation method.

GVL has been identified as a solvent with excellent properties for biomass conversion [398]. Since the δ -value of GVL ($\delta = 11.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$) is close to the ideal value ($\pm 11 \text{ cal}^{1/2}/\text{cm}^{3/2}$) for adequate

lignin solubility, it is also used to pretreat lignocellulose for selective lignin dissolution [399]. Although the δ -value decreases through adding water, GVL mixtures with water can still dissolve lignin [385]. Up to 80 % of lignin is removed from beech wood by using 80 % GVL and 20 % water at 393 K with 75 mM H₂SO₄ [399]. More than 96 % of cellulose is left as a solid residue, which can undergo enzymatic hydrolysis to sugar. The solubilized hemicellulose (including oligomeric and monomeric sugars) stays in the aqueous phase after GVL recovery through liquid CO₂ extraction. The convertibility of GVL-based cellulose is three times higher than that of other organic solvents such as tetrahydrofuran or ethanol and 20 times than that of hot water pretreatment.

Recently, Wyman et al. developed a co-solvent-enhanced lignocellulosic fractionation (CELf) method, which is realized by adding tetrahydrofuran (THF) as organic solvent in the dilute acid pretreatment. The sugars and ethanol yields are significantly improved as a result of a very high lignin removal with CELf pretreatment compared to the dilute acid pretreatment [400–402]. Up to 95 % of theoretical yield of sugar can be obtained from CELf-pretreated corn stover after enzymatic hydrolysis with very low enzyme loading (2 mg_{enzyme} g_{glucan}⁻¹) [400]. Unprecedented ethanol titers of 79.2, 81.3, and 85.6 g·L⁻¹ in batch shake flask, corresponding to ethanol yields of 90.5 %, 86.1 %, and 80.8 % at solids loadings of 20.0 wt.%, 21.5 wt.%, and 23.0 wt.%, respectively, are achieved by optimizing simultaneous saccharification and fermentation of CELf-pretreated corn stover [403]. Besides, lower enzyme loadings are required for CELf-pretreated corn stover compared to diluted acid pretreated corn stover [401,403]. The role of water and THF on different polymers (*i.e.* cellulose and lignin) is investigated by molecular simulation. Since cellulose has many hydroxyl groups, water will stay at the hydrophilic cellulose faces due to the formed hydrogen bond, while THF will stack on the hydrophobic faces. Therefore, THF and water automatically separate on the local surface of a cellulose fiber [404]. The stacking of THF to the hydrophobic sites of cellulose fibers may block the aggregation of lignin on those surfaces. The THF-water can coordinate with and expand native lignin interunit linkages to promote their acid-catalyzed cleavage [405].

Although those new pretreatment technologies have significantly improved the efficiency of bio-chemical process, the influence on the chemo-catalytic conversion of cellulose is still unclear as they are hardly investigated.

4.9. Cellulose solvents

Lindman et al. theorized that the low solubility of cellulose in water is due to both hydrogen bonding and hydrophobic interactions within cellulose [406]. Cellulose solvents that overcome this internal cohesion are generally divided into two categories: non-derivatizing and derivatizing solvents. Non-derivatizing solvents physically dissolve cellulose merely through intermolecular interactions, while derivatizing solvents dissolve cellulose in combination with the formation of unstable ether, ester, or acetal derivatives of the cellulose hydroxyl groups [407,408]. Cellulose solvents include aqueous inorganic complexes (*e.g.* copper(II) ethylenediamine (Cuen)), aqueous bases (*e.g.* 10 % NaOH), mineral acids (*e.g.* H₃PO₄), ionic liquids (*e.g.* 1-ethyl-3-methylimidazolium acetate ([emim]OAc)), molten salt hydrates (*e.g.* ZnCl₂·4H₂O), dipolar aprotic solvent/LiCl solvents (*e.g.* DMAc/LiCl), DMSO-based solvents (*e.g.* DMSO/methylamine), tricomponent solvents (*e.g.* DMSO/triethylamine/SO₂), NH₃-based solvents (*e.g.* NH₃/NH₄SCN), tertiary amine oxides (*e.g.* N-methyl-morpholine-N-oxide (NMMO)), and alkali hydroxide/urea solvents (*e.g.* LiOH/urea) [407,409,410]. Derivatizing cellulose solvents include trifluoroacetic acid, formic acid, DMF/N₂O₄ and DMSO/paraformaldehyde [407]. Ionic liquids and molten salt hydrates can be applied both as reaction solvents and as catalysts in (ligno)cellulose conversion [411–416]. Certain ionic liquids such as [emim]OAc are also able to solubilize lignin simultaneously [417].

Ionic liquids [410,411,418–420], concentrated acids (*e.g.* H₃PO₄) [421,422], trifluoroacetic acid [423]) and bases (*e.g.* NaOH, ammonia) [337] have been used for the activation of cellulose prior to enzymatic or chemo-catalytic conversion. With an H₃PO₄-pretreatment, Deng et al. reported an increase in sorbitol/mannitol yield from 13 % to 73 % during hydrolytic hydrogenation of cellulose with 1 wt% Ru/CNT, a carbon nanotube-supported ruthenium catalyst, at 458 K [422]. Best results were obtained after 40 min of H₃PO₄-pretreatment with 85 % H₃PO₄ at 323 K followed by regeneration through recovering with water, filtration, washing, and drying. This H₃PO₄-pretreatment efficiently decreased the cellulose crystallinity index from 85 % to 33 % (XRD, using the peak height method) through cellulose swelling and also decreased the cellulose DP_v from 221 to 106 through mild cellulose hydrolysis. Both pretreatment effects are expected to have a beneficial influence on the rate-determining cellulose-to-glucose hydrolysis.

During (ligno)cellulose pretreatment with ionic liquids, cellulose is generally recovered and isolated through precipitation after (ligno) cellulose dissolution *via* the addition of an anti-solvent like water or alcohol [424]. Cellulose regenerated from ionic liquids exhibits a reduced or altered (cellulose II) crystallinity, leading to increased accessibility and reactivity [425]. Combined with an acid catalyst, like *p*-toluenesulfonic acid or Amberlyst™ 15Dry, ionic liquid pretreatment can even achieve concomitant depolymerization of cellulose. Cellulose oligomers with DP of 10 were isolated after 5 h of reaction, something which is impossible to achieve in dilute acid hydrolysis due to the persistency of crystalline cellulose in aqueous slurries [414,415]. Alternatively, cellulose can also be purified from lignocellulosic biomass through ionic liquid-mediated selective lignin dissolution, followed by filtration. This so-called Ionosolv Process does not significantly alter the crystallinity of cellulose [410]. [emim]OAc and [bmim]Cl (1-butyl-3-methylimidazolium chloride) are commonly used ionic liquids in (ligno)cellulose pretreatment prior to enzymatic and chemo-catalytic cellulose conversion, respectively. After a thorough screening of twenty-one ionic liquids for cellulose and wood chip dissolution, Zavrel et al. have demonstrated [emim]OAc to be the most efficient ionic liquid for cellulose dissolution and the second most efficient for wood chip dissolution [426]. Li et al. reported a 54.4-fold increase in the initial enzymatic hydrolysis rate of the cellulose component of switchgrass after a short [emim]OAc pretreatment (3 h, 433 K), resulting in 96 % cellulose digestibility in only 24 h [427]. Without this pretreatment, only 2.7 % of cellulose digestibility was obtained in 24 h. The initial rate after [emim]OAc pretreatment was also found to be 16.7 times higher than the initial rate after dilute H₂SO₄ pretreatment. The successful pretreatment with [emim]OAc was attributed to its amorphization and delignification action. Shi et al. demonstrated that using 50–80 % [C2mim][OAc] in water can also achieve an efficient dissolution of cellulose [428]. [bmim]Cl pretreatment has been used prior to hydrolysis of pure cellulose with solid acid chemo-catalysts like cation-exchange resins, such as Nafion NR50 and Amberlyst 35, sulphated zirconia, and phosphoric acid-activated carbon [199,418,419,429]. Kim et al. reported a remarkable increase in glucose yield from 2.1 % to 35 % using Nafion NR50 after a 2 h [bmim]Cl pretreatment of microcrystalline cellulose at 403 K [418]. Benoit et al. observed an increase in glucose yield from < 1 % to 14 % using Amberlyst 35 after a 3 h [bmim]Cl pretreatment of microcrystalline cellulose at 353 K [199]. Grisel and Smit applied a [bmim]Cl-pretreatment to Avicel PH-101 microcrystalline cellulose, resulting in an increase in cellulose conversion from 11 % to 37 % (glucose yield: 5% to 26%) and from 23 % to 83 % (glucose yield: 8 % to 54 %) after 4 h of reaction at 453 K in the presence of H-mordenite (Si/Al = 45) and Norit CAP Super (NCS) solid acid catalysts, respectively [429]. Keasling et al. demonstrated that the addition of Amberlyst 15, a protic acid resin, to the [C₄mim]Cl pretreatment of switchgrass increases the sugar yield tenfold [430], which means that less cellulase is required for effective saccharification. The XRD characterization shows that pretreatment of cellulose *via* 1-N-butyl-3-methylimidazolium chloride or 1-allyl-3-

methylimidazolium chloride can convert cellulose I to cellulose II [418,431]. Hydrolysis of 1-N-butyl-3-methylimidazolium chloride pretreated cellulose can facilitate the cellulose conversion to glucose [418]. Alcoholysis of 1-allyl-3-methylimidazolium chloride pretreated cellulose in methanol over $H_3PW_{12}O_{40}$ can produce methyl glucosides with yield of 70.2 wt%, which is higher than that of untreated cellulose (46.1 wt%) [431].

Main bottlenecks for implementation of ionic liquids as a pretreatment prior to cellulose conversion processes include their high price and the need for near-complete solvent recovery and recycling due to these high costs, build-up of impurities, and downstream deactivation of certain catalysts like enzymes [432–440]. George et al. designed some low-cost ionic liquids by using inexpensive feedstock such as H_2SO_4 and simple amines [441]. The designed hydrous ammonium hydrogen sulfate ionic liquids are still 75 % as effective as [Emim]OAc. Since the best performing ionic liquids are derived from non-renewable feedstocks, Socha et al. synthesized a series of tertiary amine-based ionic liquids from lignin and hemicellulose derived aldehydes such as vanillin and furfural, to overcome this issue [442]. With respect to enzymatic hydrolysis of ionic liquid pretreated switch grass to sugar, this pretreatment performs equally efficient in terms of overall sugar yield, although the hydrolysis rate is slower than for pretreatments with the traditional ionic liquid [Emim]OAc. This proved concept shows the potential to realize a ‘closed-loop’ biorefinery (Fig. 21).

In addition to low-cost ionic liquids, efforts in the development of ionic liquid tolerant enzymes or enzyme compatible ionic liquids look promising. Shi et al. were able to obtain a one-pot [emim]OAc pretreatment and enzymatic saccharification of switchgrass to 81.2 % glucose and 87.4 % xylose (monomers and oligomers) in 72 h at 343 K using a thermophilic and ionic liquid tolerant enzyme cocktail [443]. By combination of low toxicity of bio-derived ionic liquid such as cholinium lysinate, Xu et al. achieved one-pot pretreatment, saccharification and fermentation to yield concentrated sugars and high titer bio-ethanol (41.1 g L^{-1}) with high gravity biomass ($> 30 \text{ wt.}\%$) [444]. Although one-pot integrated biomass-to-bioethanol was achieved with bio-derived ionic liquids, it is challenging due to pH adjustment. In order to solve this, Sun et al. used CO_2 to control the pH [445]. Additionally, Sun et al. developed a low cost biocompatible protonic ionic liquid, ethanolamine acetate, which realizes the one-pot integrated biomass-biofuel (bioethanol) conversion without pH adjustment [446].

Moreover, a new class of green ionic solvents called deep eutectic solvents (DESs, a subgroup of low-transition-temperature mixtures (LTTMs)) such as choline chloride/urea (ChCl/urea (1:2)), may

constitute a potential alternative for ionic liquids. They tackle the high costs and hazards of ionic liquid, while still exhibiting comparable physicochemical properties [447–450]. Although ChCl/urea (1:2) does not significantly dissolve Avicel PH-105 microcrystalline cellulose ($< 0.2 \text{ wt}\%$ solubility in 12 h at 383 K), an exchange of Cl^- by OAc^- and addition of 15 % tributylmethylammonium chloride to the DES, yielded a green and inexpensive ionic fluid ([Ch]OAc/[TBMA]Cl) capable of dissolving 6 wt% of Avicel PH-105 in just 10 min at 383 K [450]. On the other hand, [bmim]Cl, a commonly used ionic liquid for cellulose activation, was only capable of dissolving 4 wt% of Avicel PH-105 in 8 h at 383 K. After complete dissolution in [Ch]OAc/[TBMA]Cl, Avicel PH-105 can be easily regenerated in a fully amorphous form upon addition of ethanol. The ionic fluid can easily be recycled without contamination of the regenerated cellulose, which is interesting in light of subsequent enzymatic conversion processes. Kim et al. synthesized a renewable and new class of DES from lignin-derived phenolic compounds such as 4-hydroxybenzyl alcohol, catechol, vanillin or *p*-coumaric acid [451]. These DESs can achieve high lignin removal for switchgrass: 61 % of lignin is removed by choline chloride/ *p*-coumaric acid, which facilitates high sugar release during the saccharification. Similar to the closed-loop process of ionic liquid synthesized from lignin and hemicellulose derived aldehydes, the use of lignin-derived phenols to synthesize DES for lignocellulose pretreatment will provide a ‘closed-loop’ for future biorefinery [452].

4.10. Non-thermal atmospheric plasma (NTAP)

Non-thermal atmospheric plasma (NTAP) pretreatment of cellulose is a relatively new and innovative way of improving cellulose degradability by reducing cellulose DP. The work of Benoit et al. highlights the potential of this pretreatment in cellulose conversion. For instance, microcrystalline Avicel PH-105 cellulose was partially depolymerized via NTAP pretreatment (11 kV, 2 kHz, 3 h), which reduced the DP_v from 200 to 120, leading to a glucose yield improvement from < 1 to 22 % after hydrolysis with solid acid Amberlyst 35 at 423 K for 1 h [199]. Interestingly, glucose yields after NTAP pretreatment were higher compared to ball milling and ionic liquid (such as [bmim]Cl, [bmim]Et₂PO₄, and [bmim]OAc) pretreatments, validating NTAP as a promising pretreatment for cellulose valorization. Furthermore, this research underlines the importance of cellulose DP reduction for efficient aqueous cellulose dissolution and valorization. Glucose yield could be further improved to 58 % by using ball milling pretreatment prior to NTAP pretreatment to reduce cellulose crystallinity [453]. Since NTAP

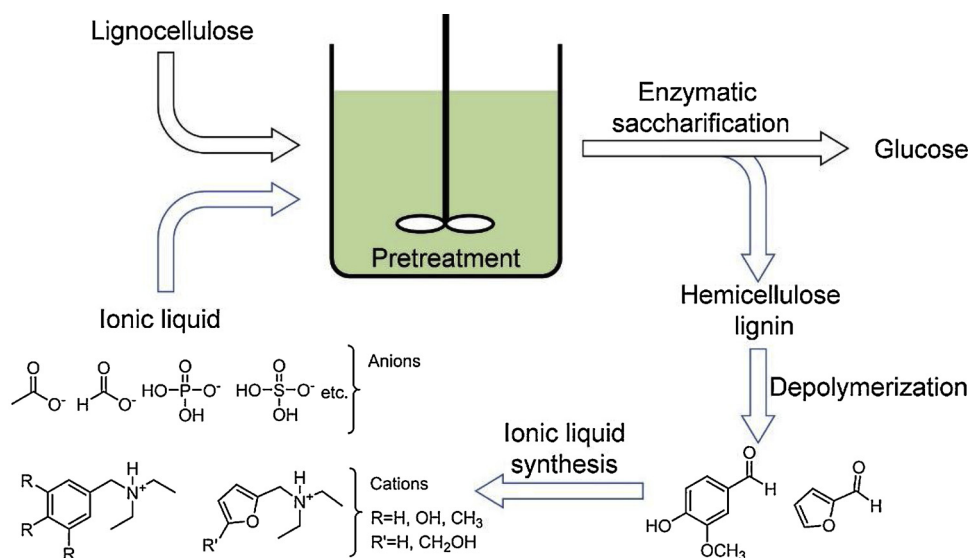


Fig. 21. Pretreatment of lignocellulose with lignin and hemicellulose-derived ionic liquid. Based on Socha et al. [442].

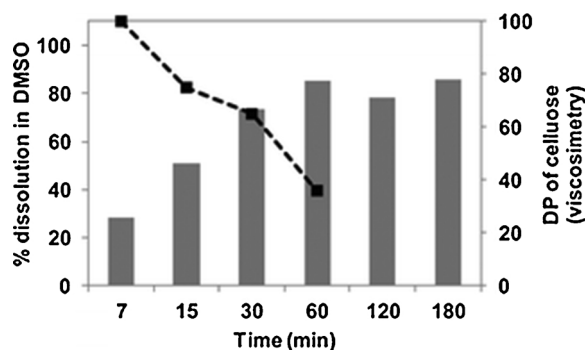


Fig. 22. Effect of the NTAP treatment time on the dissolution of cellulose in DMSO (grey bars, 150 mg in 30 mL of DMSO) and the DP_v of cellulose (dashed line). After 60 min of NTAP, DP_v could not be measured with accuracy due to the presence of undesired products that affect the measurements. Adapted from Benoit et al. [453].

pretreatment mainly affects the degree of polymerization of the amorphous cellulose areas, decrystallization through ball milling significantly influenced cellulose reactivity towards NTAP, leading to more efficient depolymerization of cellulose to low molecular weight oligomers (DP 36 measured with ¹H NMR, DP_v 40) after only 1 h of NTAP pretreatment. NTAP-induced depolymerization of ball-milled cellulose was confirmed through a reduction in measured DP_v and an improved solubility in DMSO (solubility up to 85 %, Fig. 22). Although very promising, the true working mechanism of NTAP in cellulose depolymerization requires more fundamental researches. Benoit et al. tentatively suggested that the observed depolymerization can be attributed to the hydrolytic activation of water contained in cellulose by NO_x, formed through NTAP-induced air activation. The authors also reported that NTAP did not result in cellulose oxidation. Delaux et al. reported that NTAP not only induces partial depolymerization but also causes polymerization of carbohydrate through α- and β-1,6 linkages [454].

Advantages of the NTAP process include its efficiency at low temperature, the absence of a solvent or catalyst, and an excellent selectivity since no significant amount of degradation or oxidation products were observed after NTAP pretreatment. However, the need for a preliminary, energy-intensive ball milling pretreatment to obtain high, industrial yields might limit its economic viability. Moreover, the up-scaling of NTAP has yet to be demonstrated. More discussions about pretreatment of lignocellulose using other plasma technologies (such as nitrogen/air plasma with water, ozone plasma treatment) can be found in a recent review [66].

4.11. CO₂

Supercritical CO₂ is becoming an interesting extraction solvent in industrial applications due to its non-toxicity, recyclability, and low environmental impact. Its potential applicability in lignocellulose biomass pretreatment is demonstrated as well [455–466]. Degradation of hemicellulose readily occurs when supercritical CO₂ is used in the presence of water or steam. This is caused by an increased acidity after dissolution of CO₂ in water [456,457,460,461]. Delignification can be improved through the use of additional solvents like ethanol or acetic acid [458]. Besides, the supercritical CO₂ pretreatment can also extract waxes, which results in a 20 % increase of total sugars released after saccharification compared to untreated *Miscanthus* [467].

During CO₂ explosive pretreatments, pressure is released after impregnation, causing a rupture of the lignocellulosic structure like with steam and ammonia explosion. Since CO₂ at supercritical conditions is able to penetrate the lignocellulose structure much deeper compared to CO₂ at subcritical conditions, cellulose degradation is much more effective using supercritical CO₂ for the explosion [456].

Despite the reported structural effects on lignocellulose, Pang et al. reported an unexpected decrease in corn stalk conversion (83 % to 74 %) and only a modest increase in glycol yield (3%–8%) using a solid Ni-W₂C/AC catalyst after supercritical CO₂ pretreatment, which they attributed to the removal of only soluble compounds and hemicellulose (72 %) during the CO₂ pretreatment (Fig. 17a and b; I) [110]. Furthermore, use of supercritical CO₂ as a method for lignocellulose biomass pretreatment is currently too expensive for industrial application due to high capital equipment costs and low pretreatment efficiencies [457].

4.12. Biological

Biological pretreatment of lignocellulose includes treatment with fungi (mainly brown-, white-, and soft-rot fungi), bacteria or enzymes (such as laccases) to remove hemicellulose, lignin, or antimicrobial substances in lignocellulose through oxidation. White-rot fungi are the most effective basidiomycetes for biological pretreatment due to their lignin selectivity [468–472]. Lignin degradation is achieved through the action of oxidative, lignin-degrading enzymes like lignin peroxidases, polyphenol oxidases, and laccases [473].

