AUTHOR(S): NAGARAJAN, S., SKILLEN, N.C., IRVINE, J.T.S, LAWTON, L.A. and ROBERTSON, P.K.

TITLE: Cellulose II as bioethanol feedstock and its advantages over native cellulose.

YEAR: 2017

Publisher citation: NAGARAJAN, S., SKILLEN, N.C., IRVINE, J.T.S, LAWTON, L.A. and ROBERTSON, P.K. 2017. Cellulose II as bioethanol feedstock and its advantages over native cellulose. Renewable and sustainable energy reviews [online], 77, pages 182-192. Available from: https://doi.org/10.1016/j.rser.2017.03.118

OpenAIR citation: NAGARAJAN, S., SKILLEN, N.C., IRVINE, J.T.S, LAWTON, L.A. and ROBERTSON, P.K. 2017. Cellulose II as bioethanol feedstock and its advantages over native cellulose. Renewable and sustainable energy reviews, 77, pages 182-192. Held on OpenAIR [online]. Available from: https://openair.rgu.ac.uk

Cellulose II as bioethanol feedstock and its advantages over native cellulose

Sanjay Nagarajan[1*], Nathan C. Skillen[1], John T.S. Irvine[2], Linda A. Lawton[3] and Peter K.J. Robertson[1*]

[1]Centre for the Theory and Application of Catalysis (CenTACat), School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, United Kingdom;
[2]JTSI Group, University of St. Andrews, School of Chemistry, Purdie Building, North Haugh, St Andrews, KY16 9ST, United Kingdom;
[3]School of Pharmacy and Life sciences, Sir Ian Wood Building Robert Gordon University, Garthdee Road, Aberdeen, AB10 7GJ, United Kingdom

*Corresponding authors: *snagarajan01@qub.ac.uk, p.robertson@qub.ac.uk Tel: +44 (0) 28 9097 4627*

Abstract

Alternative renewable energy must emerge to sustainably meet the energy demands of the present and future. Current alternatives to fossil fuels are electricity from solar, wind and tidal energies and biofuels. Biofuels, especially bioethanol could be produced from lignocellulosic feedstock via pre-treatment and fermentation. The cellulose I content of most lignocellulosic feedstock is significant, yet its highly crystalline amphiphilic structure interlinked with the lignin network makes it difficult to process for bioethanol production. Processing lignocellulosic biomass via a range of physico-chemical, mechanical and biological pre-treatment methods have been well established, however a relatively new area on the use of cellulose II (a polymorph of native cellulose obtained via mercerisation or regeneration) for the production of bioethanol is still in its early stages. Hence, this review discusses in detail the advantages of using cellulose II over cellulose I as feedstock for bioethanol production. Furthermore, current green and sustainable methods for cellulose II production and the advantages and disadvantages of each method are discussed. In addition, examples from literature reporting higher fermentable sugar and bioethanol yields using cellulose II as feedstock are reviewed, thereby highlighting its importance in the field of bioethanol production. The conclusion from this review suggests that, in all the cases studied, fermentable sugar and/or bioethanol production was found to be higher when cellulose II was used as feedstock instead of native cellulose/lignocellulosic biomass. This higher yield could be attributed to the modified structural and lattice arrangement of cellulose II, its porous volume and degree of polymerisation.

Keywords: cellulose II, lignocellulosic biomass, fermentable sugars, bioethanol, amphiphilic.

1. Introduction

Enhanced global utilisation of fossil fuels with the associated increase in greenhouse gas (GHG) emissions from growing anthropogenic activities is continuously debated. Global politics also influences the movement of fossil fuel stock across boundaries. It was predicted that serious fossil fuel depletion will be experienced by 2030 [1]. The International Energy Agency (IEA) estimated that global fossil fuel dependence would drop from 82% to 76% by 2035 with up to 18% of total energy consumed from renewable energy resources [2]. This emphasises the need to increase renewable energy production and accordingly investments are underway globally to expand renewable energy production (Fig. 1).

Fig. 1

There are a range of alternate energy resources available to supplement fossil fuels, including bioenergy (e.g. biogas, biodiesel, biomass and bioethanol), solar, geothermal, ocean/marine and wind. Amongst the alternatives mentioned above, bioenergy has the potential to replace current transportation fuels. Bioenergy for transportation includes, biodiesel and bioethanol. Feedstocks essential to produce biodiesel include algae, waste vegetable oils, animal fats, palm oil and non-edible oils [3]. Whereas, the feedstock required to produce bioethanol could be classified into first generation feedstocks - food crops such sugarcane and corn and second generation feedstocks - lignocellulosic materials and cellulosic wastes [4,5].

Second generation bioethanol production entirely utilises cellulose I and its wastes as feedstock for the fact that cellulose I is the most abundant naturally available organic material on earth. Shown below in Table 1 are the cellulose I contents of various lignocellulosic biomass. All the feedstock mentioned in Table 1 have varying amounts of lignin in them. Lignin is an aromatic hydrophobic compound which forms interlinking complexes with cellulose I and reduces freely available cellulose I, hence giving plants their structural stability [6]. It is expensive, both from an energy and cost perspective to breakdown the lignin network in lignocelluloses to release cellulose I followed by cellulose I degradation to release fermentable sugars for bioethanol production. In order to utilise cellulose to the fullest, it is

better to use freely available cellulose in the form of processed cellulose waste rather than lignocelluloses.

Table 1

Bioethanol production from native cellulose or lignocellulosic biomass have been extensively studied and reviewed in the past [7-13]. All the published reviews have emphasised the use of cellulose I for biofuel production, however, the review presented highlights the importance of cellulose II as feedstock for biofuel production over cellulose I. Even though cellulose II production has been in practice since 1850's, green, clean and sustainable methods for the production of cellulose II has been introduced only recently [14]. It was well established in the past decade that cellulose II was the most easily digestible polymorph of cellulose with its modified lattice arrangement, higher porous volume, higher surface wettability and lower crystallinity compared to cellulose I, however its use as feedstock for bioethanol production was not extensively studied.

The aim of this review is to emphasise the importance of cellulose II as a superior feedstock than cellulose I for bioethanol production. This was achieved by subdividing the review into three subsections. The first section explains the structural differences of cellulose I and cellulose II comparing its advantages and disadvantages. The subsequent section details modern, green and renewable methods for cellulose II production and the final section discusses recent examples from literature on the superiority of cellulose II over cellulose I as feedstock for biofuel production thereby highlighting its importance in the area of renewable energy. This review was prepared to serve as a resource for researchers working in the field of lignocellulosic biofuels to acquire knowledge on the advantages of cellulose II over cellulose I for biofuel production.