Taniguchi et al. reported that rice straw pretreatment with *Pleurotus ostreatus*, a white-rot fungus, for 60 days effected a significant glucose yield increase from 13 % to 32 % (based on the cellulose content of unpretreated rice straw) after 48 h of enzymatic hydrolysis [474]. 41 % of Klason lignin, 53 % of hemicellulose, and 28 % of cellulose were removed during pretreatment. Sugar yields were comparable to those obtained after rice straw pretreatment with NaOH, peracetic acid, and sodium chlorite (32–42 %) [475]. Saha et al. demonstrated that white-rot fungal pretreatment of corn stover can cause not only lignin removal but also the removal of hemicellulose and cellulose [476]. The enzymatic hydrolysis of corn stover is increased with this pretreatment.

Although biological pretreatments are performed in mild reaction conditions (ambient temperature, no added chemicals), industrial viability of biological pretreatment is hampered due to long pretreatment times (weeks to months) and significant loss of cellulose [55,470].

4.13. Lignin first biorefinery

Several pretreatments approaches such as alkaline pretreatment and organosolv fractionation dissolve the lignin. The dissolved lignin can be precipitated to obtain a solid residue, which is usually treated as a waste stream and used for energy production [1,71]. Although it may be possible to valorize those isolated lignins into chemicals and fuels, their conversion is strongly restricted by the recalcitrant C–C bonds, which are abundantly present, largely caused by various recondensation (such as condensation, alkylation, ...) reactions during the pretreatment. Hence, when this hurdle can be overcome, lignin can be used as an abundant renewable carbon source in the production of chemicals and fuels, preferably aromatics. It has been shown that upgrading the lignin stream can improve economic viability and environmental sustainability [2, 477]. In order to achieve both delignification and lignin valorization, a ‘lignin first biorefinery’ was recently proposed and demonstrated by several research groups [5,71,478–480]. In this biorefinery, the *in planta* lignin (lignin in lignocellulose) is selectively depolymerized to a high yield (i.e. close to the β-O-4 bond based theoretical yield) of monomers, next to oligomers (Fig. 23). The (hemi) cellulose is left as a solid residue, which can be further valorized via already developed bio- and chemo-catalysis methods [478]. The high yield of monomers is achieved by stabilization of reactive lignin-derived intermediates through catalytic methods to inhibit the undesired recondensation reactions. Since no C–C bonds are broken during lignin first processing, the obtained oligomers originate from the C–C bonds in the native lignin.

Reductive catalytic fractionation (RCF) is one of the most promising approaches, which uses hydrogenation or hydrogenolysis to

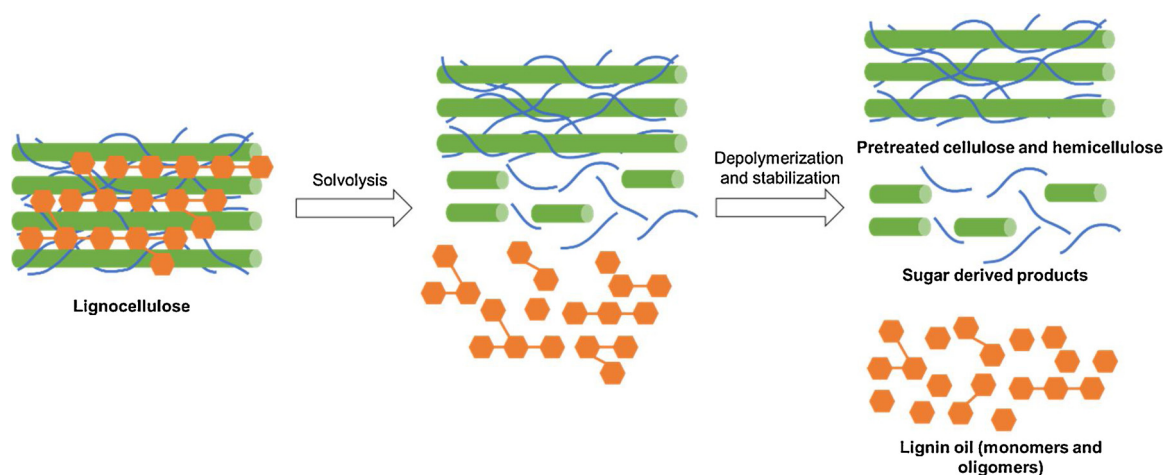


Fig. 23. Scheme of lignin-first approach.

depolymerize and stabilize the reactive intermediates in aqueous or non-aqueous organic solvents such as methanol, ethanol, and butanol in presence of hydrogen or hydrogen transfer reagents [481–485]. Sels et al. reported that reductive catalytic fractionation of birch wood in methanol with the presence of commercial Ru/C catalyst and external hydrogen at 523 K can remove more than 80 % of lignin and yield 50 % of monomers (based on Kraft lignin content) [481]. The main monomers are 4-propylsyringol and 4-propylguaiacol. More than 90 % of cellulose and 55 % of hemicellulose are kept in the solid pulp. The type of lignin-derived products depends on the catalyst, solvent, and process conditions [484,486–490]. For instance, the main monomers are 4-propanolguaiacol and 4-propanolsyringol by using Pd/C as catalyst or using butanol/H₂O as the solvent (with Ru/C catalyst).

In addition to the lignin fractionation, the remained (hemi)cellulose can be valorized and characterized. Enzymatic hydrolysis of RCF-pretreated pulp gives 95 % of the theoretical glucose yield, while only 11 % of theoretical glucose yield is obtained from untreated poplar wood under similar conditions [491]. Similarly, enzymatic hydrolysis of RCF-pretreated corn stover pulp shows higher glucan and xylan conversion rates, compared to untreated corn stover [492]. This result is consistent with reported results that removal of lignin facilitates enzymatic hydrolysis of cellulose. The poplar pulp obtained from RCF in 2-propanol/H₂O with Raney Ni catalyst gives similar glucose yields *via* enzymatic hydrolysis as an organosolv pulp [482]. Since most of the (hemi)cellulose is kept in the solid residue, the crystallinity (XRD, peak height method) of Eucalyptus cellulose after RCF-pretreatment is only slightly altered compared to untreated Eucalyptus [493]. However, the surface area is significantly improved from 1.3 m²/g to 18.8 m²/g, as measured by N₂ physisorption, with the RCF pretreatment. The enzymatic hydrolysis rate of RCF-pretreated Eucalyptus is therefore much higher than that of the intact Eucalyptus. The solvent of RCF influences the microstructure of the obtained pulp [494]. For instance, particles of aggregated fiber cells (diameters of around 100–200 μm and lengths of about 1 mm) are obtained in the birch wood pulp using RCF in methanol, whereas separated fibers with smaller diameters (about 10–20 μm) and lengths up to 1 mm are observed when the RCF is performed in ethylene glycol. Yet, the birch wood pulp obtained from RCF in methanol shows similar crystallinity, as determined by the XRD (peak height method) and ¹³C CP MAS NMR, and similar DP_v value to that in ethylene glycol. However, the impact of RCF solvent on the reactivity of cellulose was not investigated. The presence of acid or base in the RCF also influences the properties of cellulose [495]. RCF of poplar wood in the presence of NaOH causes more cellulose removal (18 %) due to partial cellulose amorphization and/or biomass swelling, whereas in the presence of acid only 9% of cellulose is removed. Hemicellulose, in contrary, is dissolving more in the presence of an acid. The crystallinity

(XRD, peak height method) of the cellulose decreases with increasing the basicity, whereas the crystallinity is not influenced by the presence of acid. However, the impact of acid and base on the reactivity of cellulose was however not revealed.

Although RCF pretreatment can selectively remove lignin from the lignocellulose matrix, the insoluble carbohydrate pulp might be contaminated by catalyst or solvent rests. Sels et al. unambiguously demonstrated that the direct contact between the lignocellulose and catalysts is not necessary to enable the extraction and depolymerisation of the native lignin [487]. In their proof, they have separated the catalyst pellets from the lignocellulose by using a metal basket which contains the solid catalyst pellets. Given similar depolymerisation results were obtained, the catalyst is considered to act on the solubilized fragments while the solvent is responsible through solvolysis of lignin to detach it from the lignocellulosic matrix. The solvent is also capable to assist in breakage of specific ether linkages in the lignin structure. Semi-simultaneous saccharification-fermentation of the non-contaminated birch wood pulp (containing both cellulose and hemicellulose) obtained from RCF in methanol using Ni/Al₂O₃ catalyst pellets yielded an ethanol titer of 36 g/L at 73 % ethanol yield. In contrast, only trace amounts of ethanol (< 2 g/L) were obtained from untreated birch wood [487].

In addition to the use of baskets in a batch reactor system, flow-through systems were recently proposed to avoid contamination of lignocellulose with catalyst. The systems comprises of two reactor units, one containing a solid bed of lignocellulose (extracting lignin) and the other containing a catalyst bed (to stabilize the lignin fragments through hydrogenation/hydrogenolysis) [496,497]. The birch pulp from such flow-through RCF can also be selectively hydrolyzed to glucose with 95 % yield on pulp basis (corresponding to 87 % on original woody cellulose basis) through mild enzymatic hydrolysis [497]. In terms of chemo-catalysis, the RCF-pretreated Miscanthus pulp generates higher yields of furfural and levulinic acid compared to untreated ones over FeCl₃ in H₂O and 2-methyltetrahydrofuran [498]. The birch wood pulp from RCF in ethylene glycol can be converted into ethylene glycol in the presence of Pd/C and H₂WO₄ [486]. Hydrolytic hydrogenation of RCF birch wood pulp with tungstosilicic acid and Ru/C can selectively produce sugar alcohol with 74 % and 82 % yield at low and high concentration, respectively [481]. Direct hydrodeoxygenation of birch wood pulp obtained from RCF in methanol while keeping the Ni/Al₂O₃ catalyst in a basket gave the same alkanes yield as the direct hydrodeoxygenation of intact birch wood [324]. These examples demonstrate that the RCF carbohydrate pulp can be selectively converted to chemicals *via* chemo-catalytic processes.

Lignin can be selectively extracted from lignocellulosic biomass in 1,4-dioxane with the presence of HCl as well. However, the extracted

lignin is as recalcitrant to valorization as the Organosolv lignin due to its dense structure resulting from recondensation chemistry during its separation [499]. Recondensation of the lignin-derived reactive intermediates can be inhibited by adding aldehydes such as formaldehyde, acetaldehyde and propionaldehyde since they form a 1,3-dioxane structure [500]. The aldehyde-stabilized lignin can be selectively hydrogenolyzed into a few phenolic monomers with close to theoretical yields (based on the β -O-4 bond content in the original lignin), while cellulose is left as a solid residue, which can be hydrolyzed to sugars. However, the binding of aldehyde to the cellulose might reduce the enzymatic digestibility of the cellulose.

RCF processes are usually conducted at severe conditions, e.g. at high temperature and pressure. To overcome such process severity, it might be interesting to perform the 'Oxidative Catalytic Fractionation (OCF)', which is usually conducted at milder reaction conditions. In this method, lignin is selectively oxidized toward aldehydes like vanillin and syringaldehyde or various oligomers in alkaline solution in the presence of oxygen or air. The cellulose remains as a solid residue [501, 502]. For example, Wang et al. reported a 21.1 % vanillin yield (on Kraft lignin basis) by processing pine wood in aqueous NaOH in presence of O₂, while 45 % of the cellulose remained as a solid residue. The hemicellulose is completely converted towards different acids and diacids. The amorphous part of cellulose has also reacted, whereas a large part of the crystalline cellulose remains unchanged. The process conditions, and especially the stirring rate, should be well controlled to maintain such high cellulose content, along with the high vanillin yield, since full degradation of cellulose was shown in conditions of strong agitation [502, 503]. Tarabanko et al. conducted OCF on pine in the presence of Copper (II) sulfate pentahydrate in aqueous NaOH [501]. By changing reaction conditions, the vanillin yield can reach 15.5 % and 18.6 %, while 93 % and 64 % of cellulose are kept, respectively. The obtained OCF cellulose performs better in enzymatic hydrolysis towards reduced sugars when compared to a Kraft cellulose. The reduced sugar yield increases with decreasing lignin content in the residue.

In addition to thermal catalysis, photocatalysis was demonstrated to remove lignin from lignocellulose and depolymerize it further to ketones [504]. The results show that 90 % of hemicellulose and 98 % of cellulose are left in the solid residue, while 27 wt.% of birch wood lignin is converted to ketones. In a first treatment of pulp, hemicellulose can be hydrolyzed with sulfuric acid to xylose with a yield of 84 %. A glucose yield of 85 % is subsequently obtained via enzymatic hydrolysis of the acid hydrolyzed residue.

In summary, the recent 'lignin first' approaches can selectively remove high levels of lignin from the lignocellulosic matrix, and leave solid cellulose and optionally also large parts of the hemicellulose fraction (depending on solvents, process conditions, etc.) behind. The beneficial influence of delignification on the biochemical transformation of (hemi)cellulose has been proven, as discussed in this section. However, the impact of delignification or even hemicellulose removal on cellulose conversion via chemo-catalytic processes is only scarcely investigated and deserves more research efforts.

5. Selection of pretreatment methods for cellulose valorisation

Like in case of enzymatic cellulose hydrolysis, pretreatment of lignocellulosic biomass substantially improves chemo-catalytic conversion processes through an increase in the reactivity of cellulose after a disassembly of the protective (ligno)cellulosic structure. This disassembly entails an increase in cellulose accessibility (through changes in e.g. particle size, porosity, crystallinity, and degree of polymerization) and/or purity (through the removal of hemicellulose, lignin, minerals, and other constituents such as waxes). The relative importance of each (ligno)cellulosic characteristic for predicting the cellulose reactivity is hard to determine and is largely case-dependent.

The degree of cellulose crystallinity can be determined with

analytical techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), solid state ¹³C cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (¹³C-CP/MAS NMR), Raman, and vibrational sum frequency generation spectroscopy (SFG). Unfortunately, the presence of hemicellulose and lignin in lignocellulosic biomass often impedes an accurate determination of the crystallinity using the aforementioned methods. Of course, this is not an issue when pure cellulose (such as microcrystalline cellulose, nanocellulose) samples are concerned in the study. The most popular and straightforward analytical method is the XRD peak height method. Although this is not the most accurate method, it is simple and fast option to relatively compare the degree of crystallinity of different cellulose samples. Solid-state ¹³C CP MAS NMR methods are generally more accurate and should, therefore, be preferred, if possible. If available, Raman and SFG can be executed to validate the X-ray or NMR results.

The degree of polymerization (DP) of cellulose can be defined in terms of weight average (DP_w), number average (DP_n), or viscosity average (DP_v). The main challenge of cellulose DP determination is the solubilization of cellulose without degradation or aggregation. Since cellulose is insoluble in almost all conventional solvents, special solvents like metal complex solutions (e.g. Cuam) are often applied. Viscometry and size-exclusion chromatography (SEC) are the most commonly used methods for cellulose DP determination. Viscometry is a popular method for DP determination due to its fast and convenient implementation, but only provides a viscosity average DP (DP_v) and supplies no information concerning the molar mass distribution in contrast to SEC. Using SEC, both weight (DP_w) and number average (DP_n) DPs can be determined, making this in our opinion the most preferable method.

In addition to an improvement in cellulose reactivity, pretreatment is useful for fractionation of lignocellulose into more or less pure streams of its three main constituents, viz. cellulose, hemicellulose, and lignin. This fractionation enables selective downstream conversions of each fraction in a biorefinery. Ideally, pretreatments simultaneously produce a high-quality cellulose pulp (with high reactivity in the biorefinery), together with a high-quality hemicellulose stream, and useful lignin degradation products, ensuring optimal use of the biologically sequestered carbon. While classic biorefineries have a carbohydrate focus, currently developed 'lignin first' biorefineries include such a kind of pretreatment method that enable value from lignin by generating separable mono- and oligomeric phenolics next to a delignified pulp fraction. Since an organic solvent is used, preferably without any acid or base, only little structural damage on the fibrous cellulose is reported besides an enhanced cellulose purity. The choice of lignocellulose pretreatment depends on the targeted product, downstream processing technology, and the economics of the pretreatment process.

Physical pretreatments like milling induce a severe improvement in cellulose accessibility, mainly through a disruption of the lignocellulosic structure and a decrease in particle size and/or crystallinity. Nevertheless, the mechanical process remains fairly energy-intensive and does not purify cellulose. Certain downstream catalytic upgrading processes, such as hydrolysis (including enzymatic) or hydrolytic hydrogenation, can therefore still be impaired by (ligno)cellulosic impurities, such as lignin and/or contaminants like sulfur. However, the conversion of cellulose to target platform molecules was demonstrated to be significantly improved in specific cases through ball milling pretreatment, whether or not in combination with acids or other pretreatments (Table 3, entries 1, 2, and 11). Nowadays, (reactive) ball milling and mixed balling of cellulose and heterogeneous catalysts are the most popular pretreatments of pure cellulose in chemo-catalytic conversion routes, studied at laboratory scale. Next to mechanical milling, other physical pretreatments: irradiation pretreatments such as microwave pretreatment, electron bombardment or sonification are used, but less frequently. Numerous positive effects on cellulose

Table 3
Selection of reported pretreatments and their effects on the aqueous chemo-catalytic valorization of cellulose to platform chemicals.

| Entry ^(a) | Feedstock | Pretreatment | Aqueous reaction | | | | | Ref. | | | | |
|----------------------|--------------------|----------------------------------|---|------------------------------------|------------------------------------|--|-------|------|------------|-------------------------------------|------------|-----------|
| | | | Method | Conditions | Main effect(s) | Catalyst | T (K) | | t (h) | Conv. ^(b) (%) | Product(s) | Yield (%) |
| 1a | MCC ^(c) | Ball milling | 25 g MCC, 24 h | Crystallinity reduction | Particle size reduction | H ₄ SiW ₁₂ O ₄₀ -Ru/C | 463 | 5 | 77 | Hexitols | 56 | [19] |
| 1b | MCC | Acid impregnation | 1.2 g IMC ^(d) (1 mmol H ₂ SO ₄ /g MCC), 800 rpm, 2 h, Fritsch Pulverisette P7 (Planetary Micro Mill) | Crystallinity reduction | DP reduction | H ₂ SO ₄ -Ru/C ^(e) | 433 | 1 | 100 | Hexitols | 100 | [219] |
| 2a | MCC | Ball milling | 10.0 g cellulose, 60 rpm, 2 days. | Crystallinity reduction | Particle size reduction | Activated carbon catalyst and 0.012 wt. % HCl | 453 | 0.33 | 40 | Glucose | 30 | [202] |
| 2b | MCC | Ball milling with solid catalyst | 10.0 g cellulose, 1.54 g solid catalyst, 60 rpm, 2 days. | Crystallinity reduction | Particle size reduction | Activated carbon catalyst and 0.012 wt. % HCl | 423 | 1 | 16 | Glucose | 5 | [98] |
| 4a | MCC | Sonication | 5 g MCC, 200 ml H ₂ O, 750 W, 20 kHz, A = 40%, 353 K, 3 h | Delignification | Particle size reduction | AC-SO ₃ H | 423 | 1 | 20 | Glucose | 14 | [110] |
| 5a | Corn stalk | Alkaline/Oxidative | 1:10 (m/v) corn stalk to solution ratio, 15 wt% NH ₃ , 333 K, 12 h followed with 2 wt% H ₂ O ₂ , 318 K, 12 h | Delignification | Delignification | 2%Ni:30 %W ₂ C/AC | 518 | 2.5 | 87.6 ± 100 | Ethylene glycol propylene glycol | 3.3 48 | [110] |
| 5b | Miscanthus | Alkaline | - | Delignification | Delignification | Mo/Pt/WO ₃ | 518 | 2 | n.d. | Ethanol | 26.3 | [349] |
| 6a | Wheat straw | Organosolv/Oxidative | Acetic acid/formic acid/H ₂ O (50:30:15 m/m), 378 K, 3.5 h followed with peracetic acid and performic acid treatment | Fractionation | Cellulose purity increase | H ₄ SiW ₁₂ O ₄₀ -Ru/C | 483 | 3 | n.d. | Isosorbide | 43.1 | [508,509] |
| 7a | Cellulose | Acid/Swelling | 85 % H ₃ PO ₄ , 323 K, 40 min | Crystallinity reduction | DP reduction | 1% Ru/CNT | 458 | 24 | n.d. | Sorbitol mannitol | 13 73 | [422] |
| 8a | MCC | Ionic liquid | 0.2 g MCC, 60 mmol [bmim]Cl, 403 K, 2h | Crystallinity reduction/alteration | Crystallinity reduction/alteration | Nafion NR50 | 433 | 4 | n.d. | Glucose | 2.1 | [418] |
| 9a | MCC | NTAP | 0.2 g MCC, 11 kV, 2 kHz, 3 h | DP reduction | DP reduction | Amberlyst 35 | 423 | 1 | n.d. | Glucose | 35 | [199] |
| 10a | MCC | Ball milling | 2 g MCC, 48 h (ball milling, Reisch PM100, planetary mill)0.18 g BMC ^(f) , air (25 ml/min), 11.2 kV, 2 kHz, 1 h (NTAP) | Crystallinity reduction | DP reduction | Amberlyst 35 | 423 | 1 | n.d. | Glucose | 22 | [199,453] |
| 10b | MCC | Ball milling | 15 wt% Ni/C, 35 bar H ₂ , MeOH, 498 K, 12 h | Delignification | Delignification | FeCl ₃ in H ₂ O/MeTHF | 473 | 1.5 | n.d. | Levulinic acid/ furfurals | 52/41 | [498] |
| 11a | Miscanthus | RCF | 5 wt.%Ru/C, 30 bar H ₂ , MeOH, 523 K, 3 h | Delignification | Delignification | 5 wt.% Ru/C, H ₄ [Si(W ₃ O ₁₀) ₄]xH ₂ O in H ₂ O | 463 | 6 | n.d. | Levulinic acid/ furfurals | 76/55 | [481] |
| 11b | Birch | RCF | 5 wt.%Ru/C, 30 bar H ₂ , MeOH, 523 K, 3 h | Delignification | Delignification | 5 wt.% Ru/C, H ₄ [Si(W ₃ O ₁₀) ₄]xH ₂ O in H ₂ O | 463 | 6 | n.d. | C5 and C6 sugar alcohols | 82 % | [481] |

[a] wherein a = untreated and b = treated. [b] Conversion to water-soluble products. [c] Microcrystalline cellulose. [d] Acid-impregnated MCC. [e] 1 mmol H₂SO₄/g MCC. [f] Ball milled cellulose.

accessibility have been reported for microwave and sonification pretreatment, but these treatments are rather expensive, high-energy-demanding, and difficult to apply on an industrial level.