2. Structure of Cellulose

Cellulose I is an amphiphilic homopolysaccharide compound [15]. Individual β-D-glucose units joined by a (1-4)-glycosidic bond as well as intermolecular and intramolecular hydrogen bonds and hydrophobic interactions give rise to a rigid cellulose structure [15,16].

Cellulose I molecules have both disordered amorphous and highly ordered crystalline regions along its chain [17]. The structure of cellulose I with chair confirmation and equatorial orientation of the glucose molecules, the β (1-4) glycosidic bond and the intramolecular and intermolecular hydrogen bonds represented by the green dotted lines are shown in Fig. 2.

Fig.2

In addition to the characteristic hydrogen bonds of cellulose I, van der Waals interactions (hydrophobic interactions) also play a major role in stabilising the structure of cellulose I. The intermolecular and intramolecular hydrogen bonds along with the van der Waals interactions make cellulose I an amphiphilic compound. Cellulose I was proposed to be an amphiphilic compound because all three hydroxyl groups of the anhydroglucose units have an equatorial orientation making it hydrophilic and the H atoms of its C-H bonds have an axial orientation making it hydrophobic [15,18-24] (Fig. 3). Clear understanding of the amphiphilic property of cellulose I is necessary to choose appropriate amphiphilic solvents to dissolve cellulose I for the purpose of cellulose II production or for further chemical processing of native cellulose. The most common solvent, water which is non-amphiphilic would not dissolve cellulose I because of this reason.

Fig. 3

Different polymorphs of cellulose could be produced from its native form as seen in Fig. 4 [25]. Physico-chemical treatments of native microcrystalline cellulose (cellulose I) yields these different polymorphs. Native cellulose Iα is produced by microbes whereas the most abundant cellulose Iβ is found in higher plants. Although cellulose Iα and Iβ have parallel strands of cellulose, they differ in their lattice arrangement with the former being triclinic and the latter having a monoclinic structure.

Fig. 4

Cellulose II could be produced from both cellulose Iα or Iβ via alkali treatment (mercerisation) or solubilising and recrystallising (regeneration) respectively. In a few rare instances, naturally occurring cellulose II has been isolated [25-27]. This naturally occurring cellulose II was isolated from a mutant *Acetobacter xylinum* strain, whereas it's wild strain generally produces cellulose Iα. Unlike cellulose I, cellulose II has an antiparallel strand arrangement and monoclinic lattice arrangement. Other polymorphs of cellulose such as cellulose III_I and cellulose III_{II} could be reversibly produced from cellulose I and cellulose II via NH_3 treatment respectively. The degree of conversion of cellulose III polymorph and the reversibility back to the parent polymorph depends on the process in which ammonia is removed from the reaction mixture [28]. This polymorph was reported to exhibit a monoclinic crystal structure similar to cellulose II [29]. Another similarity that was observed among cellulose III_I, cellulose III_{II} and cellulose II structure was the orientation of the -CH_2OH group. It was found to be in gauche-trans (gt) conformation in cellulose III_I (and cellulose III_{II}) unlike its parent polymorph, cellulose I which has the hydroxymethyl group in trans-gauche (tg) conformation [29]. When these cellulose III_I and cellulose III_{II} materials are heat treated, cellulose IV_I and cellulose IV_{II} are formed. It was reported that although cellulose IV_I and cellulose IV_{II} have similar unit cell size they have different polarity, with the former having a parallel arrangement and the latter having an antiparallel arrangement following its parent polymorphs, cellulose I and cellulose II respectively [30].

An in-depth understanding of the polymorph's characteristics is necessary for determining its end use. Cellulose I is the naturally abundant cellulose whereas, cellulose II is the most commonly used man made cellulose and for this reason there is abundant information in literature regarding the production and characterisation of these polymorphs [16,17,25,31]. It is evident from published literature that the hydrogen bonding interactions play a governing role in stabilising the molecular structure of these polymorphs. The hydrogen bonding networks for cellulose I and cellulose II are shown along the a-c axis in Fig. 5. As can be seen, there are differences in hydrogen bonding between the two polymorphs which were induced due to the irreversible transformation of cellulose I to cellulose II during mercerisation or regeneration. As a result of the transformation, the latter exists as anti-parallel chains while the former hosts a parallel chain strand arrangement.

Fig.5

The intermolecular hydrogen bonding is more complicated in cellulose II when compared to cellulose I due to its antiparallel chain arrangement. For instance, in cellulose I, the O6-H-O3 (indicated within a red circle) intermolecular hydrogen bond is formed parallel to the a-axis as a result of tg conformation of the $–CH_2OH$ group. Whereas in cellulose II, the $–CH_2OH$ group occurs in the gt conformation due to the anti-parallel chain arrangement and hence forms the O6-H-O2 (indicated within a green circle) intermolecular hydrogen bond [31]. The gt and tg conformations of the $–CH_2OH$ group not only determine the hydrogen bonding in cellulose polymorphs but also determine the fate of chemical reactivity with various radical species and chemical compounds. Apart from hydrogen bonds, glycosidic bonds are formed between the C1 of a glucose monomer and C4 of the subsequent monomer. During the transformation from cellulose I to cellulose II, it is the hydrogen bonding network that is reorganised whereas the glycosidic linkages are not affected. Furthermore, cellulose II in its hydrate (non-dried) form has superior digestibility than dried cellulose II and cellulose I [32,33]. This is because of the increased inter-planar spacing (d-spacing) created due the presence of two water molecules per two chain unit cell of cellulose II hydrate [32,33]. The increased d-spacing is also due to the weakening of the hydrophobic bonds (van der Waals interaction) thereby increasing the hydrophilicity [20,32,34]. In contrast to cellulose I, cellulose II has its glucopyranose rings stacked with each other by hydrophobic interactions along the (1 -1 0) plane, thereby resulting in an increased density of hydroxyl groups on the surface leading to increased hydrophilicity [20]. This increased density of hydroxyl groups gives cellulose II a wetting angle of 12^O which is significantly lower than many polymers such as polyvinyl alcohol, polymethyl methacrylate, starch and polyethylene [20]. Furthermore, crystallinity index (CrI) results of cellulose I and cellulose II suggests that the latter is less crystalline than the former [35]. Additionally, from literature it can also be seen that the surface area and the porous volume of cellulose II is higher than that of cellulose I [34,36]. The characterisation of both cellulose I and II clearly indicates the latter to be a far more suitable starting material for the efficient release of fermentable sugars and subsequently, biofuel production. [32,34,37].

3. Cellulose II synthesis for fermentable sugar and biofuel production

Cellulose I is difficult to process without pre-treatment, whereas cellulose II is the most commonly used man-made form which is relatively easier to process. Hence, to gain better accessibility to the cellulose structure for chemical processing, cellulose II has to be derived from cellulose I via an efficient pre-treatment process. Due to its amphiphilicity, cellulose I cannot be dissolved in water, however it can be dissolved in various other solvents such as trifluoroacetic acid, ionic liquids, onium hydroxides, molten salts and cold alkalis [15,38-41] (Table 2).

In contrast to conventional alkali dissolution, ionic liquids and onium hydroxides are considered as green amphiphilic non-derivatising cellulose I solvents having negligible volatility and greater stability at higher temperatures [39,41]. Once dissolved, the irreversibly produced cellulose II can be precipitated out by the addition of anti-solvents such as water, ethanol, acetone, dilute acids or methanol. The nature of anti-solvents used, influence the structure and reactivity of cellulose II [18].

3.1 Conventional cellulose II production method – Alkali treatment

Alkali treatment of cellulose I is one of the oldest known industrial processes. In the field of fibre production, it is known as the viscose process [42-44]. In viscose process, cellulose from pulp is converted to cellulose xanthogenate. This cellulose derivative is then dissolved in aqueous NaOH. Upon dissolution, the cellulose II derivative formed is precipitated out from solution followed by purification of cellulose II with removal of the substituent [42]. Viscose process is still being used for the production of cellophane, a packaging material.

Unlike the viscose process, mercerisation is another method to produce cellulose II from cellulose I without derivatisation. Mercerisation was introduced by J. Mercer in the 1850’s where cellulose I was allowed to swell in a concentrated NaOH aqueous solution followed by dissolution and precipitation [45,46]. Ever since mercerisation was introduced, it has been used to produce cellulose II frequently [47-55].

Table 2

Yu *et al*. tested the effect of a range of NaOH concentrations and temperatures on the mercerisation of cellulose I [54]. The feedstock material used in their experiments was ground jute fibres with an approximate particle size of 1 mm which were dispersed in aqueous NaOH solutions in the concentration range of 0 – 30% at 70 ^{O}C and 85 ^{O}C. It was determined that the highest cellulose II content was obtained with a 20% aqueous NaOH solution at 85 ^{O}C and 25% aqueous NaOH solution at 70 ^{O}C upon mercerisation (Fig. 6). It was further determined that the crystallinity index increased in the concentration range of 5 – 9% NaOH which is due to the increased reactivity of the amorphous regions in the jute fibres. Due to the increase in concentration of Na^{+} and OH^{-} ions present beyond 9% concentration, penetration of the cellulose I lattice became easier thereby producing cellulose II with the lowest crystallinity until 15% NaOH concentration. When the concentration of NaOH was further increased until 30%, viscosity of the solution increased and hence the crystallinity of the resulting cellulose II sample was higher. It was also determined that the crystallinity index of the precipitated cellulose II was lower with a higher temperature (85 ^{O}C).

Fig.6

In contrast to determining the effect of high temperatures on mercerisation, Wang and Deng tested the effect of cellulose I dissolution at sub-zero temperatures [50]. They dissolved cotton linters in 6% NaOH solution at temperatures ranging from -8 ^{O}C to -20 ^{O}C. The percentage solubility of the samples were calculated and it was found that 25 – 32% solubility was reached (and plateaued) at temperatures of -15 ^{O}C and -20 ^{O}C. It was also determined that cellulose II started to appear after 10 minutes of dissolution time at -15 ^{O}C.

3.2 New methods for cellulose II production

3.2.1 Ionic liquid treatment

Ionic liquids are molten salts with melting temperatures lower than 100 ^{O}C. Most common ionic liquids to date are air and moisture stable imidazolium based salts [56].

Currently, ionic liquids are of prime interest due to their versatility as solvents in various applications [57,58]. They are highly flexible, as a number of cation and anion combinations could be fabricated based on its end use. Methylimidazolium and methylpyridinium based cations, and chloride, acetate and formate anions are the most commonly used species for designing cellulose I dissolving ionic liquids [39], however, other anions such as Br^-, SCN^-, BF_4^- and PF_6^- among others, have been used [14,39,56]. It is believed that the OH groups of the neighbouring C6 and C3 cellulose chains form an electron donor-acceptor complex with ionic liquids to result in the dissolution of cellulose I [39].

Ever since Swatloski *et al*. [14] demonstrated the use of ionic liquids as cellulose I dissolving solvents for the irreversible production of cellulose II, numerous researchers have opted for the use of various ionic liquids for the production of regenerated cellulose [36,49,59-68]. For instance, Cheng *et al*. reported the use of an ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) to produce cellulose II from Avicel, switchgrass, eucalyptus and pine [65]. The biomass samples were milled to 40 mesh prior to EMIM-Ac treatment. The samples were heated to 120 ^{O}C for 1, 3, 6 or 12 hours. Upon dissolution, hot water was added to precipitate cellulose II out of the solution. X-ray diffraction (XRD) profiles of the dried samples revealed that after treatment with EMIM-Ac, all the samples were converted to cellulose II as seen in Fig. 7, however switch grass samples showed residual cellulose I after an hour's treatment [65,66]. This group performed further experiments at a higher temperature of 160 ^{O}C and found that the rate of cellulose II formation was higher at higher temperatures, however there are chances of cellulose I depolymerisation when dissolved at higher temperatures.

Fig. 7

Zavrel *et al*. performed a high throughput screening to compare and determine the best ionic liquid for producing cellulose II from Avicel and lignocellulose [69]. Apart from Avicel and α-cellulose as the standard cellulose I samples, lignocellulosic materials such as spruce wood, silver fir, common beech and chestnut wood of size 1-2 mm were dissolved in a range of ionic liquids. They screened 21 different ionic liquids for their ability to dissolve cellulose I (and lignocellulose) of 1 – 5 wt.% for 8 – 12 hours at 50 ^{O}C and precipitated cellulose II.

Amongst the screened ionic liquids, EMIM-Ac was found to be effective for dissolving cellulose I whereas 1-allyl-3-methylimidazolium-chloride (AMIM-Cl) was found to be effective for dissolving wood chips as observed from their light scattering measurements. In addition, it was also observed that at a higher temperature of 80 ^{O}C, the dissolution of cellulose I was quicker when compared to lower temperatures ranging from 40 – 60 ^{O}C (Fig. 8). It was elucidated that viscosity of the ionic liquids is affected at higher temperatures enabling better dissolution. Furthermore, at higher temperatures the hydrogen bonds present in cellulose I structure were destabilised thereby enhancing the rate of cellulose I dissolution.