Chemical pretreatment methods typically remove hemicellulose, lignin, and other impurities such as proteins and minerals. In addition, amorphization and even dissolution of cellulose can be achieved through chemical pretreatment with cellulose intracrystalline swelling agents and solvents. In contrast to physical methods, there is a beneficial increase in cellulose purity *via* selective removal of the protective hemicellulose and lignin during a chemical pretreatment making it a more favorable pretreatment to increase the accessibility of cellulose microfibrils in lignocellulosic material.

Hydrothermal pretreatment mainly removes hemicellulose and extractives and redistributes lignin in batch pretreatment reactor systems. In flow-through reactor systems, this method partially removes lignin as well. In order to make the cellulose accessible to bulky heterogeneous catalysts, large parts of the protective lignin matrix have to be removed. Since homogeneous acids can penetrate the lignocellulose matrix more easily, removal of this hemicellulose and lignin matrix is less important for acid hydrolysis. However, these conversion processes might benefit from an increase in cellulose purity accomplished through pretreatment, since product purity will increase and downstream sugar valorization with metal-based catalysts will be less influenced by potential poisons in the hydrolyzate.

Homogeneous acids can also be applied in lignocellulose pretreatment to selectively degrade hemicellulose in less severe conditions or to directly hydrolyze the holocellulose fraction to sugars. Sugar degradation products such as HMF and levulinic acid can also be targeted in more severe conditions, but the latter is not considered as a pretreatment per definition. HMF and furfural are known inhibitors to inhibit biochemical conversion of cellulose and their formation should thus be avoided. However, chemo-catalysts are less inhibited by these compounds. As with batch-wise aqueous pretreatment, batch-wise acid pretreatment is not considered as a useful pretreatment prior to heterogeneous chemo-catalytic processes, since practically no lignin is removed during such pretreatment. Nevertheless, both pretreatments are interesting to apply on pure microcrystalline cellulose, since they decrease the crystallinity and DP in hot compressed water and concentrated acid solutions (e.g. 85 % H₃PO₄: Table 3, entry 8).

On the other hand, alkaline and oxidative methods are excellent delignification pretreatments and are often combined due to the formation of highly active free oxygen radicals in basic medium. Oxidative pretreatment is also frequently employed after another pretreatment to effect a more thorough delignification of the feedstock (Table 3, entries 5 and 7). Some alkaline pretreatments such as pretreatment with aqueous NaOH solutions or liquid ammonia have been demonstrated to alter and reduce the crystallinity of native cellulose as well. Hence, alkaline and oxidative pretreatments seem an excellent choice for lignocellulose pretreatment prior to heterogeneous chemocatalytic conversion routes (Table 3, entries 5–7).

Another pretreatment of delignification is organosolv pretreatment, where (aqueous) organic solvents are employed to solubilize the degrading lignin fraction (e.g. with formic/acetic acid: Table 3, entry 7). The main advantage of organosolv methods over alkaline and oxidative pretreatments is the production of three separate, high-quality product streams. These are consisting of a relatively pure solid cellulose pulp, a partially saccharified aqueous hemicellulose solution and a solid lignin fraction. Therefore, in our opinion, organosolv pretreatment constitutes one of the best lignocellulosic biomass pretreatment options, especially due to its excellent applicability as an entry point in future biorefineries. The main drawback is its generation of unreactive and condense lignin streams, which have lost considerable amounts of their initial chemical functionality.

Pretreatment with cellulose solvents such as ionic liquids instead of organic solvents can also effect the fractionation of lignocellulose into separate holocellulose and lignin fractions, in addition to a decrease

and alteration of crystallinity. However, complete solvent recovery is even more crucial for these pretreatments than during organosolv pretreatment, in order to avoid downstream catalyst deactivation and high process costs (Table 3, entry 9).

Although its efficiency is not yet demonstrated on lignocellulosic substrates, non-thermal atmospheric plasma (NTAP) pretreatment constitutes an interesting pretreatment option to efficiently reduce the degree of polymerization of cellulose, which is an important parameter for the aqueous catalytic valorization of cellulose. However, pre-milling cellulose to reduce its crystallinity appears to be a requisite for efficient depolymerization (Table 3, entries 10 and 11).

Sub- and supercritical CO₂ pretreatment in the presence of water or steam can be applied to selectively remove hemicellulose, while delignification can be effected through the addition of organic solvents. Similar to batch-wise aqueous and acid pretreatment, prior removal of hemicellulose instead of lignin is not expected to significantly improve downstream cellulose conversion under heterogeneous catalysis.

Physicochemical pretreatment methods combine both physical and chemical pretreatment and therefore effect both a physical and chemical disruption of the lignocellulosic structure. Physicochemical pretreatment includes mechanocatalytic pretreatment, *viz.* ball milling after acid impregnation of the feedstock (Table 3, entry 2), steam explosion, ammonia fiber expansion (AFEX), and CO₂ explosion.

Biological pretreatments, even though they are performed under mild conditions, are less of interest due to the long pretreatment times and certain cellulose loss. However, this strategy might be feasible when combined controllably with wood storage nearby the biorefinery.

The current developed *lignin first* biorefinery is one of the ideal pretreatment methods, which simultaneously produce high-quality pulp and valuable lignin degradation products. This approach ensures an optimal use of the sequestered carbon. Although the organosolv pretreatment can be used to obtain solid lignin, it is quite recalcitrant for depolymerisation due to newly formed strong C–C bonds during the pretreatment. Compared to the organosolv pretreatment, *lignin first* biorefinery, especially the RCF approach, selectively converts lignin into a liquid lignin oil product, which contains high yields of monomers, besides oligomers. The lignin monomers fraction can be catalytically converted into phenol and propylene, while oligomers can replace nonylphenol in printing ink production [2, 505–507]. Therefore, the value of lignin is improved without losing the value of hemicellulose and cellulose (Table 3, entries 12 and 13). The economic feasibility and environmental sustainability of RCF has also been preliminarily proved with modelling results [2]. Nevertheless, some engineering points need to be solved for upscaling such as solvent and metal catalyst recuperation, and stirring regime design for large batch reactor and high biomass loading.

Indeed, in addition to pretreatment effects, economic factors such as process time, energy consumption, and costs determine the ultimate pretreatment efficiency. For instance, some lignocellulose pretreatments might be too expensive for industrial application (e.g. CO₂ explosion, irradiation pretreatment), require solvent recycling (e.g. organosolv, ionic liquid pretreatment), are corrosive and require neutralization (e.g. acid pretreatment), limiting their industrial viability. These factors have to be taken into account when selecting an appropriate pretreatment for cellulose valorization. Besides, since lignocellulose contains hemicellulose and lignin, their valorization and value should take into account for the integrated biorefinery. It is therefore advisable to first select the desired pretreatment effect (e.g. extensive lignin removal) with regard to the type of catalyst used in further downstream processing of the cellulosic feedstock and the desired properties of the resulting product mixture (e.g. product purity), before selecting the most cost-efficient pretreatment. In addition to economic feasibility, the sustainability of pretreatment method is important when selecting the appropriate method. For example, the consumption of NH₃ in AFEX is not good for the environment as it will end with NO_x. Therefore, life cycle assessments from plant growth to

end products using detailed techno-economic analysis are required to really understand the CO₂ footprint of biorefineries.

6. Conclusions

Lignocellulose - cellulose in particular - represents a promising alternative feedstock for the production of fuels and chemicals in addition to petroleum, classically used to date. This review has clearly shown that pretreatment of lignocellulosic biomass is a prerequisite not only for efficient biological, but also for chemo-catalytic conversion processes to bio-based chemicals and fuels. Since the latter is still in its infancy, we advise to include more systematically the potential beneficial effects of lignocellulosic pretreatments in chemo-catalytic studies. In addition to technical feasibility, the profitability and sustainability of pretreatment method should be considered before chosen it for future biorefinery.

Declaration of Competing Interest

Authors declare no conflict of interest.

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References

- [1] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Catalytic transformation of lignin for the production of chemicals and fuels, *Chem. Rev.* 115 (2015) 11559–11624.
- [2] Y. Liao, S.-F. Koelewijn, G. Van den Bossche, J. Van Aelst, S. Van den Bosch, T. Renders, K. Navare, T. Nicolai, K. Van Aelst, M. Maesen, H. Matsushima, J. Thevelein, K. Van Acker, B. Lagrain, D. Verboekend, B.F. Sels, A sustainable wood biorefinery for low-carbon footprint chemicals production, *Science* (2020), <https://doi.org/10.1126/science.aau1567>.
- [3] D. Esposito, M. Antonietti, Redefining biorefinery: the search for unconventional building blocks for materials, *Chem. Soc. Rev.* 44 (2015) 5821–5835.
- [4] Z. Zhang, G.W. Huber, Catalytic oxidation of carbohydrates into organic acids and furan chemicals, *Chem. Soc. Rev.* 47 (2018) 1351–1390.
- [5] Z. Sun, Bl. Fridrich, A. de Santi, S. Elangovan, K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, *Chem. Rev.* 118 (2018) 614–678.
- [6] S. Van de Vyver, J. Geboers, P.A. Jacobs, B.F. Sels, Recent advances in the catalytic conversion of cellulose, *ChemCatChem* 3 (2011) 82–94.
- [7] L.T. Mika, E. Csefalvay, A. Nemeth, Catalytic conversion of carbohydrates to initial platform chemicals: chemistry and sustainability, *Chem. Rev.* 118 (2017) 505–613.
- [8] X. Zhang, K. Wilson, A.F. Lee, Heterogeneously catalyzed hydrothermal processing of C5–C6 sugars, *Chem. Rev.* 116 (2016) 12328–12368.
- [9] M. Besson, P. Gallezot, C. Pinel, Conversion of biomass into chemicals over metal catalysts, *Chem. Rev.* (2013).
- [10] J.A. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P.A. Jacobs, B.F. Sels, Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls, *Catal. Sci. Technol.* 1 (2011) 714–726.
- [11] S. Van de Vyver, J. Geboers, W. Schutyser, M. Dusselier, P. Eloy, E. Dornez, J.W. Seo, C.M. Courtin, E.M. Gaigneaux, P.A. Jacobs, B.F. Sels, Tuning the Acid/Metal balance of carbon nanofiber-supported nickel catalysts for hydrolytic hydrogenation of cellulose, *ChemSusChem* 5 (2012) 1549–1558.
- [12] S. Van de Vyver, J. Thomas, J. Geboers, S. Keyzer, M. Smet, W. Dehaen, P.A. Jacobs, B.F. Sels, Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s, *Energy Environ. Sci.* 4 (2011) 3601–3610.
- [13] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, *Chem. Rev.* 106 (2006) 4044–4098.
- [14] B. Kamm, P.R. Gruber, M. Kamm, Biorefineries – Industrial Processes and Products Vol. 1 Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, 2006.
- [15] A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, *Chem. Rev.-Columbus* 107 (2007) 2411–2502.
- [16] S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C.J. Gommers, B. Goderis, P.A. Jacobs, B.F. Sels, Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose, *Green Chem.* 12 (2010) 1560–1563.
- [17] J.-P. Lange, Lignocellulose conversion: an introduction to chemistry, process and economics, *Biofuels Bioprod. Biorefining* 1 (2007) 39–48.
- [18] P.L. Dhepe, A. Fukuoka, Cellulose conversion under heterogeneous catalysis, *ChemSusChem* 1 (2008) 969–975.
- [19] J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs, B. Sels, Efficient catalytic conversion of concentrated cellulose feeds to hexitols with heteropoly acids and Ru on carbon, *Chem. Commun.* 46 (2010) 3577–3579.
- [20] R. Rinaldi, F. Schüth, Design of solid catalysts for the conversion of biomass, *Energy Environ. Sci.* 2 (2009) 610–626.
- [21] J.W.A. Langeveld, J. Dixon, J.F. Jaworski, Development perspectives of the bio-based economy: a review, *Crop Sci.* 50 (2010) S-142-S-151.
- [22] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Catalytic conversion of biomass to biofuels, *Green Chem.* 12 (2010) 1493–1513.
- [23] F. Cherubini, A.H. Strømman, Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems, *Biofuels Bioprod. Biorefining* 5 (2011) 548–561.
- [24] Y. Román-Leshkov, M. Moliner, J.A. Labinger, M.E. Davis, Mechanism of glucose isomerization using a solid Lewis acid catalyst in water, *Angew. Chemie Int. Ed.* 49 (2010) 8954–8957.
- [25] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, *Chem. Soc. Rev.* 41 (2012) 8075–8098.
- [26] S. Dutta, Deoxygenation of Biomass-Derived Feedstocks: Hurdles and Opportunities, *ChemSusChem* 5 (2012) 2125–2127.
- [27] H. Kobayashi, H. Ohta, A. Fukuoka, Conversion of lignocellulose into renewable chemicals by heterogeneous catalysis, *Catal. Sci. Technol.* 2 (2012) 869–883.
- [28] M. Rose, R. Palkovits, Isosorbide as a Renewable Platform chemical for Versatile Applications—Quo Vadis? *ChemSusChem* 5 (2012) 167–176.
- [29] L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes, *RSC Adv.* 2 (2012) 11184–11206.
- [30] J.O. Metzger, Production of liquid hydrocarbons from biomass, *Angew. Chemie Int. Ed.* 45 (2006) 696–698.
- [31] M.R. üschgen, Klaas, H. Schöne, Direct, high-yield conversions of cellulose into biofuel and platform chemicals—on the way to a sustainable biobased economy, *ChemSusChem* 2 (2009) 127–128.
- [32] A. Wang, T. Zhang, One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts, *Acc. Chem. Res.* (2013).
- [33] S. Van de Vyver, J. Geboers, S. Helsen, F. Yu, J. Thomas, M. Smet, W. Dehaen, B.F. Sels, Thiol-promoted catalytic synthesis of diphenolic acid with sulfonated hyperbranched poly(arylene oxindole)s, *Chem. Commun.* 48 (2012) 3497–3499.
- [34] J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs, B. Sels, Hydrolytic hydrogenation of cellulose with hydrotreated caesium salts of heteropoly acids and Ru/C, *Green Chem.* 13 (2011) 2167–2174.
- [35] J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs, B. Sels, Efficient hydrolytic hydrogenation of cellulose in the presence of Ru-loaded zeolites and trace amounts of mineral acid, *Chem. Commun.* 47 (2011) 5590–5592.
- [36] H. Olcay, A.V. Subrahmanyam, R. Xing, J. Lajoie, J.A. Dumesic, G.W. Huber, Production of renewable petroleum refinery diesel and jet fuel feedstocks from hemicellulose sugar streams, *Energy Environ. Sci.* 6 (2013) 205–216.
- [37] J.N. Chheda, G.W. Huber, J.A. Dumesic, Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals, *Angew. Chemie Int. Ed.* 46 (2007) 7164–7183.
- [38] G.W. Huber, J. Chheda, C. Barrett, J.A. Dumesic, Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates, *Science* 308 (2005) 1446–1450.
- [39] T. Werpy, G. Petersen, Top Value Added Chemicals From Biomass: Volume I—results of Screening for Potential Candidates From Sugars and Synthesis Gas, National Renewable Energy Lab., Golden, CO (US), 2004.
- [40] J. Jae, G.A. Tompsett, Y.-C. Lin, T.R. Carlson, J. Shen, T. Zhang, B. Yang, C.E. Wyman, W.C. Conner, G.W. Huber, Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis, *Energy Environ. Sci.* 3 (2010) 358–365.
- [41] Z. Si, X. Zhang, C. Wang, L. Ma, R. Dong, An overview on catalytic hydrodeoxygenation of pyrolysis oil and its model compounds, *Catalysts* 7 (2017) 169.
- [42] E. Rodríguez-Aguado, A. Infantes-Molina, D. Ballesteros-Plata, J. Cecilia, I. Barroso-Martín, E. Rodríguez-Castellón, Ni and Fe mixed phosphides catalysts for O-removal of a bio-oil model molecule from lignocellulosic biomass, *Mol. Catal.* 437 (2017) 130–139.
- [43] X. Zhang, Q. Zhang, T. Wang, B. Li, Y. Xu, L. Ma, Efficient upgrading process for production of low quality fuel from bio-oil, *Fuel* 179 (2016) 312–321.
- [44] R. Rinaldi, F. Schüth, Acid hydrolysis of cellulose as the entry point into biorefinery schemes, *ChemSusChem* 2 (2009) 1096–1107.
- [45] S. Zhu, J. Guo, X. Wang, J. Wang, W. Fan, Alcoholysis: a promising technology for conversion of lignocellulose and platform chemicals, *ChemSusChem* 10 (2017) 2547–2559.
- [46] V.P. Puri, Effect of crystallinity and degree of polymerization of cellulose on enzymatic saccharification, *Biotechnol. Bioeng.* 26 (1984) 1219–1222.
- [47] H.E. Grethlein, The effect of pore size distribution on the rate of enzymatic hydrolysis of cellulosic substrates, *Nat. Biotechnol.* 3 (1985) 155–160.
- [48] D.P. Koullas, P. Christakopoulos, D. Kekos, B.J. Macris, E.G. Koukios, Correlating the effect of pretreatment on the enzymatic hydrolysis of straw, *Biotechnol. Bioeng.* 39 (1992) 113–116.
- [49] D. Gregg, J. Saddler, A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process, *Appl. Biochem. Biotechnol.*

- 57–58 (1996) 711–727.
- [50] V. Chang, M. Holtzapfle, Fundamental factors affecting biomass enzymatic reactivity, in: M. Finkelstein, B. Davison (Eds.), *Twenty-First Symposium on Biotechnology for Fuels and Chemicals*, Humana Press, 2000, pp. 5–37.
- [51] H. Palonen, A. Thomsen, M. Tenkanen, A. Schmidt, L. Viikari, Evaluation of wet oxidation pretreatment for enzymatic hydrolysis of softwood, *Appl. Biochem. Biotechnol.* 117 (2004) 1–17.
- [52] L. Laureano-Perez, F. Teymour, H. Alizadeh, B. Dale, Understanding factors that limit enzymatic hydrolysis of biomass, in: B. Davison, B. Evans, M. Finkelstein, J. McMillan (Eds.), *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*, Humana Press, 2005, pp. 1081–1099.
- [53] A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, *Bioresour. Technol.* 100 (2009) 10–18.
- [54] M.J. Taherzadeh, K. Karimi, Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review, *Int. J. Mol. Sci.* 9 (2008) 1621–1651.
- [55] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresour. Technol.* 83 (2002) 1–11.
- [56] P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production, *Ind. Eng. Chem. Res.* 48 (2009) 3713–3729.
- [57] X. Zhao, K. Cheng, D. Liu, Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis, *Appl. Microbiol. Biotechnol.* 82 (2009) 815–827.
- [58] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapfle, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 96 (2005) 673–686.
- [59] P. Alvirá, E. Tomás-Pejó, M. Ballesteros, M.J. Negro, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review, *Bioresour. Technol.* 101 (2010) 4851–4861.
- [60] F. Carvalheiro, L.C. Duarte, F.M. Gfrio, Hemicellulose biorefineries: a review on biomass pretreatments, *J. Sci. Ind. Res.* 67 (2008) 849–864.
- [61] D.F. Caulfield, W.E. Moore, Effect of varying crystallinity of cellulose on enzymic hydrolysis, *Wood Sci.* 6 (1974) 375–379.
- [62] W.R. Grous, A.O. Converse, H.E. Grethlein, Effect of steam explosion pretreatment on pore size and enzymatic hydrolysis of poplar, *Enzyme Microb. Technol.* 8 (1986) 274–280.
- [63] D.N. Thompson, H.-C. Chen, H.E. Grethlein, Comparison of pretreatment methods on the basis of available surface area, *Bioresour. Technol.* 39 (1992) 155–163.
- [64] C.E. Wyman, *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons Ltd, West Sussex, United Kingdom, 2013.
- [65] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapfle, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 96 (2005) 673–686.
- [66] J. Vanneste, T. Ennaert, A. Vanhulsel, B. Sels, Unconventional pretreatment of lignocellulose with low-temperature plasma, *ChemSusChem* 10 (2017) 14–31.
- [67] F. Jérôme, Non-thermal atmospheric plasma: opportunities for the synthesis of valuable oligosaccharides from biomass, *Curr. Opin. Green Sustain. Chem.* 2 (2016) 10–14.
- [68] M.J. Bussemaker, D. Zhang, Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications, *Ind. Eng. Chem. Res.* 52 (2013) 3563–3580.
- [69] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, *Chem. Rev.* (Washington, DC, U. S.) 110 (2010) 3552–3599.
- [70] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, *Lignin Valorization: Improving Lignin Processing in the Biorefinery*, Science 344 (2014).
- [71] W. Schutyser, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G. Beckham, B.F. Sels, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, *Chem. Soc. Rev.* 47 (2018) 852–908.
- [72] N.S. Thompson, *Hemicellulose*, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc, 2000.
- [73] J.L. Wertz, O. Bédué, *Lignocellulosic Biorefineries*, EFPL Press, 2013.
- [74] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Cellulose: fascinating biopolymer and sustainable raw material, *Angew. Chemie Int. Ed.* 44 (2005) 3358–3393.
- [75] H.A. Krässig, *Cellulose: Structure, Accessibility, and Reactivity*, Gordon and Breach Science Publishers, Switzerland, 1993.
- [76] K. Kulasinski, S. Ketten, S. Churakov, D. Derome, J. Carmeliet, A comparative molecular dynamics study of crystalline, paracrystalline and amorphous states of cellulose, *Cellulose* 21 (2014) 1103–1116.
- [77] M. Jarvis, Cellulose stacks up, *Nature* 426 (2003) 611–612.
- [78] Y. Nishiyama, P. Langan, H. Chanzy, Crystal structure and hydrogen-bonding system in cellulose I β from synchrotron X-ray and neutron Fiber diffraction, *J. Am. Chem. Soc.* 124 (2002) 9074–9082.
- [79] S.K. Cousins, R.M. Brown Jr, Cellulose I microfibril assembly: computational molecular mechanics energy analysis favours bonding by van der Waals forces as the initial step in crystallization, *Polymer* 36 (1995) 3885–3888.
- [80] W. Glasser, R. Atalla, J. Blackwell, R. Malcolm Brown Jr, W. Burchard, A. French, D. Klemm, Y. Nishiyama, About the structure of cellulose: debating the Lindman hypothesis, *Cellulose* 19 (2012) 589–598.
- [81] A. O'Sullivan, Cellulose: the structure slowly unravels, *Cellulose* 4 (1997) 173–207.
- [82] P. Zugenmaier, Conformation and packing of various crystalline cellulose fibers, *Prog. Polym. Sci.* 26 (2001) 1341–1417.
- [83] S.K. Ritter, Calling all chemists, *Chem. Eng. News* 86 (2008) 59–68.
- [84] H. Kobayashi, T. Komanoya, S.K. Guha, K. Hara, A. Fukuoka, Conversion of cellulose into renewable chemicals by supported metal catalysis, *Appl. Catal. A Gen.* 409–410 (2011) 13–20.
- [85] H.V. Scheller, P. Ulvskov, Hemicelluloses, *Annu. Rev. Plant Biol.* 61 (2010) 263–289.
- [86] M. Crocker, R. Andrews, Chapter 1 The Rationale for Biofuels, *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*, The Royal Society of Chemistry, 2010, pp. 1–25.
- [87] D. Fengel, G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin and New York, 1984.
- [88] T. Koshijima, T. Watanabe, *Association Between Lignin and Carbohydrates in Wood and Other Plant Tissues*, Springer-Verlag, Berlin Heidelberg, 2003.
- [89] R.C. Pettersen, The chemical composition of wood, in: R.M. Rowell (Ed.), *The Chemistry of Solid Wood*, Advances in Chemistry, American Chemical Society, Washington, DC, 1984, pp. 57–126.
- [90] S.Y. Lin, C.W. Dence, *Methods in Lignin Chemistry*, Springer-Verlag, Berlin Heidelberg, 1992.
- [91] R. Weingarten, A. Rodriguez-Beuerman, F. Cao, J.S. Luterbacher, D.M. Alonso, J.A. Dumesic, G.W. Huber, Selective conversion of cellulose to hydroxymethylfurfural in polar aprotic solvents, *ChemCatChem* 6 (2014) 2229–2234.
- [92] F. Cao, T.J. Schwartz, D.J. McClelland, S.H. Krishna, J.A. Dumesic, G.W. Huber, Dehydration of cellulose to levoglucosone using polar aprotic solvents, *Energy Environ. Sci.* 8 (2015) 1808–1815.
- [93] B. Saha, M.M. Abu-Omar, Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents, *Green Chem.* 16 (2014) 24–38.
- [94] R. Kumar, C.E. Wyman, Physical and chemical features of pretreated biomass that influence macro-/micro-accessibility and biological processing, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons Ltd, West Sussex, United Kingdom, 2013, pp. 281–310.
- [95] R. Xu, Particle Characterization: Light Scattering Methods, Springer, 2001.
- [96] M. Vaezi, V. Pandey, A. Kumar, S. Bhattacharyya, Lignocellulosic biomass particle shape and size distribution analysis using digital image processing for pipeline hydro-transportation, *Biosyst. Eng.* 114 (2013) 97–112.
- [97] M. Gil, E. Teruel, I. Arauzo, Analysis of standard sieving method for milled biomass through image processing. Effects of particle shape and size for poplar and corn stover, *Fuel* 116 (2014) 328–340.
- [98] Q. Zhang, M. Benoit, K. De Oliveira Vigier, J. Barraut, G. Jegou, M. Philippe, F. Jerome, Pretreatment of microcrystalline cellulose by ultrasounds: effect of particle size in the heterogeneously-catalyzed hydrolysis of cellulose to glucose, *Green Chem.* 15 (2013) 963–969.
- [99] S.H. Kothari, V. Kumar, G.S. Banker, Comparative evaluations of powder and mechanical properties of low crystallinity celluloses, microcrystalline celluloses, and powdered celluloses, *Int. J. Pharm.* 232 (2002) 69–80.
- [100] L.T. Fan, Y.-H. Lee, D.H. Beardmore, Mechanism of the enzymatic hydrolysis of cellulose: effects of major structural features of cellulose on enzymatic hydrolysis, *Biotechnol. Bioeng.* 22 (1980) 177–199.
- [101] X. Meng, M. Foston, J. Leisen, J. DeMartini, C.E. Wyman, A.J. Ragauskas, Determination of porosity of lignocellulosic biomass before and after pretreatment by using Simons' stain and NMR techniques, *Bioresour. Technol.* 144 (2013) 467–476.
- [102] S. Ardizzone, F.S. Dioguardi, T. Mussini, P.R. Mussini, S. Rondinini, B. Vercelli, A. Vertova, Microcrystalline cellulose powders: structure, surface features and water sorption capability, *Cellulose* 6 (1999) 57–69.
- [103] H. Peng, H. Chen, Y. Qu, H. Li, J. Xu, Bioconversion of different sizes of microcrystalline cellulose pretreated by microwave irradiation with/without NaOH, *Appl. Energy* 117 (2014) 142–148.
- [104] M.K. Inglesby, S.H. Zeronian, Direct dyes as molecular sensors to characterize cellulose substrates, *Cellulose* 9 (2002) 19–29.
- [105] R. Chandra, S. Ewanick, C. Hsieh, J.N. Saddler, The characterization of pretreated lignocellulosic substrates prior to enzymatic hydrolysis, part 1: a modified Simons' staining technique, *Biotechnol. Prog.* 24 (2008) 1178–1185.
- [106] M. Wiman, D. Dienes, M.A.T. Hansen, T. van der Meulen, G. Zacchi, G. Lidén, Cellulose accessibility determines the rate of enzymatic hydrolysis of steam-pretreated spruce, *Bioresour. Technol.* 126 (2012) 208–215.
- [107] C.A. Carrillo, D. Saloni, O.J. Rojas, Evaluation of O/W microemulsions to penetrate the capillary structure of woody biomass: interplay between composition and formulation in green processing, *Green Chem.* (2013).
- [108] A.M. Bellocq, J. Biais, P. Bothorel, B. Clin, G. Fourche, P. Lalanne, B. Lemaire, B. Lemanceau, D. Roux, Microemulsions, *Adv. Colloid Interface Sci.* 20 (1984) 167–272.
- [109] D. Langevin, Microemulsions - interfacial aspects, *Adv. Colloid Interface Sci.* 34 (1991) 583–595.
- [110] J. Pang, M. Zheng, A. Wang, T. Zhang, Catalytic hydrogenation of corn stalk to ethylene glycol and 1,2-Propylene glycol, *Ind. Eng. Chem. Res.* 50 (2011) 6601–6608.
- [111] C. Li, M. Zheng, A. Wang, T. Zhang, One-pot catalytic hydrocracking of raw woody biomass into chemicals over supported carbide catalysts: simultaneous conversion of cellulose, hemicellulose and lignin, *Energy Environ. Sci.* 5 (2012) 6383–6390.
- [112] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts, *Angew. Chemie Int. Ed.* 47 (2008) 8510–8513.
- [113] A.P. Imeson, W. Humphreys, Microcrystalline cellulose, in: A. Imeson (Ed.), *Thickening and Gelling Agents for Food*, Springer, US, 1997, pp. 180–198.
- [114] M. Ielovich, A. Leykin, O. Figovsky, Study of cellulose paracrystallinity, *BioResources* 5 (2010) 1393–1407.

- [115] M. Loelovitch, M. Gordeev, Crystallinity of cellulose and its accessibility during deuteration, *Acta Polym.* 45 (1994) 121–123.
- [116] I.L. Wadehra, R.S.J. Manley, Recrystallization of amorphous cellulose, *J. Appl. Polym. Sci.* 9 (1965) 2627–2630.
- [117] K. Schenzel, S. Fischer, E. Brendler, New method for determining the degree of cellulose I crystallinity by means of FT raman spectroscopy, *Cellulose* 12 (2005) 223–231.
- [118] A.L. Barnette, L.C. Bradley, B.D. Veres, E.P. Schreiner, Y.B. Park, J. Park, S. Park, S.H. Kim, Selective detection of crystalline cellulose in plant cell walls with sum-frequency-generation (SFG) vibration spectroscopy, *Biomacromolecules* 12 (2011) 2434–2439.
- [119] S. Park, J. Baker, M. Himmel, P. Parilla, D. Johnson, Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance, *Biotechnol. Biofuels* 3 (2010) 10.
- [120] U.P. Agarwal, Analysis of cellulose and lignocellulose materials by Raman spectroscopy: a review of the current status, *Molecules* 24 (2019) 1659.
- [121] S. Kim, C. Lee, K. Kafle, Characterization of crystalline cellulose in biomass: basic principles, applications, and limitations of XRD, NMR, IR, Raman, and SFG, *Korean J. Chem. Eng.* 30 (2013) 2127–2141.
- [122] M. Makarem, C.M. Lee, K. Kafle, S. Huang, I. Chae, H. Yang, J.D. Kubicki, S.H. Kim, Probing cellulose structures with vibrational spectroscopy, *Cellulose* 26 (2019) 35–79.
- [123] S. Nishikawa, S. Ono, Transmission of X-rays through fibrous, lamellar and granular substances, *Proc. Phys.-Math. Soc.* 7 (1913) 131–138.
- [124] P.H. Hermans, A. Weidinger, Quantitative X-Ray investigations on the crystallinity of cellulose fibers. A background analysis, *J. Appl. Phys.* 19 (1948) 491–506.
- [125] P.H. Hermans, A. Weidinger, X-ray studies on the crystallinity of cellulose, *J. Polym. Sci.* 4 (1949) 135–144.
- [126] P.H. Hermans, A. Weidinger, Quantitative investigation of the X-Ray diffraction picture of some typical rayon specimens: part I, *Text. Res. J.* 31 (1961) 558–571.
- [127] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An empirical method for estimating the degree of crystallinity of native cellulose using the X-Ray diffractometer, *Text. Res. J.* 29 (1959) 786–794.
- [128] A.D. French, M.S. Cintrón, Cellulose polymorphism, crystallite size, and the Segal crystallinity index, *Cellulose* 20 (2013) 583–588.
- [129] S. Nam, A.D. French, B.D. Condon, M. Concha, Segal crystallinity index revisited by the simulation of X-ray diffraction patterns of cotton cellulose I β and cellulose II, *Carbohydr. Polym.* 135 (2016) 1–9.
- [130] X. Ju, M. Bowden, E.E. Brown, X. Zhang, An improved X-ray diffraction method for cellulose crystallinity measurement, *Carbohydr. Polym.* 123 (2015) 476–481.
- [131] W. Ruland, X-ray determination of crystallinity and diffuse disorder scattering, *Acta Crystallogr.* 14 (1961) 1180–1185.
- [132] C. Vonk, Computerization of Ruland's X-ray method for determination of the crystallinity in polymers, *J. Appl. Crystallogr.* 6 (1973) 148–152.
- [133] K. Kafle, C. Lee, H. Shin, J. Zoppe, D. Johnson, S. Kim, S. Park, Effects of delignification on crystalline cellulose in lignocellulose biomass characterized by vibrational sum frequency generation spectroscopy and X-ray diffraction, *Bioenergy Res.* (2015) 1–9.
- [134] E.-L. Hult, T. Iversen, J. Sugiyama, Characterization of the supermolecular structure of cellulose in wood pulp fibres, *Cellulose* 10 (2003) 103–110.
- [135] R. Teeäär, R. Serimaa, T. Paakkari, Crystallinity of cellulose, as determined by CP/MAS NMR and XRD methods, *Polym. Bull.* 17 (1987) 231–237.
- [136] J. He, S. Cui, S.-y. Wang, Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate, *J. Appl. Polym. Sci.* 107 (2008) 1029–1038.
- [137] C.J. Garvey, I.H. Parker, G.P. Simon, On the interpretation of X-Ray diffraction powder patterns in terms of the nanostructure of cellulose I fibres, *Macromol. Chem. Phys.* 206 (2005) 1568–1575.
- [138] P. Ahvenainen, I. Kontro, K. Svedström, Comparison of sample crystallinity determination methods by X-ray diffraction for challenging cellulose I materials, *Cellulose* 23 (2016) 1073–1086.
- [139] P. Debye, Zerstreuung von röntgenstrahlen, *Ann. Phys.* 351 (1915) 809–823.
- [140] H. Rietveld, Line profiles of neutron powder-diffraction peaks for structure refinement, *Acta Crystallogr.* 22 (1967) 151–152.
- [141] H. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.* 2 (1969) 65–71.
- [142] R.T. O'Connor, E.F. DuPré, D. Mitcham, Applications of infrared absorption spectroscopy to investigations of cotton and modified cottons: part I: physical and crystalline modifications and oxidation, *Text. Res. J.* 28 (1958) 382–392.
- [143] S.Y. Oh, D.I. Yoo, Y. Shin, H.C. Kim, H.Y. Kim, Y.S. Chung, W.H. Park, J.H. Youk, Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy, *Carbohydr. Res.* 340 (2005) 2376–2391.
- [144] M.L. Nelson, R.T. O'Connor, Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part II. A new infrared ratio for estimation of crystallinity in celluloses I and II, *J. Appl. Polym. Sci.* 8 (1964) 1325–1341.
- [145] P. Calvini, A. Gorassini, G. Luciano, E. Franceschi, FTIR and WAXS analysis of periodate oxycellulose: evidence for a cluster mechanism of oxidation, *Vib. Spectrosc.* 40 (2006) 177–183.
- [146] K.K. Pandey, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, *J. Appl. Polym. Sci.* 71 (1999) 1969–1975.
- [147] U.P. Agarwal, R.S. Reiner, S.A. Ralph, Cellulose I crystallinity determination using FT-raman spectroscopy: univariate and multivariate methods, *Cellulose* 17 (2010) 721–733.
- [148] U.P. Agarwal, R.R. Reiner, S.A. Ralph, Estimation of cellulose crystallinity of lignocelluloses using near-IR FT-Raman spectroscopy and comparison of the Raman and Segal-WAXS methods, *J. Agric. Food Chem.* 61 (2012) 103–113.
- [149] S.H. Kim, C.M. Lee, K. Kafle, Characterization of crystalline cellulose in biomass: basic principles, applications, and limitations of XRD, NMR, IR, Raman, and SFG, *Korean J. Chem. Eng.* 30 (2013) 2127–2141.
- [150] C.M. Lee, A. Mittal, A.L. Barnette, K. Kafle, Y.B. Park, H. Shin, D.K. Johnson, S. Park, S.H. Kim, Cellulose polymorphism study with sum-frequency-generation (SFG) vibration spectroscopy: identification of exocyclic CH 2 OH conformation and chain orientation, *Cellulose* 20 (2013) 991–1000.
- [151] C.M. Lee, K. Kafle, Y.B. Park, S.H. Kim, Probing crystal structure and mesoscale assembly of cellulose microfibrils in plant cell walls, tunicate tests, and bacterial films using vibrational sum frequency generation (SFG) spectroscopy, *J. Chem. Soc. Faraday Trans.* 16 (2014) 10844–10853.
- [152] R.H. Newman, Homogeneity in Cellulose Crystallinity Between Samples of Pinus radiata Wood, *Walter de Gruyter*, 2004.
- [153] G. Zuckertstätter, G. Schild, P. Wollboldt, T. Röder, H.K. Weber, H. Sixta, The elucidation of cellulose supramolecular structure by ¹³C CP MAS NMR, *Lenzinger Berichte* 87 (2009) 38–46.
- [154] T. Liitiä, S. Maunu, B. Hortling, T. Tamminen, O. Pekkala, A. Varhimo, Cellulose crystallinity and ordering of hemicelluloses in pine and birch pulps as revealed by solid-state NMR spectroscopic methods, *Cellulose* 10 (2003) 307–316.
- [155] B.B. Hallac, P. Sannigrahi, Y. Pu, M. Ray, R.J. Murphy, A.J. Ragauskas, Biomass characterization of *Buddleja davidii*: a potential feedstock for biofuel production, *J. Agric. Food Chem.* 57 (2009) 1275–1281.
- [156] T. Liitiä, S.L. Maunu, B. Hortling, Solid state NMR studies on cellulose crystallinity in fines and bulk fibres separated from refined kraft pulp, *Holzforschung* 54 (2000) 618–624.
- [157] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, Effects of crystallinity on dilute acid hydrolysis of cellulose by cellulose ball-milling study, *Energy Fuels* 20 (2005) 807–811.
- [158] S. Andersson, H. Wikberg, E. Pesonen, S. Maunu, R. Serimaa, Studies of crystallinity of Scots pine and Norway spruce cellulose, *Trees* 18 (2004) 346–353.
- [159] E.-L. Hult, P. Larsson, T. Iversen, A comparative CP/MAS ¹³C-NMR study of cellulose structure in spruce wood and kraft pulp, *Cellulose* 7 (2000) 35–55.
- [160] Y. Pu, C. Ziemer, A.J. Ragauskas, CP/MAS ¹³C NMR analysis of cellulose treated bleached softwood kraft pulp, *Carbohydr. Res.* 341 (2006) 591–597.
- [161] X. Nocanda, P.T. Larsson, A. Spark, T. Bush, A. Olsson, A. Bissessur, T. Iversen, Cross polarisation/magic angle spinning ¹³C-NMR spectroscopic studies of cellulose structural changes in hardwood dissolving pulp process, *Holzforschung* 61 (2007) 675–679.
- [162] P.T. Larsson, E.-L. Hult, K. Wickholm, E. Pettersson, T. Iversen, CP/MAS ¹³C-NMR spectroscopy applied to structure and interaction studies on cellulose I, *Solid State Nucl. Magn. Reson.* 15 (1999) 31–40.
- [163] R. Newman, J. Hemmingson, Determination of the degree of cellulose crystallinity in wood by carbon-13 nuclear magnetic resonance spectroscopy, *Holzforschung-Int. J. Biol. Chem. Phys. Technol. Wood* 44 (1990) 351–356.
- [164] S. Park, D. Johnson, C. Ishizawa, P. Parilla, M. Davis, Measuring the crystallinity index of cellulose by solid state ¹³C nuclear magnetic resonance, *Cellulose* 16 (2009) 641–647.
- [165] L.R. Schroeder, V.M. Gentile, R.H. Atalla, Nondegradative preparation of amorphous cellulose, *J. Wood Chem. Technol.* 6 (1986) 1–14.
- [166] P. Sannigrahi, A.J. Ragauskas, Fundamentals of biomass pretreatment by fractionation, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons, Ltd, West Sussex, United Kingdom, 2013, pp. 201–222.
- [167] Y.-H.P. Zhang, L.R. Lynd, Toward an aggregated understanding of enzymatic hydrolysis of cellulose: noncomplexed cellulase systems, *Biotechnol. Bioeng.* 88 (2004) 797–824.
- [168] Y.-H.P. Zhang, M.E. Himmel, J.R. Mielenz, Outlook for cellulase improvement: screening and selection strategies, *Biotechnol. Adv.* 24 (2006) 452–481.
- [169] B.B. Hallac, A.J. Ragauskas, Analyzing cellulose degree of polymerization and its relevancy to cellulose ethanol, *Biofuels Bioprod. Biorefining* 5 (2011) 215–225.
- [170] R. Evans, R.H. Wearne, A.F.A. Wallis, Molecular weight distribution of cellulose as its tricarbanilate by high performance size exclusion chromatography, *J. Appl. Polym. Sci.* 37 (1989) 3291–3303.
- [171] C.A. Hubbell, A.J. Ragauskas, Effect of acid-chlorite delignification on cellulose degree of polymerization, *Bioresour. Technol.* 101 (2010) 7410–7415.
- [172] E. Sjöholm, K. Gustafsson, B. Eriksson, W. Brown, A. Colmsjö, Aggregation of cellulose in lithium chloride/N,N-dimethylacetamide, *Carbohydr. Polym.* 41 (2000) 153–161.
- [173] M. Strlič, J. Kolar, M. Žigon, B. Pihlar, Evaluation of size-exclusion chromatography and viscometry for the determination of molecular masses of oxidised cellulose, *J. Chromatogr. A* 805 (1998) 93–99.
- [174] K. Karimi, M.J. Taherzadeh, A critical review on analysis in pretreatment of lignocelluloses: degree of polymerization, adsorption/desorption, and accessibility, *Bioresour. Technol.* 203 (2016) 348–356.
- [175] A.-L. Dupont, G. Mortha, Comparative evaluation of size-exclusion chromatography and viscometry for the characterisation of cellulose, *J. Chromatogr. A* 1026 (2004) 129–141.
- [176] R. Berggren, F. Berthold, E. Sjöholm, M. Lindström, Improved methods for evaluating the molar mass distributions of cellulose in kraft pulp, *J. Appl. Polym. Sci.* 88 (2003) 1170–1179.
- [177] Y.-H.P. Zhang, L.R. Lynd, Determination of the number-average degree of polymerization of cellobextrins and cellulose with application to enzymatic hydrolysis, *Biomacromolecules* 6 (2005) 1510–1515.
- [178] H. Krässig, J. Schurz, R.G. Steadman, K. Schliefer, W. Albrecht, M. Mohring, H. Schlosser, *Cellulose*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-