Fig. 8

Vitz *et al*. performed cellulose I dissolution studies using various imidazolium based ionic liquids containing odd or even numbered alkyl side chains in combination with a range of anions [70]. Few ionic liquids used in their study were commercially available whereas the remaining were synthesised before the dissolution experiments. A concentration of 8 wt.% of cellulose I (Avicel PH 101) was dissolved in the ionic liquids at 100 ^{O}C. In some cases, microwave irradiation was used to dissolve cellulose I in ionic liquids. Upon dissolution for 1 hour, cellulose II was precipitated with the addition of excess methanol. From their experiments it was primarily concluded that moisture free ionic liquids were needed to achieve high dissolution of cellulose I. Furthermore, they deduced that the moisture uptake by ionic liquids with various anions followed the resulting order CH_3COO^- ≈ $(CH_3)_2PO_4^-$ > $(CN_2)N^-$ > triflate > BF_4^- > PF_6^-. Secondly, they established that imidazolium based ionic liquids with shorter even numbered side chains (two or four) combined with chloride anions showed good cellulose I dissolving properties. In addition to chloride anions, acetate and phosphate anions were shown to have good cellulose I dissolution properties. Results upon microwave irradiation revealed that the yield of cellulose II was 86% for 1-ethyl-3-methylimidazolium chloride whereas the yield from ionic liquid, 1-ethyl-3-methylimidazolium diethyl phosphate was 96%. This was attributed to the degradation of cellulose I in chloride containing ionic liquid under microwave irradiation.

Zhang *et al*. performed nuclear magnetic resonance (NMR) spectroscopic studies on the dissolution of cellobiose (a disaccharide containing two anhydroglucose units) in EMIM-

Ac to understand the mechanism of cellulose I dissolution in ionic liquids [71]. They provided evidence that the acetate ion in EMIM-Ac forms a hydrogen bond with the hydrogen atoms of the cellobiose hydroxyl group whereas the imidazolium ion bonds with the oxygen atoms of the cellobiose hydroxyl group thereby dissolving it.

It can be seen from literature that ionic liquids for cellulose II production is ever expanding. Despite the high versatility for fabrication of ionic liquids and negligible vapour pressure, its high viscosity at room temperature, instability in the presence of water and the requirement of temperatures higher than room temperature to dissolve cellulose I does not make it completely “environmental friendly” for the production of cellulose II.

3.2.2 Onium hydroxide treatment

Solvents containing onium and hydroxide ions are termed as onium hydroxides. Examples of onium hydroxides are tetrabutylammonium hydroxide (TBAH), tetramethylammonium hydroxide (TMAH) or tertabutylphosphonium hydroxide (TBPH). Onium hydroxides, unlike ionic liquids, are usually found as aqueous solutions and have the capability to dissolve wet cellulose I samples. Solvents of this class also have the added advantage of lower viscosity when compared to their ionic liquid counterparts. They are also liquid at room temperature and they do not require heating to dissolve cellulose I. Additionally, Toth *et al.* demonstrated that an aqueous onium hydroxide, TMAH was a better Mercerising agent than aqueous NaOH [72].

Abe *et al*. demonstrated the use of onium hydroxides, TBAH and TBPH for the production of cellulose II from cellulose I [40]. They dissolved cellulose I in various concentrations of aqueous TBAH and TBPH ranging from 40 – 70 wt.% at room temperature (25 ^{O}C). It was determined that a concentration range of 50 – 60% TBAH and 50 – 70% TBPH in water was required for complete cellulose I dissolution at room temperature. Cellulose I was insoluble in all the other concentrations of onium hydroxides used. Upon dissolution, hot ethanol was added to precipitate cellulose II. H-NMR studies were further conducted to study the mechanism of cellulose dissolution in onium hydroxides. It was established from these studies that the hydroxide ion of the onium hydroxides formed hydrogen bonds with the

hydroxyl groups of cellulose. This mechanism of cellulose dissolution observed is similar to that in ionic liquids as mentioned earlier. This provides further evidence that an amphiphilic compound such as cellulose could only be dissolved in amphiphilic solvents.

Furthermore, Abe *et al*. published a follow up paper to their above mentioned work (in 2012) to examine the effect of different onium cations on their cellulose I dissolution capability [73]. They used a range of commercially available and tailor made onium hydroxides such as TBPH, tetraethylphosphonium hydroxide (TEPH), tri-n-hexylphosphine tetramethylammonium hydroxide (THTMAH), tetraethylammonium hydroxide (TEAH), TBAH, tri-n-butylmethylphosphonium hydroxide and tetra-n-hexylammonium hydroxide and determined the effect of temperature and cellulose I loading on cellulose I solubility. All the onium hydroxides used, dissolved a concentration of 15 wt.% cellulose I, whereas TBPH and TBAH dissolved 20 wt.% cellulose I. THTMAH and TEAH did not dissolve any cellulose I. The non-dissolving ability of TEAH was attributed to the low hydrophobicity of the cation which was determined via C-NMR studies. Furthermore, they also observed that a similar onium hydroxide, TEPH dissolved up to 15 wt.% cellulose I because the phosphonium cation had a higher hydrophobicity than the ammonium cation in TEAH. This established the amphiphilic nature of both the onium hydroxides and cellulose I. When an amphiphilic solvent such as aqueous TBAH or TBPH was employed for cellulose I dissolution, an optimum amount of water was required in solution to form hydrogen bonds between the hydroxyl groups of cellulose I (hydrophilic regions) and water. Addition of cellulose I to such an amphiphilic solvent disrupts the inter and intramolecular hydrogen bonds within the cellulose I structure forming new hydrogen bonds with the surrounding water molecule. Furthermore, hydrophobic cations in these amphiphilic solvents interact with the respective hydrophobic regions in cellulose I causing complete dissolution of cellulose I. Further details on the characteristics of amphiphilic solvents used for cellulose I dissolution could be found elsewhere [15,18,23,41,74].

Wei *et al*. performed cellulose I dissolution experiments in aqueous TBAH at different temperatures to determine the effect of temperature on the production of cellulose II [75]. They dissolved 376 mg cellulose I in 5 ml aqueous TBAH (40 and 60 wt.%) in a temperature range of 16 – 28 ^{O}C for 60 minutes. It was determined that better solubility of cellulose I was

achieved with 40 wt.% TBAH at 16 ^{O}C. Although, cellulose I dissolved at 16 ^{O}C showed superior solubility, upon regeneration using hot water, all the samples showed a peak shift in the XRD spectra thereby suggesting the conversion to cellulose II. Since the ionic structure of TBAH was stable at a lower temperature, it was suggested that a strong hydrogen bond network was formed between the onium hydroxide and cellulose I enabling higher solubility.