- VCH Verlag GmbH & Co, KGaA, Weinheim, 2004.
- [179] G. Thoores, F. Krier, B. Leclercq, B. Carlin, B. Evrard, Microcrystalline cellulose, a direct compression binder in a quality by design environment—a review, *Int. J. Pharm.* 473 (2014) 64–72.
- [180] S. TAPPI, TAPPI Standards: Regulations and Style Guidelines, TAPPI Press, Atlanta, USA, 1996.
- [181] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of structural carbohydrates and lignin in biomass, *Laboratory analytical procedure 1617* (2008) 1–16.
- [182] E.L. Springer, J.F. Harris, Procedures for determining the neutralizing capacity of wood during hydrolysis with mineral acid solutions, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 485–489.
- [183] W.J.J. Huijgen, A.T. Smit, J.H. Reith, H.D. Uil, Catalytic organosolv fractionation of willow wood and wheat straw as pretreatment for enzymatic cellulose hydrolysis, *J. Chem. Technol. Biotechnol.* 86 (2011) 1428–1438.
- [184] A. Berlin, M. Balakshin, N. Gilkes, J. Kadla, V. Maximenko, S. Kubo, J. Saddler, Inhibition of cellulase, xylanase and β -glucosidase activities by softwood lignin preparations, *J. Biotechnol.* 125 (2006) 198–209.
- [185] Y. Kim, E. Ximenes, N.S. Mosier, M.R. Ladisch, Soluble inhibitors/deactivators of cellulase enzymes from lignocellulosic biomass, *Enzyme Microb. Technol.* 48 (2011) 408–415.
- [186] M. Besson, P. Gallezot, Deactivation of metal catalysts in liquid phase organic reactions, *Catal. Today* 81 (2003) 547–559.
- [187] V.I. Sharkov, Production of polyhydric alcohols from wood polysaccharides, *Angew. Chemie Int. Ed. English* 2 (1963) 405–409.
- [188] J. Pang, M. Zheng, A. Wang, R. Sun, H. Wang, Y. Jiang, T. Zhang, Catalytic conversion of concentrated miscanthus in water for ethylene glycol production, *AIChE J.* 60 (2014) 2254–2262.
- [189] J. Pang, M. Zheng, R. Sun, L. Song, A. Wang, X. Wang, T. Zhang, Catalytic conversion of cellulosic biomass to ethylene glycol: effects of inorganic impurities in biomass, *Bioresour. Technol.* 175 (2015) 424–429.
- [190] C. Yang, H. Kobayashi, A. Fukuoka, Removal of catalyst poisons for the production of sugar alcohols from a real biomass molasses using a heterogeneous Ni catalyst, *Fuel Process. Technol.* 196 (2019) 106155.
- [191] W.S.L. Mok, M.J. Antal, Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water, *Ind. Eng. Chem. Res.* 31 (1992) 1157–1161.
- [192] N. Yan, C. Zhao, P.J. Dyson, C. Wang, L.-t. Liu, Y. Kou, Selective degradation of wood lignin over noble-metal catalysts in a two-step process, *ChemSusChem* 1 (2008) 626–629.
- [193] E. Sjöström, *Wood Chemistry: Fundamentals and Applications*, 2nd ed., Gulf Professional Publishing, 1993.
- [194] A. Vehniäinen, P. Haikkala, T. Suhonen, Future outlook in papermaking science and technology, in: B. Lönnberg (Ed.), *Mechanical Pulping, Paper Engineers' Association/Paperi Ja Puu Oy, Helsingfors (Helsinki)*, 2009, p. 516.
- [195] S. Haghghi Mood, A. Hossein Golfeshan, M. Tabatabaei, G. Salehi Jouzani, G.H. Najafi, M. Gholami, M. Ardjmand, Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment, *Renew. Sustain. Energy Rev.* 27 (2013) 77–93.
- [196] B. Vidal Jr., B. Dien, K.C. Ting, V. Singh, Influence of feedstock particle size on lignocellulose conversion—a review, *Appl. Biochem. Biotechnol.* 164 (2011) 1405–1421.
- [197] M. Ago, T. Endo, T. Hirotsu, Crystalline transformation of native cellulose from cellulose I to cellulose II polymorph by a ball-milling method with a specific amount of water, *Cellulose* 11 (2004) 163–167.
- [198] M.H. Sipponen, S. Laakso, S. Baumberger, Impact of ball milling on maize (*Zea mays* L.) stem structural components and on enzymatic hydrolysis of carbohydrates, *Ind. Crops Prod.* 61 (2014) 130–136.
- [199] M. Benoit, A. Rodrigues, Q. Zhang, E. Fourré, K. De Oliveira Vigier, J.-M. Tatibouët, F. Jérôme, Depolymerization of cellulose assisted by a nonthermal atmospheric plasma, *Angew. Chemie* 123 (2011) 9126–9129.
- [200] F. de Clippel, M. Dusselier, S. Van de Vyver, L. Peng, P.A. Jacobs, B.F. Sels, Tailoring nanohybrids and nanocomposites for catalytic applications, *Green Chem.* 15 (2013) 1398–1430.
- [201] J. Pang, A. Wang, M. Zheng, T. Zhang, Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures, *Chem. Commun.* 46 (2010) 6935–6937.
- [202] H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita, A. Fukuoka, High-yielding one-pot synthesis of glucose from cellulose using simple activated carbons and trace hydrochloric acid, *ACS Catal.* 3 (2013) 581–587.
- [203] R.J. Grisel, A.T. Smit, Thermochemical saccharification of cellulose: the benefit of adding a scavenger, *Appl. Catal. A Gen.* 475 (2014) 438–445.
- [204] S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Voshch, L. Zhang, G. Van Tendeloo, P.A. Jacobs, B.F. Sels, Selective bifunctional catalytic conversion of cellulose over reshaped Ni particles at the tip of carbon nanofibers, *ChemSusChem* 3 (2010) 698–701.
- [205] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P.L. Dhepe, K. Kasai, K. Hara, A. Fukuoka, Synthesis of sugar alcohols by hydrolytic hydrogenation of cellulose over supported metal catalysts, *Green Chem.* 13 (2011) 326–333.
- [206] Y. Liao, Q. Liu, T. Wang, J. Long, L. Ma, Q. Zhang, Zirconium phosphate combined with Ru/C as a highly efficient catalyst for the direct transformation of cellulose to C 6 aldol, *Green Chem.* 16 (2014) 3305–3312.
- [207] T. Ennaert, B.O. de Beeck, J. Vanneste, A.T. Smit, W.J. Huijgen, A. Vanhulsel, P.A. Jacobs, B.F. Sels, The importance of pretreatment and feedstock purity in the reductive splitting of (ligno) cellulose by metal supported USY zeolite, *Green Chem.* 18 (2016) 2095–2105.
- [208] J. Pang, M. Zheng, X. Li, J. Sebastian, Y. Jiang, Y. Zhao, A. Wang, T. Zhang, Unlock the compact structure of lignocellulosic biomass by mild ball milling for ethylene glycol production, *ACS Sustain. Chem. Eng.* 7 (2018) 679–687.
- [209] S. Liu, M. Tamura, Y. Nakagawa, K. Tomishige, One-pot conversion of cellulose into n-hexane over the Ir-ReO_x/SiO₂ catalyst combined with HZSM-5, *ACS Sustain. Chem. Eng.* 2 (2014) 1819–1827.
- [210] A.S.A. da Silva, R.S.S. Teixeira, R. de Oliveira Moutta, V.S. Ferreira-Leitão, R.d.R.O. de Barros, M.A. Ferrara, E.P. da Silva Bon, Sugarcane and woody biomass pretreatments for ethanol production, in: A.K. Chandel, S.S. da Silva (Eds.), *Sustainable Degradation of Lignocellulosic Biomass - Techniques, Applications and Commercialization*, InTech, 2013.
- [211] M. Laser, D. Schulman, S.G. Allen, J. Lichwa, M.J. Antal Jr., L.R. Lynd, A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol, *Bioresour. Technol.* 81 (2002) 33–44.
- [212] N. Meine, R. Rinaldi, F. Schüth, Solvent-Free Catalytic Depolymerization of Cellulose to Water-Soluble Oligosaccharides, *ChemSusChem* 5 (2012) 1449–1454.
- [213] G. Kaupp, Waste-free large-scale syntheses without auxiliaries for sustainable production omitting purifying workup, *CrystEngComm* 8 (2006) 794–804.
- [214] Q. Zhang, F. Jérôme, Mechanocatalytic deconstruction of cellulose: an emerging entry into biorefinery, *ChemSusChem* (2013) n/a-n/a.
- [215] S.M. Hick, C. Griebel, D.T. Restrepo, J.H. Truitt, E.J. Buker, C. Bylde, R.G. Blair, Mechanocatalysis for biomass-derived chemicals and fuels, *Green Chem.* 12 (2010) 468–474.
- [216] M. Källdström, N. Meine, C. Farès, F. Schüth, R. Rinaldi, Deciphering 'water-soluble lignocellulose' obtained by mechanocatalysis: new insights into the chemical processes leading to deep depolymerization, *Green Chem.* 16 (2014) 3528–3538.
- [217] F. Schüth, R. Rinaldi, N. Meine, M. Källdström, J. Hilgert, M.K. Rechulski, Mechanocatalytic depolymerization of cellulose and raw biomass and downstream processing of the products, *Catal. Today* 234 (2014) 24–30.
- [218] M. Källdström, N. Meine, C. Farès, R. Rinaldi, F. Schüth, Fractionation of 'water-soluble lignocellulose' into C 5/C 6 sugars and sulfur-free lignins, *Green Chem.* 16 (2014) 2454–2462.
- [219] J. Hilgert, N. Meine, R. Rinaldi, F. Schüth, Mechanocatalytic depolymerization of cellulose combined with hydrogenolysis as a highly efficient pathway to sugar alcohols, *Energy Environ. Sci.* 6 (2013) 92–96.
- [220] A. Shrotri, L.K. Lambert, A. Tanksale, J. Beltrami, Mechanical depolymerisation of acidulated cellulose: understanding the solubility of high molecular weight oligomers, *Green Chem.* 15 (2013) 2761–2768.
- [221] R. Carrasquillo-Flores, M. Källdström, F. Schüth, J.A. Dumesic, R. Rinaldi, Mechanocatalytic depolymerization of dry (Ligno)cellulose as an entry process for high-yield production of furfurals, *ACS Catal.* 3 (2013) 993–997.
- [222] M.D. Kaufman Rechulski, M. Källdström, U. Richter, F. Schüth, R. Rinaldi, Mechanocatalytic depolymerization of lignocellulose performed on hectogram and kilogram scales, *Ind. Eng. Chem. Res.* 54 (2015) 4581–4592.
- [223] S. Liu, Y. Okuyama, M. Tamura, Y. Nakagawa, A. Imai, K. Tomishige, Production of Renewable Hexanols from Mechanocatalytically Depolymerized Cellulose by Using Ir-ReO_x/SiO₂ catalyst, *ChemSusChem* 8 (2015) 628–635.
- [224] L. Schneider, J. Haverinen, M. Jaakkola, U. Lassi, Pretreatment and fractionation of lignocellulosic barley straw by mechanocatalysis, *Chem. Eng. J.* 327 (2017) 898–905.
- [225] A. Shrotri, H. Kobayashi, A. Fukuoka, Mechanochemical synthesis of a carboxylated carbon catalyst and its application in cellulose hydrolysis, *ChemCatChem* 8 (2016) 1059–1064.
- [226] A. Shrotri, H. Kobayashi, A. Fukuoka, Cellulose depolymerization over heterogeneous catalysts, *Acc. Chem. Res.* 51 (2018) 761–768.
- [227] P. Chen, A. Shrotri, A. Fukuoka, Soluble Cello-Oligosaccharides Produced by Carbon-Catalyzed Hydrolysis of Cellulose, *ChemSusChem* (2019).
- [228] A. Shrotri, H. Kobayashi, H. Kaiki, M. Yabushita, A. Fukuoka, Cellulose hydrolysis using oxidized carbon catalyst in a plug-flow slurry process, *Ind. Eng. Chem. Res.* 56 (2017) 14471–14478.
- [229] M. Yabushita, H. Kobayashi, K. Hara, A. Fukuoka, Quantitative evaluation of ball-milling effects on the hydrolysis of cellulose catalysed by activated carbon, *Catal. Sci. Technol.* 4 (2014) 2312–2317.
- [230] A. Shrotri, H. Kobayashi, A. Fukuoka, Air oxidation of activated carbon to synthesize a biomimetic catalyst for hydrolysis of cellulose, *ChemSusChem* 9 (2016) 1299–1303.
- [231] H. Kobayashi, H. Kaiki, A. Shrotri, K. Techikawara, A. Fukuoka, Hydrolysis of woody biomass by a biomass-derived reusable heterogeneous catalyst, *Chem. Sci.* 7 (2016) 692–696.
- [232] Y. Liao, Q. Liu, T. Wang, J. Long, Q. Zhang, L. Ma, Y. Liu, Y. Li, Promoting hydrolytic hydrogenation of cellulose to sugar alcohols by mixed ball milling of cellulose and solid acid catalyst, *Energy Fuels* 28 (2014) 5778–5784.
- [233] F. Boissou, N. Sayoud, K. De Oliveira Vigier, A. Barakat, S. Marinkovic, B. Estrine, F. Jérôme, Acid-Assisted Ball Milling of Cellulose as an Efficient Pretreatment Process for the Production of Butyl Glycosides, *ChemSusChem* 8 (2015) 3263–3269.
- [234] S. Ouajai, R. Shanks, Solvent and enzyme induced recrystallization of mechanically degraded hemp cellulose, *Cellulose* 13 (2006) 31–44.
- [235] F. Yu, R. Zhong, H. Chong, M. Smet, W. Dehaen, B.F. Sels, Fast catalytic conversion of recalcitrant cellulose into alkyl levulinates and levulinic acid in the presence of soluble and recoverable sulfonated hyperbranched poly (arylene oxindole) s, *Green Chem.* 19 (2017) 153–163.
- [236] C. Polk, E. Postow, *Handbook of Biological Effects of Electromagnetic Fields*, Third Edition - 2 Volume Set, Taylor & Francis, 1995.
- [237] M.R. Al-Masri, M. Zarkawi, Effects of gamma irradiation on cell-wall constituents of some agricultural residues, *Radiat. Phys. Chem.* 44 (1994) 661–663.
- [238] M. Kumakura, I. Kaetsu, Radiation-induced decomposition and enzymatic

- hydrolysis of cellulose, *Biotechnol. Bioeng.* 20 (1978) 1309–1315.
- [239] E. Betiku, O. Adetunji, T. Ojumu, B. Solomon, A comparative study of the hydrolysis of gamma irradiated lignocelluloses, *Braz. J. Chem. Eng.* 26 (2009) 251–255.
- [240] M. Kumakura, I. Kaetsu, Effect of radiation pretreatment of bagasse on enzymatic and acid hydrolysis, *Biomass* 3 (1983) 199–208.
- [241] J.S. Bak, Electron beam irradiation enhances the digestibility and fermentation yield of water-soaked lignocellulosic biomass, *Biotechnol. Rep.* 4 (2014) 30–33.
- [242] O. Merino-Pérez, R. Martínez-Palou, J. Labidi, R. Luque, Microwave-assisted pretreatment of lignocellulosic biomass to produce biofuels and value-added products, in: Z. Fang, J.R.L. Smith, X. Qi (Eds.), *Production of Biofuels and Chemicals With Microwave*, Springer, Netherlands, 2015, pp. 197–224.
- [243] H. Li, Y. Qu, Y. Yang, S. Chang, J. Xu, Microwave irradiation—A green and efficient way to pretreat biomass, *Bioresour. Technol.* 199 (2016) 34–41.
- [244] X. Lu, B. Xi, Y. Zhang, I. Angelidaki, Microwave pretreatment of rape straw for bioethanol production: focus on energy efficiency, *Bioresour. Technol.* 102 (2011) 7937–7940.
- [245] M.M. de Souza Moretti, D.A. Bocchini-Martins, C.d.C.C. Nunes, M.A. Villena, O.M. Perrone, R. da Silva, M. Boscolo, E. Gomes, Pretreatment of sugarcane bagasse with microwaves irradiation and its effects on the structure and on enzymatic hydrolysis, *Appl. Energy* 122 (2014) 189–195.
- [246] Y. Wu, Z. Fu, D. Yin, Q. Xu, F. Liu, C. Lu, L. Mao, Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids, *Green Chem.* 12 (2010) 696–700.
- [247] J. Fan, M. De bruyn, V.L. Budarin, M.J. Gronnow, P.S. Shuttleworth, S. Breeden, D.J. Macquarrie, J.H. Clark, Direct microwave-assisted hydrothermal depolymerization of cellulose, *J. Am. Chem. Soc.* 135 (2013) 11728–11731.
- [248] Y. Luo, J. Fan, V.L. Budarin, C. Hu, J.H. Clark, Microwave-assisted hydrothermal selective dissolution and utilisation of cellulose in *Phyllostachys heterocycla* cv. *Pubescens*, *Green Chem.* 19 (2017) 4889–4899.
- [249] J. Remón, T. Li, C.J. Chuck, A.S. Matharu, J.H. Clark, Toward Renewable-Based, Food-Applicable Prebiotics from Biomass: A One-Step, Additive-Free, Microwave-Assisted Hydrothermal Process for the Production of High Purity Xylo-oligosaccharides from Beech Wood Hemicellulose, *ACS Sustain. Chem. Eng.* 7 (2019) 16160–16172.
- [250] Z. He, Z. Wang, Z. Zhao, S. Yi, J. Mu, X. Wang, Influence of ultrasound pretreatment on wood physicochemical structure, *Ultrason. Sonochem.* 34 (2017) 136–141.
- [251] B. Yang, L. Tao, C.E. Wyman, Strengths, challenges, and opportunities for hydrothermal pretreatment in lignocellulosic biorefineries, *Biofuels Bioprod. Biorefining* 12 (2018) 125–138.
- [252] H. Kobayashi, Y. Yamakoshi, Y. Hosaka, M. Yabushita, A. Fukuoka, Production of sugar alcohols from real biomass by supported platinum catalyst, *Catal. Today* 226 (2014) 204–209.
- [253] M. Pedersen, A.S. Meyer, Lignocellulose pretreatment severity – relating pH to biomatrix opening, *N. Biotechnol.* 27 (2010) 739–750.
- [254] N.S. Mosier, Fundamentals of aqueous pretreatment of biomass, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons, Ltd., West Sussex, United Kingdom, 2013, pp. 129–143.
- [255] F. Jin, H. Enomoto, Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: chemistry of acid/base-catalysed and oxidation reactions, *Energy Environ. Sci.* 4 (2011) 382–397.
- [256] B. Yang, C.E. Wyman, Effect of xylan and lignin removal by batch and flowthrough pretreatment on the enzymatic digestibility of corn stover cellulose, *Biotechnol. Bioeng.* 86 (2004) 88–95.
- [257] G. Moeller-Chavez, S. Gonzalez-Martinez, Two combined techniques to enhance anaerobic digestion of sludge, *Water science and technology: a journal of the International Association on Water Pollution Research* 46 (2002) 167–172.
- [258] J. Kim, C. Park, T.-H. Kim, M. Lee, S. Kim, S.-W. Kim, J. Lee, Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, *J. Biosci. Bioeng.* 95 (2003) 271–275.
- [259] T. DiStefano, A. Ambulkar, Methane production and solids destruction in an anaerobic solid waste reactor due to post-reactor caustic and heat treatment, *Water Sci. Technol.* 53 (2006) 33–41.
- [260] J. Li, G. Henriksson, G. Gellerstedt, Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion, *Bioresour. Technol.* 98 (2007) 3061–3068.
- [261] B.S. Donohoe, S.R. Decker, M.P. Tucker, M.E. Himmel, T.B. Vinzant, Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatment, *Biotechnol. Bioeng.* 101 (2008) 913–925.
- [262] S. Deguchi, K. Tsujii, K. Horikoshi, Cooking cellulose in hot and compressed water, *Chem. Commun.* (2006) 3293–3295.
- [263] S. Deguchi, K. Tsujii, K. Horikoshi, Crystalline-to-amorphous transformation of cellulose in hot and compressed water and its implications for hydrothermal conversion, *Green Chem.* 10 (2008) 191–196.
- [264] R.L. Silveira, S.R. Stoyanov, A. Kovalenko, M.S. Skaf, Cellulose aggregation under hydrothermal pretreatment conditions, *Biomacromolecules* 17 (2016) 2582–2590.
- [265] M.R. Sturgeon, S. Kim, K. Lawrence, R.S. Paton, S.C. Chmely, M. Nimlos, T.D. Foust, G.T. Beckham, A mechanistic investigation of acid-catalyzed cleavage of aryl-ether linkages: implications for lignin depolymerization in acidic environments, *ACS Sustain. Chem. Eng.* 2 (2013) 472–485.
- [266] S. Jung, H.L. Trajano, C.G. Yoo, M.B. Foston, F. Hu, A.K. Tolbert, C.E. Wyman, A.J. Ragauskas, Topochemical understanding of lignin distribution during hydrothermal flowthrough pretreatment, *ChemistrySelect* 3 (2018) 9348–9352.
- [267] N. Mosier, R. Hendrickson, N. Ho, M. Sedlak, M.R. Ladisch, Optimization of pH controlled liquid hot water pretreatment of corn stover, *Bioresour. Technol.* 96 (2005) 1986–1993.
- [268] N. Mosier, R. Hendrickson, M. Brewer, N. Ho, M. Sedlak, R. Dreshel, G. Welch, B. Dien, A. Aden, M. Ladisch, Industrial scale-up of pH-controlled liquid hot water pretreatment of corn fiber for fuel ethanol production, *Appl. Biochem. Biotechnol.* 125 (2005) 77–97.
- [269] C.E. Wyman, B.E. Dale, R.T. Elander, M. Holtzapfel, M.R. Ladisch, Y.Y. Lee, C. Mitchinson, J.N. Saddler, Comparative sugar recovery and fermentation data following pretreatment of poplar wood by leading technologies, *Biotechnol. Prog.* 25 (2009) 333–339.
- [270] Y.G. Sun, Y. Ma, Z. Wang, J. Yao, Evaluating and optimizing pretreatment technique for catalytic hydrogenolysis conversion of corn stalk into polyol, *Bioresour. Technol.* 158 (2014) 307–312.
- [271] C.J. Biermann, *Handbook of Pulping and Papermaking*, Elsevier Science, 1996.
- [272] H. Trajano, C.E. Wyman, Fundamentals of biomass pretreatment at Low pH, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons, Ltd., West Sussex, United Kingdom, 2013, pp. 103–128.
- [273] X. Meng, T. Wells, Q. Sun, F. Huang, A. Ragauskas, Insights into the effect of dilute acid, hot water or alkaline pretreatment on the cellulose accessible surface area and the overall porosity of Populus, *Green Chem.* 17 (2015) 4239–4246.
- [274] F. Bergius, Conversion of wood to carbohydrates and problems in the industrial use of concentrated hydrochloric acid, *Ind. Eng. Chem.* 29 (1937) 247–253.
- [275] W.L. Faith, Development of the scholler process in the United States, *Ind. Eng. Chem.* 37 (1945) 9–11.
- [276] R. Erckel, R. Franz, R. Woernle, T. Riehm, Process for hydrolyzing cellulose-containing material with gaseous hydrogen fluoride, in: H. Aktiengesellschaft (Ed.), *Germany*, 1985.
- [277] D.L. Brink, *Method of Treating Biomass Material*, (1994).
- [278] C.J. Israillides, G.A. Grant, Y.W. Han, Sugar Level, Fermentability, and Acceptability of Straw Treated with Different Acids, *Appl. Environ. Microbiol.* 36 (1978) 43–46.
- [279] A.M. Kootstra, H. Beftink, E. Scott, J. Sanders, Optimization of the dilute maleic acid pretreatment of wheat straw, *Biotechnol. Biofuels* 2 (2009) 31.
- [280] A. Kootstra, H. Beftink, E. Scott, J. Sanders, Comparison of dilute mineral and organic acid pretreatment for enzymatic hydrolysis of wheat straw, *Biochem. Eng. J.* 46 (2009) 126–131.
- [281] D. Scordia, S.L. Cosentino, J.-W. Lee, T.W. Jeffries, Dilute oxalic acid pretreatment for biorefining giant reed (*Arundo donax* L.), *Biomass Bioenergy* 35 (2011) 3018–3024.
- [282] H.Q. Lam, Y.L. Bigot, M. Delmas, E.G. Avignon, Formic acid pulping of rice straw, *Ind. Crops Prod.* 14 (2001) 65–71.
- [283] R.A. Young, J.L. Davis, E.-B. Wiesmann, Organic acid pulping of wood-part II. Acetic acid pulping of Aspen, *Holzforchung-Int. J. Biol. Chem. Phys. Technol.* Wood 40 (1986) 99–108.
- [284] Y. Ogasawara, S. Itagaki, K. Yamaguchi, N. Mizuno, Saccharification of natural lignocellulose biomass and polysaccharides by highly negatively charged heteropolycids in concentrated aqueous solution, *ChemSusChem* 4 (2011) 519–525.
- [285] Y. Lu, N.S. Mosier, Biomimetic catalysis for hemicellulose hydrolysis in corn stover, *Biotechnol. Prog.* 23 (2007) 116–123.
- [286] N.S. Mosier, C.M. Ladisch, M.R. Ladisch, Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation, *Biotechnol. Bioeng.* 79 (2002) 610–618.
- [287] D.W. Rackemann, W.O.S. Doherty, The conversion of lignocellulosics to levulinic acid, *Biofuels Bioprod. Biorefining* 5 (2011) 198–214.
- [288] G.R. Akien, L. Qi, I.T. Horvath, Molecular mapping of the acid catalysed dehydration of fructose, *Chem. Commun.* 48 (2012) 5850–5852.
- [289] J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural—a promising platform for lignocellulosic biofuels, *ChemSusChem* 5 (2012) 150–166.
- [290] D.J. Braden, C.A. Henao, J. Heltzel, C.C. Maravelias, J.A. Dumesic, Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid, *Green Chem.* 13 (2011) 1755–1765.
- [291] A. Mukherjee, M.-J. Dumont, V. Raghavan, Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities, *Biomass Bioenergy* 72 (2015) 143–183.
- [292] D.J. Hayes, S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, The biofine process – production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks, in: B. Kamm, P.R. Gruber, M. Kamm (Eds.), *Biorefineries – Industrial Processes and Products*, Wiley-VCH, Weinheim, 2006, pp. 139–163.
- [293] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B.F. Sels, Lactic acid as a platform chemical in the biobased economy: the role of chemocatalysis, *Energy Environ. Sci.* 6 (2013) 1415–1442.
- [294] K. Iris, D.C. Tsang, Conversion of biomass to hydroxymethylfurfural: a review of catalytic systems and underlying mechanisms, *Bioresour. Technol.* 238 (2017) 716–732.
- [295] R.-J. Van Putten, J.C. Van Der Waal, E. De Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, *Chem. Rev.* 113 (2013) 1499–1597.
- [296] T. Wang, M.W. Nolte, B.H. Shanks, Catalytic dehydration of C 6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical, *Green Chem.* 16 (2014) 548–572.
- [297] K. Garves, Acid catalyzed degradation of cellulose in alcohols, *J. Wood Chem. Technol.* 8 (1988) 121–134.
- [298] R. Grisel, J. Van Der Waal, E. De Jong, W. Huijgen, Acid catalysed alcoholysis of wheat straw: towards second generation furan-derivatives, *Catal. Today* 223 (2014) 3–10.
- [299] N. Villandier, A. Corma, Transformation of cellulose into biodegradable alkyl

- glycosides by following two different chemical routes, *ChemSusChem* 4 (2011) 508–513.
- [300] A.V. Puga, A. Corma, Direct conversion of cellulose into alkyl glycoside surfactants, *ChemistrySelect* 2 (2017) 2495–2498.
- [301] D. Ding, J. Xi, J. Wang, X. Liu, G. Lu, Y. Wang, Production of methyl levulinate from cellulose: selectivity and mechanism study, *Green Chem.* 17 (2015) 4037–4044.
- [302] Y.-B. Huang, T. Yang, Y.-T. Lin, Y.-Z. Zhu, L.-C. Li, H. Pan, Facile and high-yield synthesis of methyl levulinate from cellulose, *Green Chem.* 20 (2018) 1323–1334.
- [303] K.-i. Tominaga, A. Mori, Y. Fukushima, S. Shimada, K. Sato, Mixed-acid systems for the catalytic synthesis of methyl levulinate from cellulose, *Green Chem.* 13 (2011) 810–812.
- [304] W. Deng, M. Liu, Q. Zhang, Y. Wang, Direct transformation of cellulose into methyl and ethyl glucosides in methanol and ethanol media catalyzed by heteropolyacids, *Catal. Today* 164 (2011) 461–466.
- [305] M. Dusselier, R. De Clercq, R. Cornelis, B.F. Sels, Tin triflate-catalyzed conversion of cellulose to valuable (α -hydroxy-) esters, *Catal. Today* 279 (2017) 339–344.
- [306] R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi, A. Ruppert, Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts, *Green Chem.* 12 (2010) 972–978.
- [307] R. Palkovits, K. Tajvidi, A.M. Ruppert, J. Procelewska, Heteropoly acids as efficient acid catalysts in the one-step conversion of cellulose to sugar alcohols, *Chem. Commun.* 47 (2011) 576–578.
- [308] J. Michael Robinson, C.E. Burgess, M.A. Bently, C.D. Brasher, B.O. Horne, D.M. Lillard, J.M. Macias, H.D. Mandall, S.C. Mills, K.D. O'Hara, J.T. Pon, A.F. Raigoza, E.H. Sanchez, J.S. Villarreal, The use of catalytic hydrogenation to intercept carbohydrates in a dilute acid hydrolysis of biomass to effect a clean separation from lignin, *Biomass Bioenergy* 26 (2004) 473–483.
- [309] A. Fukuoka, P.L. Dhepe, Catalytic conversion of cellulose into sugar alcohols, *Angew. Chemie Int. Ed.* 45 (2006) 5161–5163.
- [310] A. Yamaguchi, O. Sato, N. Mimura, Y. Hirosaki, H. Kobayashi, A. Fukuoka, M. Shirai, Direct production of sugar alcohols from wood chips using supported platinum catalysts in water, *Catal. Commun.* 54 (2014) 22–26.
- [311] H. Kobayashi, A. Fukuoka, Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass, *Green Chem.* 15 (2013) 1740–1763.
- [312] A.M. Ruppert, K. Weinberg, R. Palkovits, Hydrogenolysis Goes bio: from carbohydrates and sugar alcohols to platform chemicals, *Angew. Chemie Int. Ed.* 51 (2012) 2564–2601.
- [313] H. Kobayashi, A. Fukuoka, Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass, *Green Chem.* (2013).
- [314] G.W. Huber, J.A. Dumesic, An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery, *Catal. Today* 111 (2006) 119–132.
- [315] N. Li, G.W. Huber, Aqueous-phase hydrodeoxygenation of sorbitol with Pt/SiO₂-Al₂O₃: identification of reaction intermediates, *J. Catal.* 270 (2010) 48–59.
- [316] X. Liu, X. Liu, G. Xu, Y. Zhang, C. Wang, Q. Lu, L. Ma, Highly efficient catalytic conversion of cellulose into acetol over Ni–Sn supported on nanosilica and the mechanism study, *Green Chem.* 21 (2019) 5647–5656.
- [317] H. Wang, C. Zhu, Q. Liu, J. Tan, C. Wang, Z. Liang, L. Ma, Selective Conversion of Cellulose to Hydroxyacetone and 1-Hydroxy-2-Butanone with Sn–Ni Bimetallic Catalysts, *ChemSusChem* (2019).
- [318] R. Sun, T. Wang, M. Zheng, W. Deng, J. Pang, A. Wang, X. Wang, T. Zhang, Versatile Nickel–Lanthanum (III) catalyst for direct conversion of cellulose to glycols, *ACS Catal.* 5 (2015) 874–883.
- [319] R. Sun, M. Zheng, J. Pang, X. Liu, J. Wang, X. Pan, A. Wang, X. Wang, T. Zhang, Selectivity-switchable conversion of cellulose to glycols over Ni–Sn catalysts, *ACS Catal.* 6 (2016) 191–201.
- [320] Y. Liu, C. Luo, H. Liu, Tungsten trioxide promoted selective conversion of cellulose into propylene glycol and ethylene glycol on a ruthenium catalyst, *Angew. Chemie Int. Ed.* 51 (2012) 3249–3253.
- [321] Y. Liu, L. Chen, T. Wang, Q. Zhang, C. Wang, J. Yan, L. Ma, One-pot catalytic conversion of raw lignocellulosic biomass into gasoline alkanes and chemicals over LiTaMoO₆ and Ru/C in aqueous phosphoric acid, *ACS Sustain. Chem. Eng.* 3 (2015) 1745–1755.
- [322] L. Jin, W. Li, Q. Liu, L. Ma, C. Hu, A.T. Ogunbiyi, M. Wu, Q. Zhang, High performance of Mo-promoted Ir/SiO₂ catalysts combined with HZSM-5 toward the conversion of cellulose to C₅/C₆ alkanes, *Bioresour. Technol.* (2019) 122492.
- [323] B.O. de Beeck, M. Dusselier, J. Geboers, J. Holsbeek, E. Morré, S. Oswald, L. Giebeler, B.F. Sels, Direct catalytic conversion of cellulose to liquid straight-chain alkanes, *Energy Environ. Sci.* 8 (2015) 230–240.
- [324] A. Deneyer, E. Peeters, T. Renders, S. Van den Bosch, N. Van Oeckel, T. Ennaert, T. Szarvas, T.I. Korányi, M. Dusselier, B.F. Sels, Direct upstream integration of biogasoline production into current light straight run naphtha petrorefinery processes, *Nat. Energy* 3 (2018) 969.
- [325] A. Deneyer, T. Ennaert, G. Cavents, J. Dijkmans, J. Vanneste, C. Courtin, M. Dusselier, B. Sels, Compositional and structural feedstock requirements of a liquid phase cellulose-to-naphtha process in a carbon-and hydrogen-neutral biorefinery context, *Green Chem.* 18 (2016) 5594–5606.
- [326] R.S. Ramirez, M. Holtzapfel, N. Piamonte, Fundamentals of biomass pretreatment at high pH, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons, Ltd., West Sussex, United Kingdom, 2013, pp. 145–167.
- [327] R.A. Silverstein, Y. Chen, R.R. Sharma-Shivappa, M.D. Boyette, J. Osborne, A comparison of chemical pretreatment methods for improving saccharification of cotton stalks, *Bioresour. Technol.* 98 (2007) 3000–3011.
- [328] M. Beccari, M. Majone, M.P. Papini, L. Torrisi, Enhancement of anaerobic treatability of olive oil mill effluents by addition of Ca(OH)₂ and bentonite without intermediate solid/liquid separation, *Water Sci. Technol.* 43 (2001) 275–282.
- [329] Z. Xu, Q. Wang, Z. Jiang, X.-x. Yang, Y. Ji, Enzymatic hydrolysis of pretreated soybean straw, *Biomass Bioenergy* 31 (2007) 162–167.
- [330] G. Bali, X. Meng, J.I. Deneff, Q. Sun, A.J. Ragauskas, The effect of alkaline pretreatment methods on cellulose structure and accessibility, *ChemSusChem* 8 (2015) 275–279.
- [331] C.J. Knill, J.F. Kennedy, Degradation of cellulose under alkaline conditions, *Carbohydr. Polym.* 51 (2003) 281–300.
- [332] X. Zhao, L. Zhang, D. Liu, Comparative study on chemical pretreatment methods for improving enzymatic digestibility of crofton weed stem, *Bioresour. Technol.* 99 (2008) 3729–3736.
- [333] J.F. Revol, D.A.I. Goring, On the mechanism of the mercerization of cellulose in wood, *J. Appl. Polym. Sci.* 26 (1981) 1275–1282.
- [334] D. Fengel, H. Jakob, C. Strobel, Influence of the alkali concentration on the formation of cellulose II. Study by X-ray diffraction and FTIR spectroscopy, *Holzforchung-Int. J. Biol. Chem. Phys. Technol. Wood* 49 (1995) 505–511.
- [335] A. Isogai, R.H. Atalla, Dissolution of cellulose in aqueous NaOH solutions, *Cellulose* 5 (1998) 309–319.
- [336] A.A. Saapan, S.H. Kandil, A.M. Habib, Liquid Ammonia and caustic mercerization of cotton fibers using X-Ray, infrared, and sorption measurements, *Text. Res. J.* 54 (1984) 863–867.
- [337] A. Mittal, R. Katahira, M. Himmel, D. Johnson, Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility, *Biotechnol. Biofuels* 4 (2011) 41.
- [338] P. Weimer, A. French, T. Calamari, Differential fermentation of cellulose alcohols by ruminal cellulolytic bacteria, *Appl. Environ. Microbiol.* 57 (1991) 3101–3106.
- [339] S. Kumar, R. Gupta, Y.Y. Lee, R.B. Gupta, Cellulose pretreatment in subcritical water: effect of temperature on molecular structure and enzymatic reactivity, *Bioresour. Technol.* 101 (2010) 1337–1347.
- [340] M. Wada, M. Ike, K. Tokuyasu, Enzymatic hydrolysis of cellulose I is greatly accelerated via its conversion to the cellulose II hydrate form, *Polym. Degrad. Stab.* 95 (2010) 543–548.
- [341] A.J. Barry, F.C. Peterson, A.J. King, X-ray studies of reactions of cellulose in nonaqueous systems. I. Interaction of cellulose and liquid ammonia, *J. Am. Chem. Soc.* 58 (1936) 333–337.
- [342] C. Schuerch, Plasticizing wood with liquid ammonia, *Ind. Eng. Chem.* 55 (1963) 39.
- [343] M. Lewin, L.G. Roldan, The effect of liquid anhydrous ammonia in the structure and morphology of cotton cellulose, *J. Polym. Sci. Part C Polym. Symp.* 36 (1971) 213–229.
- [344] J. Hayashi, A. Sufoka, J. Ohkita, S. Watanabe, The confirmation of existences of cellulose III, IIII, IVI, and IVII by the X-ray method, *J. Polym. Sci. Polym. Lett. Ed.* 13 (1975) 23–27.
- [345] M. Wada, H. Chanzy, Y. Nishiyama, P. Langan, Cellulose IIII crystal structure and hydrogen bonding by synchrotron X-ray and neutron Fiber diffraction, *Macromolecules* 37 (2004) 8548–8555.
- [346] K. Igarashi, T. Uchihashi, A. Koivula, M. Wada, S. Kimura, T. Okamoto, M. Penttilä, T. Ando, M. Samejima, Traffic jams reduce hydrolytic efficiency of cellulase on cellulose surface, *Science* 333 (2011) 1279–1282.
- [347] M. Goswami, S. Meena, S. Navatha, K.N. Prasanna Rani, A. Pandey, R.K. Sukumaran, R.B.N. Prasad, B.L.A. Prabhavathi Devi, Hydrolysis of biomass using a reusable solid carbon acid catalyst and fermentation of the catalytic hydrolysate to ethanol, *Bioresour. Technol.* 188 (2015) 99–102.
- [348] C. Li, G. Xu, C. Wang, L. Ma, Y. Qiao, Y. Zhang, Y. Fu, One-pot chemocatalytic transformation of cellulose to ethanol over Ru-WO_x/HZSM-5, *Green Chem.* 21 (2019) 2234–2239.
- [349] M. Yang, H. Qi, F. Liu, Y. Ren, X. Pan, L. Zhang, X. Liu, H. Wang, J. Pang, M. Zheng, One-pot production of cellulosic ethanol via tandem catalysis over a multifunctional Mo/Pt/WO_x catalyst, *Joule* (2019).
- [350] H. Song, P. Wang, S. Li, W. Deng, Y. Li, Q. Zhang, Y. Wang, Direct conversion of cellulose into ethanol catalyzed by a combination of tungstic acid and zirconia-supported Pt nanoparticles, *Chem. Commun.* 55 (2019) 4303–4306.
- [351] Q. Liu, H. Wang, H. Xin, C. Wang, L. Yan, Y. Wang, Q. Zhang, X. Zhang, Y. Xu, G.W. Huber, Selective cellulose hydrogenolysis to ethanol using Ni@C combined with phosphoric acid catalysts, *ChemSusChem* (2019).
- [352] V. Balan, B. Bals, S.P. Chundawat, D. Marshall, B.E. Dale, Lignocellulosic Biomass Pretreatment Using AFEX Biofuels: Methods and Protocols, (2009), pp. 61–77.
- [353] S.P.S. Chundawat, R. Vismeh, L.N. Sharma, J.F. Humpala, L. da Costa Sousa, C.K. Chambliss, A.D. Jones, V. Balan, B.E. Dale, Multifaceted characterization of cell wall decomposition products formed during ammonia fiber expansion (AFEX) and dilute acid based pretreatments, *Bioresour. Technol.* 101 (2010) 8429–8438.
- [354] S.P.S. Chundawat, B.S. Donohoe, L. da Costa Sousa, T. Elder, U.P. Agarwal, F. Lu, J. Ralph, M.E. Himmel, V. Balan, B.E. Dale, Multi-scale visualization and characterization of lignocellulosic plant cell wall deconstruction during thermochemical pretreatment, *Energy Environ. Sci.* 4 (2011) 973–984.
- [355] M. Holtzapfel, J.-H. Jun, G. Ashok, S. Patibandla, B. Dale, The ammonia freeze explosion (AFEX) process, *Appl. Biochem. Biotechnol.* 28–29 (1991) 59–74.
- [356] Z. Fang, F. Zhang, H.-Y. Zeng, F. Guo, Production of glucose by hydrolysis of cellulose at 423 K in the presence of activated hydrotalcite nanoparticles, *Bioresour. Technol.* 102 (2011) 8017–8021.
- [357] S.P. Chundawat, G. Bellesia, N. Uppugundla, L. da Costa Sousa, D. Gao, A.M. Chel, U.P. Agarwal, C.M. Bianchetti, G.N. Phillips Jr., P. Langan, Restructuring the crystalline cellulose hydrogen bond network enhances its depolymerization rate,