To emphasise the amphiphilicity of cellulose I and TBAH, Alves *et al*. compared the dissolution of cellulose I in aqueous TBAH and NaOH [41]. A concentration of 1 wt.% cellulose I was dispersed in 8 wt.% aqueous NaOH and frozen at -20 ^{O}C for 24 hours, followed by thawing at room temperature with gentle mixing. Similarly, 1 wt.% cellulose I was mixed with 40 wt.% aqueous TBAH at room temperature for 30 minutes. After dissolution, dilute H_2SO_4 was added to the mixture to precipitate and regenerate cellulose II. A clear cellulose I solution was obtained when both TBAH and NaOH were used as solvents indicating complete dissolution when observed with the naked eye. When viewed under a polarised light microscope, however, cellulose I fragments were seen in the aqueous NaOH solution but not in the case of aqueous TBAH solution. Furthermore, SEM images revealed that needle-like crystallite structures were observed in NaOH solution and a wrinkled film like morphology was observed in the TBAH solution indicating that complete cellulose I dissolution occurred in the latter but not the former. Dynamic light scattering measurements revealed that the average particle size in the TBAH system was between 10 – 20 nm whereas in the case of the NaOH system it was 200 nm. Additionally, the lower crystallinity index of the TBAH extracted cellulose II when compared to cellulose I and NaOH extracted cellulose II supported their results. Thus it can be seen that near molecular level dissolution was achieved when TBAH was used as a solvent. The authors attributed this to the amphiphilic nature of cellulose I and TBAH emphasising the superiority of onium hydroxides over alkalis as solvents for dissolving cellulose I. The advantage of using onium hydroxides over alkali metal hydroxides and (aqueous) ionic liquids for cellulose I dissolution was established by Abe *et al*. and is shown in Fig. 9 [73].

Fig. 9

3.2.3 Phosphoric acid treatment

Jia *et al*. dissolved cellulose I in phosphoric acid and produced cellulose II via regeneration with the addition of water [76]. They prepared a range of cellulose I - phosphoric acid concentrations with 0.5 – 3% wt./v cellulose I and 77 – 85 wt.% phosphoric acid in the temperature range of 5 – 75 ^{O}C. An esterification reaction occurred when cellulose I was mixed with phosphoric acid forming a cellulose I - phosphoric acid ester. Upon dissolution, when water was added to regenerate cellulose II, phosphoric acid in the complex was displaced by the water molecules. The transformation of cellulose I to cellulose II was confirmed with the XRD and FTIR (Fourier Transform Infrared spectroscopy) spectra. Furthermore, they determined that a higher concentration of phosphoric acid (≥ 83 wt.%) was required to completely dissolve cellulose I whereas in any other lower concentration, only swelling occurs. In addition, they also established that up to 3% wt./v cellulose I could be dissolved in phosphoric acid and any concentration above that would cause the dispersion of cellulose I but not dissolution in phosphoric acid. When dissolution experiments were performed under different temperatures, it was determined that complete dissolution was favoured at lower temperatures as monitored by an UV-visible spectrometer.

3.2.4 Trifluoroacetic acid treatment

Zhao *et al*. introduced a new non-derivatising method to produce cellulose II from cotton linters using trifluoroacetic acid (TFA) at low temperatures [77]. Cotton linters was mixed in 99% TFA in mass ratios of 1:15 at different temperatures ranging from 0 – 65 ^{O}C for 3 hours. The swollen samples were washed with water to remove traces of TFA and recover cellulose II. The production of cellulose II was confirmed using XRD measurements. They observed an inverse temperature effect for the production of cellulose II using TFA as the solvent. At 0 ^{O}C, cellulose I was completely converted to cellulose II whereas with an increase in temperature only partial conversion was observed. The reason for this partial conversion was attributed to the lack of TFA cyclic dimer formation at higher temperatures. As proposed, TFA tend to form cyclic dimers at lower temperatures but not at higher temperatures. Weak interactions were suggested to be formed between the C=O of the TFA dimers and cellulose I at 0 ^{O}C. These interactions could disrupt the hydrogen bonding network thereby facilitating cellulose I decrystallisation, but the TFA monomers formed at higher temperatures were not able to disrupt the hydrogen bonds favouring only partial conversion. In addition, SEM

analysis showed that the supramolecular structure of cellulose was undisturbed before and after TFA treatment which confirms that treatment with TFA would only partially produce cellulose II. Although the inverse temperature effect for cellulose II production was established, risks involved in the handling and use of TFA makes it a less preferred solvent for cellulose II production.

3.2.5 Supercritical water solubilisation

Sasaki *et al*. proposed a new method for cellulose II production from native cellulose (cellulose I) using near and supercritical water as a solvent [78]. A concentration of 10 wt.% cellulose I was mixed with water in a microreactor and rapidly heated for 0.02 – 0.6 s at 320 – 400 ^{O}C and 25 – 33 MPa pressure. It was determined that at 320 ^{O}C and 25 MPa, cellulose II was not produced instead, soluble saccharides of cellulose were formed. In the range of 360 – 380 ^{O}C, partial cellulose I dissolution occurred and in the range of 375 – 380 ^{O}C, 50% cellulose I conversion was achieved accounting for both cellulose II and soluble saccharides of cellulose. At 400 ^{O}C cellulose I disappeared within 0.02 s and both cellulose II and soluble saccharides of cellulose were obtained. It was further established that at temperatures higher than 380 ^{O}C, cellulose I conversion was constant and was independent of the pressure.

At the near and supercritical water temperatures, the intermolecular and intramolecular hydrogen bonds become weaker in cellulose I thereby facilitating bond cleavage. Also, at higher temperatures, the density and dielectric constant of water decreases with the increase in hydrophobicity and diffusion coefficient which favours the partial dissolution and hydrolysis of cellulose I. Although advantages such as the use of environment friendly solvent (water) and one pot cellulose II production was emphasised by the authors, the disadvantages such as non-selectivity, decomposition of desired products at high temperatures and high energy input overshadow its advantages.