- J. Am. Chem. Soc. 133 (2011) 11163–11174.
- Y. D. Gao, S.P. Chundawat, A. Sethi, V. Balan, S. Gnanakaran, B.E. Dale, Increased enzyme binding to substrate is not necessary for more efficient cellulose hydrolysis, *Proc. Natl. Acad. Sci.* 110 (2013) 10922–10927.
- Z. L. da Costa Sousa, M. Jin, S.P. Chundawat, V. Bokade, X. Tang, A. Azarpira, F. Lu, U. Avci, J. Humpula, N. Uppugundla, Next-generation ammonia pretreatment enhances cellulosic biofuel production, *Energy Environ. Sci.* 9 (2016) 1215–1223.
- AA. U. Avci, X. Zhou, S. Pattathil, S.D. Leonardo, M.G. Hahn, B. Dale, Y. Xu, V. Balan, Effects of extractive ammonia pretreatment on the ultrastructure and glycan composition of corn stover, *Front. Energy Res.* 7 (2019) 85.
- AB. L. da Costa Sousa, M. Foston, V. Bokade, A. Azarpira, F. Lu, A.J. Ragauskas, J. Ralph, B. Dale, V. Balan, Isolation and characterization of new lignin streams derived from extractive-ammonia (EA) pretreatment, *Green Chem.* 18 (2016) 4205–4215.
- AC. M. Jin, L. da Costa Sousa, C. Schwartz, Y. He, C. Sarks, C. Gunawan, V. Balan, B.E. Dale, Toward lower cost cellulosic biofuel production using ammonia based pretreatment technologies, *Green Chem.* 18 (2016) 957–966.
- AD. J.M. Gould, Alkaline peroxide delignification of agricultural residues to enhance enzymatic saccharification, *Biotechnol. Bioeng.* 26 (1984) 46–52.
- AE. P.F. Vidal, J. Molinier, Ozonolysis of lignin — improvement of in vitro digestibility of poplar sawdust, *Biomass* 16 (1988) 1–17.
- AF. G.D. McGinnis, W.W. Wilson, C.E. Mullen, Biomass pretreatment with water and high-pressure oxygen. The wet-oxidation process, *Ind. Eng. Chem. Prod. Res. Dev.* 22 (1983) 352–357.
- AG. L. Teixeira, J. Linden, H. Schroeder, Alkaline and peracetic acid pretreatments of biomass for ethanol production, in: B. Davison, M. Finkelstein (Eds.), *Twentieth Symposium on Biotechnology for Fuels and Chemicals*, Humana Press, 1999, pp. 19–34.
- AH. Y.-J. Lee, C.-H. Chung, D.F. Day, Sugarcane bagasse oxidation using a combination of hypochlorite and peroxide, *Bioresour. Technol.* 100 (2009) 935–941.
- AI. P.A. Ahlgren, D.A.I. Goring, Removal of wood components during chlorite delignification of black spruce, *Can. J. Chem.* 49 (1971) 1272–1275.
- AJ. G. Panagiotou, L. Olsson, Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates, *Biotechnol. Bioeng.* 96 (2007) 250–258.
- AK. D. Guay, B. Cole, R. Fort Jr., J. Genco, M. Hausman, Mechanisms of Oxidative Degradation of Carbohydrates During Oxygen Delignification. I. Reaction of Methyl β -D-Glucopyranoside with Photochemically Generated Hydroxyl Radicals, *J. Wood Chem. Technol.* 20 (2000) 375–394.
- AL. L. Zhou, X. Yang, J. Xu, M. Shi, F. Wang, C. Chen, J. Xu, Depolymerization of cellulose to glucose by oxidation–hydrolysis, *Green Chem.* 17 (2015) 1519–1524.
- AM. G.I. Mantanis, R.A. Young, R.M. Rowell, Swelling of wood. Part II. Swelling in organic liquids, *Holzforchung-Int. J. Biol. Chem. Phys. Technol. Wood* 48 (1994) 480–490.
- AN. G.I. Mantanis, R.A. Young, R.M. Rowell, Swelling of compressed cellulose fiber webs in organic liquids, *Cellulose* 2 (1995) 1–22.
- AO. Y. Boluk, Acid–base interactions and swelling of cellulose fibers in organic liquids, *Cellulose* 12 (2005) 577–593.
- AP. P. Sannigrahi, S.J. Miller, A.J. Ragauskas, Effects of organosolv pretreatment and enzymatic hydrolysis on cellulose structure and crystallinity in Loblolly pine, *Carbohydr. Res.* 345 (2010) 965–970.
- AQ. Z. Fang, *Pretreatment Techniques for Biofuels and Biorefineries*, Springer Berlin Heidelberg, 2013.
- AR. J. Wildschut, A.T. Smit, J.H. Reith, W.J.J. Huijgen, Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose, *Bioresour. Technol.* 135 (2013) 58–66.
- AS. W.J.J. Huijgen, J.H. Reith, H. den Uil, Pretreatment and fractionation of wheat straw by an acetone-based organosolv process, *Ind. Eng. Chem. Res.* 49 (2010) 10132–10140.
- AT. G. Brudecki, I. Cybulska, K. Rosentrater, Optimization of clean fractionation process applied to switchgrass to produce pulp for enzymatic hydrolysis, *Bioresour. Technol.* 131 (2013) 101–112.
- AU. R. Sindhu, P. Binod, K. Satyanagalakshmi, K. Janu, K. Sajna, N. Kurien, R. Sukumaran, A. Pandey, Formic acid as a potential pretreatment agent for the conversion of sugarcane bagasse to bioethanol, *Appl. Biochem. Biotechnol.* 162 (2010) 2313–2323.
- AV. X. Pan, Y. Sano, Fractionation of wheat straw by atmospheric acetic acid process, *Bioresour. Technol.* 96 (2005) 1256–1263.
- AW. D. Haverty, K. Dussan, A.V. Piterina, J.J. Leahy, M.H.B. Hayes, Autothermal, single-stage, performic acid pretreatment of *Miscanthus x giganteus* for the rapid fractionation of its biomass components into a lignin/hemicellulose-rich liquor and a cellulose-digestible pulp, *Bioresour. Technol.* 109 (2012) 173–177.
- AX. W. Fang, H. Sixta, Advanced biorefinery based on the fractionation of biomass in γ -Valerolactone and water, *ChemSusChem* 8 (2015) 73–76.
- AY. J. Quesada-Medina, F.J. López-Cremades, P. Olivares-Carrillo, Organosolv extraction of lignin from hydrolyzed almond shells and application of the δ -value theory, *Bioresour. Technol.* 101 (2010) 8252–8260.
- AZ. H.Q. Lê, A. Zaitseva, J.P. Pokki, M. Ståhl, V. Alopaevs, H. Sixta, Solubility of Organosolv Lignin in γ -Valerolactone/Water Binary Mixtures, *ChemSusChem* 9 (2016) 2939–2947.
- BA. C. Loerbros, R. Rinaldi, W. Thiel, The electronic nature of the 1,4- β -Glycosidic bond and its chemical environment: DFT insights into cellulose chemistry, *Chem. Eur. J.* 19 (2013) 16282–16294.
- BB. L. Kham, Y. Le Bigot, M. Delmas, G. Avignon, Delignification of wheat straw using a mixture of carboxylic acids and peroxyacids, *Ind. Crops Prod.* 21 (2005) 9–15.
- BC. T.N. Kleinert, *Organosolv Pulping and Recovery Process*, (1971).
- [389] A.L. Jimenez, D.J.C. Garcia, O.I. Perez, Influence of cooking variables in the organosolv pulping of wheat straw using mixtures of ethanol, acetone, and water, *Tappi J.* 2 (2003) 27–31.
- [390] W.J.J. Huijgen, A.T. Smit, P.J. de Wild, H. den Uil, Fractionation of wheat straw by prehydrolysis, organosolv delignification and enzymatic hydrolysis for production of sugars and lignin, *Bioresour. Technol.* 114 (2012) 389–398.
- [391] G. Dahlmann, M. Schroeter, The Organocel process: pulping with the environment in mind, *Tappi J.* 73 (1990) 237–240.
- [392] E.K. Pye, J.H. Lora, The Alcell™ process: a proven alternative to kraft pulping, *Tappi J.* 74 (1991) 113–118.
- [393] P.M. Grande, J. Viell, N. Theysen, W. Marquardt, P. Dominguez de Maria, W. Leitner, Fractionation of lignocellulosic biomass using the OrganoCat process, *Green Chem.* 17 (2015) 3533–3539.
- [394] S.-X. Li, M.-F. Li, J. Bian, S.-N. Sun, F. Peng, Z.-M. Xue, Biphasic 2-methyltetrahydrofuran/oxalic acid/water pretreatment to enhance cellulose enzymatic hydrolysis and lignin valorization, *Bioresour. Technol.* 243 (2017) 1105–1111.
- [395] T. Damm, P.M. Grande, N.D. Jablonowski, B. Thiele, U. Disko, U. Mann, U. Schurr, W. Leitner, B. Usadel, P.D. de María, OrganoCat pretreatment of perennial plants: synergies between a biogenic fractionation and valuable feedstocks, *Bioresour. Technol.* 244 (2017) 889–896.
- [396] A. Morone, R. Pandey, T. Chakrabarti, Evaluation of OrganoCat process as a pretreatment during bioconversion of rice straw, *Ind. Crops Prod.* 99 (2017) 7–18.
- [397] D. Weidener, H. Klose, W. Leitner, U. Schurr, B. Usadel, P. Domínguez de María, P.M. Grande, One-Step Lignocellulose Fractionation by using 2, 5-Furandicarboxylic Acid as a Biogenic and Recyclable Catalyst, *ChemSusChem* 11 (2018) 2051–2056.
- [398] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass, *Green Chem.* 15 (2013) 584–595.
- [399] L. Shuai, Y.M. Questell-Santiago, J.S. Luterbacher, A mild biomass pretreatment using γ -valerolactone for concentrated sugar production, *Green Chem.* 18 (2016) 937–943.
- [400] T.Y. Nguyen, C.M. Cai, R. Kumar, C.E. Wyman, Co-solvent pretreatment reduces costly enzyme requirements for high sugar and ethanol yields from lignocellulosic biomass, *ChemSusChem* 8 (2015) 1716–1725.
- [401] T.Y. Nguyen, C.M. Cai, O. Osman, R. Kumar, C.E. Wyman, CELF pretreatment of corn stover boosts ethanol titers and yields from high solids SSF with low enzyme loadings, *Green Chem.* 18 (2016) 1581–1589.
- [402] A.S. Patri, L. McAlister, C.M. Cai, R. Kumar, C.E. Wyman, CELF significantly reduces milling requirements and improves soaking effectiveness for maximum sugar recovery of Alamo switchgrass over dilute sulfuric acid pretreatment, *Biotechnol. Biofuels* 12 (2019) 177.
- [403] T.Y. Nguyen, C.M. Cai, R. Kumar, C.E. Wyman, Overcoming factors limiting high-solids fermentation of lignocellulosic biomass to ethanol, *Proc. Natl. Acad. Sci.* 114 (2017) 11673–11678.
- [404] B. Mostofian, C.M. Cai, M.D. Smith, L. Petridis, X. Cheng, C.E. Wyman, J.C. Smith, Local phase separation of co-solvents enhances pretreatment of biomass for bioenergy applications, *J. Am. Chem. Soc.* 138 (2016) 10869–10878.
- [405] A.S. Patri, B. Mostofian, Y. Pu, N. Cifano, M. Soliman, M.D. Smith, R. Kumar, X. Cheng, C.E. Wyman, L. Tetard, A multifunctional cosolvent pair reveals molecular principles of biomass deconstruction, *J. Am. Chem. Soc.* 141 (2019) 12545–12557.
- [406] B. Lindman, G. Karlström, L. Stigsson, On the mechanism of dissolution of cellulose, *J. Mol. Liq.* 156 (2010) 76–81.
- [407] T. Heinze, A. Koschella, Solvents applied in the field of cellulose chemistry: a mini review, *Polymer* 15 (2005) 84–90.
- [408] T. Heinze, T. Liebert, Unconventional methods in cellulose functionalization, *Prog. Polym. Sci.* 26 (2001) 1689–1762.
- [409] J. Cai, L. Zhang, Rapid dissolution of cellulose in LiOH/Urea and NaOH/Urea aqueous solutions, *Macromol. Biosci.* 5 (2005) 539–548.
- [410] A. Brandt, J. Graskvik, J.P. Hallett, T. Welton, Deconstruction of lignocellulosic biomass with ionic liquids, *Green Chem.* 15 (2013) 550–583.
- [411] S. Singh, B.A. Simmons, Ionic liquid pretreatment: mechanism, performance, and challenges, in: C.E. Wyman (Ed.), *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley and Sons, Ltd., West Sussex, United Kingdom, 2013, pp. 223–238.
- [412] Z.-D. Ding, J.-C. Shi, J.-J. Xiao, W.-X. Gu, C.-G. Zheng, H.-J. Wang, Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst, *Carbohydr. Polym.* 90 (2012) 792–798.
- [413] F. Tao, H. Song, L. Chou, Hydrolysis of cellulose in SO₃H-functionalized ionic liquids, *Bioresour. Technol.* 102 (2011) 9000–9006.
- [414] R. Rinaldi, R. Palkovits, F. Schüth, Depolymerization of cellulose using solid catalysts in ionic liquids, *Angew. Chemie Int. Ed.* 47 (2008) 8047–8050.
- [415] R. Rinaldi, N. Meine, J. vom Stein, R. Palkovits, F. Schüth, Which Controls the Depolymerization of Cellulose in Ionic Liquids: The Solid Acid Catalyst or Cellulose? *ChemSusChem* 3 (2010) 266–276.
- [416] R.M. de Almeida, J. Li, C. Nederlof, P. O'Connor, M. Makkee, J.A. Moulijn, Cellulose conversion to isosorbide in molten salt hydrate media, *ChemSusChem* 3 (2010) 325–328.
- [417] S.H. Lee, T.V. Doherty, R.J. Linhardt, J.S. Dordick, Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis, *Biotechnol. Bioeng.* 102 (2009) 1368–1376.
- [418] S.-J. Kim, A.A. Dwiatmoko, J.W. Choi, Y.-W. Suh, D.J. Suh, M. Oh, Cellulose pretreatment with 1-n-butyl-3-methylimidazolium chloride for solid acid-catalyzed hydrolysis, *Bioresour. Technol.* 101 (2010) 8273–8279.
- [419] J. Zakzeski, R.J.H. Grisel, A.T. Smit, B.M. Weckhuysen, Solid acid-catalyzed