4. Fermentable sugar and biofuel production with cellulose II

With a view towards biofuel production, Mittal *et al*. dissolved four types of cellulose I obtained from various sources (Avicel PH-101, α-cellulose, cotton linters and cellulose

extracted from corn stover) in 16.5 wt% aqueous NaOH at 25 ^{O}C under a nitrogen atmosphere [47]. Upon dissolution and precipitation, the cellulose I samples were found to be converted to cellulose II. In addition to the conversion, they tested the enzymatic digestibility of these cellulose I and cellulose II samples using Genencor GC220 cellulase enzyme preparation. They determined that the enzymatic digestibility of cellulose II was superior to that of cellulose I from their experiments. The initial enzymatic hydrolysis rate of cellulose II was found to be two times faster than cellulose I. The superior digestibility was attributed towards the increased non-crystalline regions present in cellulose II as a result of mercerisation.

Ma *et al*. used pyrrolidonium based ionic liquids to extract regenerated cellulose from corn stalk for fermentable sugar production via enzymatic hydrolysis [79]. Ionic liquids such as N-methyl-2-pyrrolidonium hydrogen sulfate (MPHS), N-methyl-2-pyrrolidonium dihydrogen phosphate (MPDP), N-methyl-2-pyrrolidonium chloride (MPC) and N-methyl-2-pyrrolidonium methanesulfonate (MPMS) and their respective aqueous solutions were synthesised for dissolving the lignocellulosic feedstock. A concentration of 0.05 wt% corn stalk was added to the ionic liquids and the mixture was heated to 90 ^{O}C and stirred for 30 minutes. Then 20 ml of 1:1 acetone/deionised water solution was added to the mixture to precipitate regenerated cellulose. Reduced crystallinity of the regenerated cellulose samples was confirmed using the FTIR spectra obtained. These regenerated cellulose samples (1 g/ml) were subjected to enzymatic hydrolysis for the production of fermentable sugars. Commercial *Aspergillus niger* cellulase (0.02 g) was used for enzymatic hydrolysis. The enzymatic hydrolysis experiments were performed at 50 ^{O}C for 72 hours at a pH 4.8, maintained using 0.1 M sodium citrate buffer. Highest yield of fermentable sugars of 91.81% followed by 73.59% and 70.18% were produced from regenerated cellulose obtained with aqueous MPC, MPMS and MPC treatment respectively. These high sugar yields were attributed to the hydrogen bonding capability and the acidity of the ionic liquids which effectively removed the bound hemicelluloses and lignin in the corn stalk in addition to the reduced crystallinity of the obtained regenerated cellulose.

Shafiei *et al*. dissolved either spruce wood chips or powder in ionic liquids EMIM-Ac, and 1-butyl-3-methylimidazolium acetate (BMIM-Ac) and an organic solvent N-methylmorpholine-N-oxide (NMMO) [68]. Wood chips or powder (5%) was mixed with the

ionic liquids at 120 ^{O}C in an oil bath for varied experiment times. Upon dissolution, 20 ml of boiling water was added to the solution to precipitate cellulose II from the mixture. The precipitated cellulose II was filtered through a filter paper and washed with excess water to remove any bound ionic liquids. As a result of ionic liquid pre-treatment, cellulose II was formed with lower crystallinity than the untreated wood samples. Furthermore, enzymatic hydrolysis of cellulose II and cellulose I (wood chips and powder) samples was carried out at 45 ^{O}C for 72 h in citrate buffer with a mixture of cellulase and β-glucosidase enzymes. The fermentable sugar yield from EMIM-Ac (66%) and BMIM-Ac (57%) treated wood chips samples were found to be significantly higher than the NMMO (38%) treated and untreated samples (2%). After hydrolysis, the hydrolysates were separated and subjected to ethanol fermentation using *Saccharomyces cerevisiae* CCUG53310 at 32 ^{O}C for 24 hours. A higher yield of ethanol production for EMIM-Ac (67%) and BMIM-Ac (52%) in comparison to NMMO (36%) treated and untreated (3%) samples upon fermentation was observed. The reason for a higher yield of fermentable sugars and bioethanol production was attributed towards the lower crystallinity of the raw material, cellulose II.

In addition to the example mentioned above and various well documented evidences mentioned earlier on the use of ionic liquids for cellulose II production, there has also been a techno-economic study published by Klein-Marcuschamer *et al*. in 2011 on the feasibility of ionic liquids for ligno-cellulosic biorefineries [80]. Based on their study it can be inferred that the key barrier to scale-up is the cost of ionic liquids needed for cellulose I dissolution which dominates the proportion of total costs involved followed by the cost of ionic liquid loading and the rate of ionic liquid recycling. In order to compensate for the ionic liquid loading, aqueous ionic liquid mixtures have been used by Fu and Mazza [63]. They dissolved triticale straw in 5%, 25%, 50% and pure EMIM-Ac to obtain cellulose II for enzymatic hydrolysis. As can be seen from their results in Fig. 10, when pure EMIM-Ac was used to dissolve straw, almost complete cellulose II hydrolysis was seen after approximately 8 hours, with decreasing the ionic liquid loading to 50%, cellulose II hydrolysis fell from 100% to 80% at 8 hours. With a further decrease in the EMIM-Ac loading to 25% and 5%, an even lower cellulose II amount was hydrolysed. According to the feasibility study conducted by Klein-Marcuschamer *et al*., there has to be an optimum trade-off between the ionic liquid loading and the hydrolysate produced. Furthermore, their economic analysis also revealed that the revenue generated by the lignin by-products could offset a part of the investment costs.

Fig. 10

5. Conclusion

Current global energy scenario demands an increase in the use of renewable energy to mitigate emissions, particularly in the transportation sector. The use of biofuels for transportation would help to achieve the emission targets. To make biofuels attractive, the price of it must however match the current oil price. This would be feasible when biofuel industries turn into biorefineries and offset the costs by

(i) improving the biofuel yields and

(ii) producing value added by-products.

To improve the yield of biofuels, especially bioethanol, a more easily accessible cellulose feedstock has to be input. It is evident from this review that cellulose II has distinct advantages over cellulose I (and lignocellulosic biomass) as feedstock for biofuel production. When lignocellulosic materials are used in biorefineries, interfering lignin network hinders the complete utilisation of cellulose. Even though when cellulose I is separated from lignin using appropriate pre-treatment methods such as steam explosion, ammonia explosion or acid/alkali hydrolysis [81], the crystalline structure of native cellulose combined with the hydrophobic interactions and the intra and intermolecular hydrogen bond network makes it difficult to process further via microbiological, enzymatic or chemical routes.

To overcome this problem, lignocellulose pre-treatment focussing on delignification combined with simultaneous production of cellulose II have been used. Cellulose II could be produced by simply dissolving cellulose I or lignocellulosic feedstock in an appropriate amphiphilic solvent followed by regeneration using an anti-solvent such as water, ethanol, methanol, dilute acids or acetone. Cellulose II has been well established to have a lower crystallinity than cellulose I. The former is also said to have the highest wettability, porous volume and surface area than cellulose I [20,34,36]. These advantages make cellulose II an easily digestible polymorph of

cellulose, however it has not been used extensively for biofuel production purposes. Though the use of cellulose II as biofuel feedstock has not been comprehensively studied, the limited results reported have strongly established the fact that cellulose II is a better feedstock than native cellulose (and lignocellulosic wastes) for biofuel production.

A range of solvents have been used for the production of cellulose II. With mercerisation dating back to 1850's, until today, there has been significant developments in the field of dissolution and regeneration of cellulose. Of all the solvents used, molecular level dissolution could be achieved only when ionic liquids or onium hydroxides are used as solvents. This is because of the amphiphilic nature of both the cellulose I and the solvents, however an optimum solvent loading is required to make biorefineries profitable. Ionic liquids' cellulose I dissolving ability is affected when they come in contact with water and hence aqueous onium hydroxide solution can be used as a substitute for ionic liquids. Also from an energy perspective, onium hydroxides offer an advantage over ionic liquids as preferred solvents for cellulose I dissolution due to their high cellulose I dissolving capacity at room temperature. Although there are room temperature ionic liquids available for cellulose dissolution, their high viscosity limits its use.

The prospect of using cellulose II as feedstock for biofuel production has been experimented but requires more research considering the advantages it offers. Literature evidence available suggests that the potential of cellulose II for biofuel production is higher than cellulose I as discussed in this review. These initial results from most researchers are promising but several research gaps such as the scalability, selectivity, recyclability of cellulose I solvents, use of wet biomass for integrated biofuel production and economic viability needs to be addressed to proceed further. Hence cellulose II needs to be seriously considered as an alternative feedstock option if cellulosic biorefineries are to become a feasible reality.

Acknowledgements

The authors would like to acknowledge the funding support from Engineering and Physical Sciences Research Council (Project number EP/K036769/1) and Queen's University Belfast's PhD studentship. The authors would also like to thank Professor A. Prasanna de Silva, School of Chemistry and Chemical Engineering, Queen's University Belfast, for his valuable contribution during the progress meetings.

References

[1] Wigley TML, Richels R, Edmonds JA. Economic and environmental choices in the stabilization of atmospheric CO_2 concentrations. Nature 1996;379:240-243.

[2] van der Hoeven M. World Energy Outlook Report 2013.

[3] Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy 2008;33:1646-1653.

[4] Nagarajan S, Chou SK, Cao S, Wu C, Zhou Z. An updated comprehensive techno-economic analysis of algae biodiesel. Bioresour Technol 2013;145:150-156.

[5] Linoj KN, Prabha D, Anandajit G, Sameer M. Liquid Biofuels in South Asia: Resources and Technologies. Asian Biotechnology Development Review 2006;8:31.

[6] Betts WB, Dart RK, Ball AS, Pedlar SL. Biosynthesis and Structure of Lignocellulose. In: Betts WB., editors.Springer London; 1991, p. 139-155.

[7] Brown TR, Brown RC. A review of cellulosic biofuel commercial-scale projects in the United States. Biofuels, Bioprod Bioref 2013;7:235-245.

[8] Carroll A, Somerville C. Cellulosic Biofuels. Annu Rev Plant Biol 2009;60:165-182.

[9] Sticklen MB. Plant genetic engineering for biofuel production: towards affordable cellulosic ethanol. Nat Rev Genet 2008;9:433.

[10] Sannigrahi P, Ragauskas AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. Biofuels, Bioprod Bioref 2010;4:209-226.

[11] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: A comprehensive review. Renew Sust Energ Rev 2010;14:578-597.

[12] David K, Ragauskas AJ. Switchgrass as an energy crop for biofuel production: A review of its ligno-cellulosic chemical properties. Energy Environ Sci 2010;3:1182-1190.

[13] Weng J, Li X, Bonawitz ND, Chapple C. Emerging strategies of lignin engineering and degradation for cellulosic biofuel production. Curr Opin Biotechnol 2008;19:166-172.

[14] Swatloski RP, Spear SK, Holbrey JD, Rogers RD. Dissolution of Cellose with Ionic Liquids. J Am Chem Soc 2002;124:4974-4975.

[15] Lindman B, Karlström G, Stigsson L. On the mechanism of dissolution of cellulose. Journal of Molecular Liquids 2010;156:76-81.

[16] Silverstein RA. A Comparison of Chemical Pretreatment Methods for Converting Cotton Stalks to Ethanol 2005.

[17] Sjöström E. Wood Chemistry: Fundamentals and Applications Academic Press; 1993.

[18] Medronho B, Lindman B. Brief overview on cellulose dissolution/regeneration interactions and mechanisms. Adv Colloid Interface Sci 2015;222:502-508.

[19] Xi J, Du W, Zhong L. Probing the Interaction between Cellulose and Cellulase with a Nanomechanical Sensor. In: Van de Ven T and Godbout L., editors. Cellulose - Medical, Pharmaceutical and Electronic Applications, InTech; 2013, p. 125.

[20] Yamane C, Aoyagi T, Ago M, Sato K, Okajima K, Takahashi T. Two Different Surface Properties of Regenerated Cellulose due to Structural Anisotropy. Polym J 2006;38:819-826.

[21] Biermann O, Hädicke E, Koltzenburg S, Müller-Plathe F. Hydrophilicity and Lipophilicity of Cellulose Crystal Surfaces. Angew Chem Int Ed 2001;40:3822-3825.

[22] Glasser WG, Atalla RH, Blackwell J, Malcolm Brown R, Burchard W, French AD, Klemm DO, Nishiyama Y. About the structure of cellulose: debating the Lindman hypothesis. Cellulose 2012;19:589-598.

[23] Medronho B, Lindman B. Competing forces during cellulose dissolution: From solvents to mechanisms. Current Opinion in Colloid & Interface Science 2014;19:32-40.

[24] Medronho B, Duarte H, Alves L, Antunes FE, Romano A, Valente AJM. The role of cyclodextrin-tetrabutylammonium complexation on the cellulose dissolution. Carbohydr Polym 2016;140:136-143.

[25] O'Sullivan A. Cellulose: the structure slowly unravels. Cellulose 1997;4:173-207.

[26] Shibazaki H, Saito M, Kuga S, Okano T. Native Cellulose II Production by Acetobacter Xylinum Under Physical Constraints. Cellulose 1998;5:165-173.