- cellulose hydrolysis monitored by in situ ATR-IR spectroscopy, *ChemSusChem* 5 (2012) 430–437.
- [420] H. Tadesse, R. Luque, Advances on biomass pretreatment using ionic liquids: an overview, *Energy Environ. Sci.* 4 (2011) 3913–3929.
- [421] J. Zhang, B. Zhang, J. Zhang, L. Lin, S. Liu, P. Ouyang, Effect of phosphoric acid pretreatment on enzymatic hydrolysis of microcrystalline cellulose, *Biotechnol. Adv.* 28 (2010) 613–619.
- [422] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, Conversion of cellulose into sorbitol over carbon nanotube-supported ruthenium catalyst, *Catal Lett* 133 (2009) 167–174.
- [423] H. Zhao, J.E. Holladay, J.H. Kwak, Z.C. Zhang, Inverse temperature-dependent pathway of cellulose decrystallization in trifluoroacetic acid, *J. Phys. Chem. B* 111 (2007) 5295–5300.
- [424] D.C. Dibble, C. Li, L. Sun, A. George, A. Cheng, O.P. Cetinkol, P. Benke, B.M. Holmes, S. Singh, B.A. Simmons, A facile method for the recovery of ionic liquid and lignin from biomass pretreatment, *Green Chem.* 13 (2011) 3255–3264.
- [425] G. Cheng, P. Varanasi, C. Li, H. Liu, Y.B. Melnichenko, B.A. Simmons, M.S. Kent, S. Singh, Transition of Cellulose Crystalline Structure and Surface Morphology of Biomass as a Function of Ionic Liquid Pretreatment and Its Relation to Enzymatic Hydrolysis, *Biomacromolecules* 12 (2011) 933–941.
- [426] M. Zavrel, D. Bross, M. Funke, J. Büchs, A.C. Spiess, High-throughput screening for ionic liquids dissolving (ligno-)cellulose, *Bioresour. Technol.* 100 (2009) 2580–2587.
- [427] C. Li, B. Knierim, C. Manisseri, R. Arora, H.V. Scheller, M. Auer, K.P. Vogel, B.A. Simmons, S. Singh, Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification, *Bioresour. Technol.* 101 (2010) 4900–4906.
- [428] J. Shi, K. Balamurugan, R. Parthasarathi, N. Sathitsuksanoh, S. Zhang, V. Stavila, V. Subramanian, B.A. Simmons, S. Singh, Understanding the role of water during ionic liquid pretreatment of lignocellulose: co-solvent or anti-solvent? *Green Chem.* 16 (2014) 3830–3840.
- [429] R.J.H. Grisel, A.T. Smit, Thermochemical saccharification of cellulose: the benefit of adding a scavenger, *Appl. Catal. A Gen.* 475 (2014) 438–445.
- [430] D. Groff, A. George, N. Sun, N. Sathitsuksanoh, G. Bokinsky, B.A. Simmons, B.M. Holmes, J.D. Keasling, Acid enhanced ionic liquid pretreatment of biomass, *Green Chem.* 15 (2013) 1264–1267.
- [431] W. Zheng, Y. Cui, Z. Xu, L. Zhao, W. Sun, Cellulose transformation into methyl glucosides catalyzed by H3PW12O40: enhancement of ionic liquid pretreatment, *Can. J. Chem. Eng.* 96 (2018) 1250–1255.
- [432] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, *J. Am. Chem. Soc.* 124 (2002) 4974–4975.
- [433] O.A. El Seoud, A. Koschella, L.C. Fidade, S. Dorn, T. Heinze, Applications of ionic liquids in carbohydrate chemistry: a window of opportunities, *Biomacromolecules* 8 (2007) 2629–2647.
- [434] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: recent progress from knowledge to applications, *Appl. Catal. A Gen.* 373 (2010) 1–56.
- [435] A. Pinkert, K.N. Marsh, S. Pang, M.P. Staiger, Ionic liquids and their interaction with cellulose, *Chem. Rev.* 109 (2009) 6712.
- [436] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, *Chem. Soc. Rev.* 37 (2008) 123–150.
- [437] M.E. Zakrzewska, E. Bogel-Lukasik, R. Bogel-Lukasik, Solubility of carbohydrates in ionic liquids, *Energy Fuels* 24 (2010) 737–745.
- [438] Y. Zhang, J.Y.G. Chan, Sustainable chemistry: imidazolium salts in biomass conversion and CO₂ fixation, *Energy Environ. Sci.* 3 (2010) 408–417.
- [439] S. Zhu, Use of ionic liquids for the efficient utilization of lignocellulosic materials, *J. Chem. Technol. Biotechnol.* 83 (2008) 777–779.
- [440] S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, Dissolution of cellulose with ionic liquids and its application: a mini-review, *Green Chem.* 8 (2006) 325–327.
- [441] A. George, A. Brandt, K. Tran, S.M.N.S. Zahari, D. Klein-Marcuschamer, N. Sun, N. Sathitsuksanoh, J. Shi, V. Stavila, R. Parthasarathi, Design of low-cost ionic liquids for lignocellulosic biomass pretreatment, *Green Chem.* 17 (2015) 1728–1734.
- [442] A.M. Socha, R. Parthasarathi, J. Shi, S. Pattathil, D. Whyte, M. Bergeron, A. George, K. Tran, V. Stavila, S. Venkatachalam, Efficient biomass pretreatment using ionic liquids derived from lignin and hemicellulose, *Proc. Natl. Acad. Sci.* 111 (2014) E3587–E3595.
- [443] J. Shi, J.M. Gladden, N. Sathitsuksanoh, P. Kambam, L. Sandoval, D. Mitra, S. Zhang, A. George, S.W. Singer, B.A. Simmons, S. Singh, One-pot ionic liquid pretreatment and saccharification of switchgrass, *Green Chem.* 15 (2013) 2579–2589.
- [444] F. Xu, J. Sun, N.M. Konda, J. Shi, T. Dutta, C.D. Scown, B.A. Simmons, S. Singh, Transforming biomass conversion with ionic liquids: process intensification and the development of a high-gravity, one-pot process for the production of cellulosic ethanol, *Energy Environ. Sci.* 9 (2016) 1042–1049.
- [445] J. Sun, N.M. Konda, J. Shi, R. Parthasarathi, T. Dutta, F. Xu, C.D. Scown, B.A. Simmons, S. Singh, CO₂ enabled process integration for the production of cellulosic ethanol using bionic liquids, *Energy Environ. Sci.* 9 (2016) 2822–2834.
- [446] J. Sun, N.M. Konda, R. Parthasarathi, T. Dutta, M. Valiev, F. Xu, B.A. Simmons, S. Singh, One-pot integrated biofuel production using low-cost biocompatible protic ionic liquids, *Green Chem.* 19 (2017) 3152–3163.
- [447] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jerome, Deep eutectic solvents: syntheses, properties and applications, *Chem. Soc. Rev.* 41 (2012) 7108–7146.
- [448] M. Francisco, A. van den Bruinhorst, M.C. Kroon, Low-transition-Temperature mixtures (LTTMs): a new generation of designer solvents, *Angew. Chemie Int. Ed.* 52 (2013) 3074–3085.
- [449] M. Francisco, A. van den Bruinhorst, M.C. Kroon, New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing, *Green Chem.* 14 (2012) 2153–2157.
- [450] Q. Zhang, M. Benoit, K. De Oliveira Vigier, J. Barrault, F. Jérôme, Green and inexpensive choline-derived solvents for cellulose decrystallization, *Chem. Eur. J.* 18 (2012) 1043–1046.
- [451] K.H. Kim, T. Dutta, J. Sun, B. Simmons, S. Singh, Biomass pretreatment using deep eutectic solvents from lignin derived phenols, *Green Chem.* 20 (2018) 809–815.
- [452] K.H. Kim, A. Eudes, K. Jeong, C.G. Yoo, C.S. Kim, A. Ragauskas, Integration of renewable deep eutectic solvents with engineered biomass to achieve a closed-loop biorefinery, *Proc. Natl. Acad. Sci.* (2019) 201904636.
- [453] M. Benoit, A. Rodrigues, K. De Oliveira Vigier, E. Fourre, J. Barrault, J.-M. Tatibouet, F. Jerome, Combination of ball-milling and non-thermal atmospheric plasma as physical treatments for the saccharification of microcrystalline cellulose, *Green Chem.* (2012).
- [454] J. Delaux, M. Nigen, E. Fourré, J.-M. Tatibouët, A. Barakat, L. Atencio, J.M.G. Fernández, K.D.O. Vigier, F. Jérôme, Fast and solvent free polymerization of carbohydrates induced by non-thermal atmospheric plasma, *Green Chem.* 18 (2016) 3013–3019.
- [455] Y. Zheng, G. Tsao, Avicel hydrolysis by cellulase enzyme in supercritical CO₂, *Biotechnol. Lett.* 18 (1996) 451–454.
- [456] Y. Zheng, H.-M. Lin, J. Wen, N. Cao, X. Yu, G. Tsao, Supercritical carbon dioxide explosion as a pretreatment for cellulose hydrolysis, *Biotechnol. Lett.* 17 (1995) 845–850.
- [457] K.H. Kim, J. Hong, Supercritical CO₂ pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis, *Bioresour. Technol.* 77 (2001) 139–144.
- [458] D. Pasquini, M.T.B. Pimenta, L.H. Ferreira, A.Ad.S. Curvelo, Extraction of lignin from sugar cane bagasse and Pinus taeda wood chips using ethanol-water mixtures and carbon dioxide at high pressures, *J. Supercrit. Fluids* 36 (2005) 31–39.
- [459] C. Park, Y. Ryu, C. Kim, Kinetics and rate of enzymatic hydrolysis of cellulose in supercritical carbon dioxide, *Korean J. Chem. Eng.* 18 (2001) 475–478.
- [460] V.P. Puri, H. Marners, Explosive pretreatment of lignocellulosic residues with high-pressure carbon dioxide for the production of fermentation substrates, *Biotechnol. Bioeng.* 25 (1983) 3149–3161.
- [461] Y. Zheng, H.M. Lin, G.T. Tsao, Pretreatment for cellulose hydrolysis by carbon dioxide explosion, *Biotechnol. Prog.* 14 (1998) 890–896.
- [462] E. Demessie, A. Hassan, K. Levien, S. Kumar, J. Morrell, Supercritical carbon dioxide treatment: effect on permeability of Douglas-Fir Heartwood, *Wood and Fiber Science* 27 (1995) 296–300.
- [463] D. Ritter, A. Campbell, Supercritical carbon dioxide extraction of southern pine and ponderosa pine, *Wood and Fiber Science* 23 (1991) 98–113.
- [464] J.S. Luterbacher, J.W. Tester, L.P. Walker, High-solids biphasic CO₂-H₂O pretreatment of lignocellulosic biomass, *Biotechnol. Bioeng.* 107 (2010) 451–460.
- [465] M.-j. Zhao, Q.-q. Xu, G.-m. Li, Q.-z. Zhang, D. Zhou, J.-z. Yin, H.-s. Zhan, Pretreatment of agricultural residues by supercritical CO₂ at 50–80 °C to enhance enzymatic hydrolysis, *J. Energy Chem.* 31 (2019) 39–45.
- [466] K. Wu, G. Feng, Y. Liu, C. Liu, X. Zhang, S. Liu, B. Liang, H. Lu, Enhanced hydrolysis of mechanically pretreated cellulose in water/CO₂ system, *Bioresour. Technol.* 261 (2018) 28–35.
- [467] T.M. Attard, C.R. McElroy, R.J. Gammons, J.M. Slattery, N. Supanchaiyamat, C.L.A. Kamei, O. Dolstra, L.M. Trindade, N.C. Bruce, S.J. McQueen-Mason, Supercritical CO₂ extraction as an effective pretreatment step for wax extraction in a Miscanthus biorefinery, *ACS Sustain. Chem. Eng.* 4 (2016) 5979–5988.
- [468] J. Schurz, T.K. Ghose (Ed.), Bioconversion of Cellulosic Substances into Energy, Chemicals, and Microbial Protein: Symposium Proceedings, Indian Institute of Technology, New Delhi, 1978, p. 37.
- [469] L.-T. Fan, M.M. Gharpuray, Y.-H. Lee, Enzymatic hydrolysis, Cellulose Hydrolysis, Springer, Berlin, 1987, p. 57.
- [470] C. Wan, Y. Li, Fungal pretreatment of lignocellulosic biomass, *Biotechnol. Adv.* 30 (2012) 1447–1457.
- [471] R. Sindhu, P. Binod, A. Pandey, Biological pretreatment of lignocellulosic biomass—An overview, *Bioresour. Technol.* 199 (2016) 76–82.
- [472] H.K. Sharma, C. Xu, W. Qin, Biological pretreatment of lignocellulosic biomass for biofuels and bioproducts: an overview, *Waste Biomass Valorization* 10 (2019) 235–251.
- [473] R.A. Blanchette, Delignification by wood-decay Fungi, *Annu. Rev. Phytopathol.* 29 (1991) 381–403.
- [474] M. Taniguchi, H. Suzuki, D. Watanabe, K. Sakai, K. Hoshino, T. Tanaka, Evaluation of pretreatment with *Pleurotus ostreatus* for enzymatic hydrolysis of rice straw, *J. Biosci. Bioeng.* 100 (2005) 637–643.
- [475] M. Taniguchi, M. Tanaka, R. Matsuno, T. Kamikubo, Evaluation of chemical pretreatment for enzymatic solubilization of rice straw, *European J. Appl. Microbiol. Biotechnol.* 14 (1982) 35–39.
- [476] B.C. Saha, N. Qureshi, G.J. Kennedy, M.A. Cotta, Biological pretreatment of corn stover with white-rot fungus for improved enzymatic hydrolysis, *Int. Biodeterior. Biodegradation* 109 (2016) 29–35.
- [477] A.J. Ragauskas, G.T. Beckham, M.J. Bidy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, Lignin valorization: improving lignin processing in the biorefinery, *Science* 344 (2014) 1246843.
- [478] T. Renders, S. Van den Bosch, S.-F. Koelewijn, W. Schutyser, B. Sels, Lignin-first biomass fractionation: the advent of active stabilisation strategies, *Energy Environ. Sci.* 10 (2017) 1551–1557.
- [479] R. Rinaldi, R. Jastrzebski, M.T. Clough, J. Ralph, M. Kennema, P.C. Bruijninx, B.M. Weckhuysen, Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis, *Angew. Chemie Int. Ed.* 55 (2016) 8164–8215.

- [480] M.V. Galkin, J.S. Samec, Lignin valorization through catalytic lignocellulose fractionation: a fundamental platform for the future biorefinery, *ChemSusChem* 9 (2016) 1544–1558.
- [481] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.-F. Koelewijn, T. Renders, B. De Meester, W. Huijgen, W. Dehaen, C. Courtin, Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps, *Energy Environ. Sci.* 8 (2015) 1748–1763.
- [482] P. Ferrini, R. Rinaldi, Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions, *Angew. Chemie Int. Ed.* 53 (2014) 8634–8639.
- [483] T. Renders, S. Van den Bosch, T. Vangeel, T. Ennaert, S.-F. Koelewijn, G. Van den Bossche, C.M. Courtin, W. Schutyser, B.F. Sels, Synergetic effects of alcohol/water mixing on the catalytic reductive fractionation of poplar wood, *ACS Sustain. Chem. Eng.* 4 (2016) 6894–6904.
- [484] T. Renders, E. Cooreman, S. Van den Bosch, W. Schutyser, S.-F. Koelewijn, T. Vangeel, A. Deneyer, G. Van den Bossche, C. Courtin, B. Sels, Catalytic lignocellulose biorefining in n-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose, *Green Chem.* 20 (2018) 4607–4619.
- [485] M.V. Galkin, J.S. Samec, Selective Route to 2-Propenyl Aryls Directly from Wood by a Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis, *ChemSusChem* 7 (2014) 2154–2158.
- [486] S. Van den Bosch, W. Schutyser, S.-F. Koelewijn, T. Renders, C. Courtin, B. Sels, Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood, *Chem. Commun.* 51 (2015) 13158–13161.
- [487] S. Van den Bosch, T. Renders, S. Kennis, S.-F. Koelewijn, G. Van den Bossche, T. Vangeel, A. Deneyer, D. Depuydt, C. Courtin, J. Thevelein, Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al 2 O 3 catalyst pellets during lignin-first fractionation, *Green Chem.* 19 (2017) 3313–3326.
- [488] X. Liu, H. Li, L.-P. Xiao, R.-C. Sun, G. Song, Chemodivergent hydrogenolysis of eucalyptus lignin with Ni@ ZIF-8 catalyst, *Green Chem.* 21 (2019) 1498–1504.
- [489] Y. Huang, Y. Duan, S. Qiu, M. Wang, C. Ju, H. Cao, Y. Fang, T. Tan, Lignin-first biorefinery: a reusable catalyst for lignin depolymerization and application of lignin oil to jet fuel aromatics and polyurethane feedstock, *Sustain. Energy Fuels* 2 (2018) 637–647.
- [490] R. Rinaldi, R.T. Woodward, P. Ferrini, H.J. Rivera, Lignin-first biorefining of lignocellulose: the impact of process severity on the uniformity of lignin oil composition, *J. Braz. Chem. Soc.* 30 (2019) 479–491.
- [491] T. Parsell, S. Yohe, J. Degenstein, T. Jarrell, I. Klein, E. Gencer, B. Hewetson, M. Hurt, J. Im Kim, H. Choudhari, A synergistic biorefinery based on catalytic conversion of lignin prior to cellulose starting from lignocellulosic biomass, *Green Chem.* 17 (2015) 1492–1499.
- [492] E.M. Anderson, R. Katahira, M. Reed, M.G. Resch, E.M. Karp, G.T. Beckham, Y. Román-Leshkov, Reductive catalytic fractionation of corn stover lignin, *ACS Sustain. Chem. Eng.* 4 (2016) 6940–6950.
- [493] J. Sun, H. Li, L.-P. Xiao, X. Guo, Y. Fang, R.-C. Sun, G. Song, Fragmentation of Woody Lignocellulose into primary monolignols and their derivatives, *ACS Sustain. Chem. Eng.* 7 (2019) 4666–4674.
- [494] W. Schutyser, S. Van den Bosch, T. Renders, T. De Boe, S.-F. Koelewijn, A. Dewaele, T. Ennaert, O. Verkinderen, B. Goderis, C. Courtin, Influence of bio-based solvents on the catalytic reductive fractionation of birch wood, *Green Chem.* 17 (2015) 5035–5045.
- [495] T. Renders, W. Schutyser, S. Van den Bosch, S.-F. Koelewijn, T. Vangeel, C.M. Courtin, B.F. Sels, Influence of acidic (H₃PO₄) and alkaline (NaOH) additives on the catalytic reductive fractionation of lignocellulose, *ACS Catal.* 6 (2016) 2055–2066.
- [496] E.M. Anderson, M.L. Stone, R. Katahira, M. Reed, G.T. Beckham, Y. Román-Leshkov, Flowthrough reductive catalytic fractionation of biomass, *Joule* 1 (2017) 613–622.
- [497] I. Kumaniaev, E. Subbotina, J. Sävmarker, M. Larhed, M.V. Galkin, J.S. Samec, Lignin depolymerization to monophenolic compounds in a flow-through system, *Green Chem.* 19 (2017) 5767–5771.
- [498] H. Luo, I.M. Klein, Y. Jiang, H. Zhu, B. Liu, H.I. Kenttämä, M.M. Abu-Omar, Total utilization of Miscanthus biomass, lignin and carbohydrates, using earth abundant nickel catalyst, *ACS Sustain. Chem. Eng.* 4 (2016) 2316–2322.
- [499] D.S. Argyropoulos, H.I. Bolker, Condensation of lignin in dioxane-water-HCl, *J. Wood Chem. Technol.* 7 (1987) 1–23.
- [500] W. Lan, M.T. Amiri, C.M. Hunston, J.S. Luterbacher, Protection group effects during α , γ -diol lignin stabilization promote high-selectivity monomer production, *Angew. Chemie Int. Ed.* 57 (2018) 1356–1360.
- [501] V.E. Tarabanko, K.L. Kaygorodov, E.A. Skiba, N. Tarabanko, Y.V. Chelbina, O.V. Baybakova, B.N. Kuznetsov, L. Djakovitch, Processing pine wood into vanillin and glucose by sequential catalytic oxidation and enzymatic hydrolysis, *J. Wood Chem. Technol.* 37 (2017) 43–51.
- [502] Y. Zhu, Y. Liao, W. Lv, J. Liu, X. Song, L. Chen, C. Wang, B.F. Sels, L. Ma, Complementing vanillin and cellulose production by oxidation of lignocellulose with stirring control, *ACS Sustain. Chem. Eng.* 8 (2020) 2361–2374.
- [503] W. Schutyser, J.S. Kruger, A.M. Robinson, R. Katahira, D.G. Brandner, N.S. Cleveland, A. Mittal, D.J. Peterson, R. Meilan, Y. Román-Leshkov, Revisiting alkaline aerobic lignin oxidation, *Green Chem.* 20 (2018) 3828–3844.
- [504] X. Wu, X. Fan, S. Xie, J. Lin, J. Cheng, Q. Zhang, L. Chen, Y. Wang, Solar energy-driven lignin-first approach to full utilization of lignocellulosic biomass under mild conditions, *Nat. Catal.* 1 (2018) 772–780.
- [505] D. Verboekend, Y. Liao, W. Schutyser, B.F. Sels, Alkylphenols to phenol and olefins by zeolite catalysis: a pathway to valorize raw and fossilized lignocellulose, *Green Chem.* 18 (2016) 297–306.
- [506] Y. Liao, R. Zhong, E. Makshina, M. d'Halluin, Y. van Limbergen, D. Verboekend, B.F. Sels, Propylphenol to phenol and propylene over acidic zeolites: role of shape selectivity and presence of steam, *ACS Catal.* 8 (2018) 7861–7878.
- [507] Y. Liao, M. d'Halluin, E. Makshina, D. Verboekend, B.F. Sels, Shape selectivity vapor-phase conversion of lignin-derived 4-ethylphenol to phenol and ethylene over acidic aluminosilicates: impact of acid properties and pore constraint, *Appl. Catal. B* 234 (2018) 117–129.
- [508] B. Op de Beeck, J. Geboers, S. Van de Vyver, J. Van Lishout, J. Snelders, W.J.J. Huijgen, C.M. Courtin, P.A. Jacobs, B.F. Sels, Conversion of (Ligno)Cellulose feeds to Isosorbide with heteropoly acids and Ru on carbon, *ChemSusChem* 6 (2013) 199–208.