[27] Kuga S, Takagi S, Brown RM. Native folded-chain cellulose II. Polymer 1993;34:3293-3297.

[28] Yatsu LY, Calamari TA, Benerito RR. Conversion of Cellulose I to Stable Cellulose III. Text Res J 1986;56:419-424.

[29] Wada M, Chanzy H, Nishiyama Y, Langan P. Cellulose IIII Crystal Structure and Hydrogen Bonding by Synchrotron X-ray and Neutron Fiber Diffraction. Macromolecules 2004;37:8548-8555.

[30] Isogai A, Usuda M, Kato T, Uryu T, Atalla RH. Solid-state CP/MAS carbon-13 NMR study of cellulose polymorphs. Macromolecules 1989;22:3168-3172.

[31] Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W. General Considerations on Structure and Reactivity of Cellulose: Section 2.1-2.1.4. In: Anonymous , editors. Comprehensive Cellulose Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA; 1998, p. 9-29.

[32] Wada M, Ike M, Tokuyasu K. Enzymatic hydrolysis of cellulose I is greatly accelerated via its conversion to the cellulose II hydrate form. Polym Degrad Stab 2010;95:543-548.

[33] Sakurada I, Hutino K. Über die intramizellare Quellung der Zellulose durch Wasser. Kolloid Z 1936;77:346-351.

[34] Boissou F, Muhlbauer A, De OV, Leclercq L, Kunz W, Marinkovic S, Estrine B, Nardello-Rataj V, Jerome F. Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, gamma]-valerolactone and water. Green Chem 2014;16:2463-2471.

[35] Kljun A, Benians TAS, Goubet F, Meulewaeter F, Knox JP, Blackburn RS. Comparative Analysis of Crystallinity Changes in Cellulose I Polymers Using ATR-FTIR, X-ray Diffraction, and Carbohydrate-Binding Module Probes. Biomacromolecules 2011;12:4121-4126.

[36] Dadi AP, Varanasi S, Schall CA. Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step. Biotechnol Bioeng 2006;95:904-910.

[37] Wahlstrom RM, Suurnakki A. Enzymatic hydrolysis of lignocellulosic polysaccharides in the presence of ionic liquids. Green Chem 2015;17:694-714.

[38] Zhao H, Holladay EJ, Kwak JH, Zhang ZC. A New Route to Improved Glucose Yields in Cellulose Hydrolysis. J Biobased Mater Bio 2007;1:210.

[39] Pinkert A, Marsh KN, Pang S, Staiger MP. Ionic Liquids and Their Interaction with Cellulose. Chem Rev 2009;109:6712-6728.

[40] Abe M, Fukaya Y, Ohno H. Fast and facile dissolution of cellulose with tetrabutylphosphonium hydroxide containing 40 wt% water. Chem Commun 2012;48:1808-1810.

[41] Alves L, Medronho BF, Antunes FE, Romano A, Miguel MG, Lindman B. On the role of hydrophobic interactions in cellulose dissolution and regeneration: Colloidal aggregates and molecular solutions. Colloids Surf Physicochem Eng Aspects 2015;483:257-263.

[42] Klemm D, Heublein B, Fink H, Bohn A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew Chem Int Ed 2005;44:3358-3393.

[43] Cross CF, Bevan EJ, Beadle C. Die Chemie der Pflanzenfasern. Cellulosen, Oxycellulosen, Lignocellulosen. Ber Dtsch Chem Ges 1893;26:2520-2533.

[44] Cross CF, Bevan ET, Beadle C. Thiokohlensäureester der Cellulose. Ber Dtsch Chem Ges 1893;26:1090-1097.

[45] Guenet J. Chapter 5 - Cellulose. In: Guenet J., editors. Polymer-Solvent Molecular Compounds, Elsevier; 2008, p. 57-69.

[46] Mercer J. Improvements in the preparation of cotton and other fabrics and other fibrous materials. British Patent 1850;13296.

[47] Mittal A, Katahira R, Himmel ME, Johnson DK. Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility. Biotechnol Biofuels 2011;4:1-16.

[48] Dinand E, Vignon M, Chanzy H, Heux L. Mercerization of primary wall cellulose and its implication for the conversion of cellulose I→cellulose II. Cellulose 2002;9:7-18.

[49] Liu W, Zhao S, Li L, Xin XZ. Enhancement of cellulose reactivity using an ionic liquid pretreatment step. Cellul Chem Technol 2015;49:397-403.

[50] Wang Y, Deng Y. The kinetics of cellulose dissolution in sodium hydroxide solution at low temperatures. Biotechnol Bioeng 2009;102:1398-1405.

[51] Sharma S, Nair SS, Zhang Z, Ragauskas AJ, Deng Y. Characterization of micro fibrillation process of cellulose and mercerized cellulose pulp. RSC Adv 2015;5:63111-63122.

[52] Halonen H, Larsson PT, Iversen T. Mercerized cellulose biocomposites: a study of influence of mercerization on cellulose supramolecular structure, water retention value and tensile properties. Cellulose 2012;20:57-65.

[53] Revol JF, Dietrich A, Goring DAI. Effect of mercerization on the crystallite size and crystallinity index in cellulose from different sources. Can J Chem 1987;65:1724-1725.

[54] Yu L, Lin J, Tian F, Li X, Bian F, Wang J. Cellulose nanofibrils generated from jute fibers with tunable polymorphs and crystallinity. J Mater Chem A 2014;2:6402-6411.

[55] Jin E, Guo J, Yang F, Zhu Y, Song J, Jin Y, Rojas OJ. On the polymorphic and morphological changes of cellulose nanocrystals (CNC-I) upon mercerization and conversion to CNC-II. Carbohydr Polym 2016;143:327-335.

[56] Wilkes JS, Zaworotko MJ. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. J Chem Soc , Chem Commun 1992;13:965-967.

[57] Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. Chem Soc Rev 2008;37:123-150.

[58] Earle MJ, Seddon KR. Ionic Liquids: Green Solvents for the Future. In: Abraham MA and Moens L., editors. Clean Solvents: Alternative Media for Chemical Reactions and Processing , American Chemical Society; 2002, p. 10-25.

[59] Dutta S, De S, Alam MI, Abu-Omar MM, Saha B. Direct conversion of cellulose and lignocellulosic biomass into chemicals and biofuel with metal chloride catalysts. J Catal 2012;288:8-15.

[60] Hou X, Smith TJ, Li N, Zong M. Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin. Biotechnol Bioeng 2012;109:2484-2493.

[61] Xiao S, Liu B, Wang Y, Fang Z, Zhang Z. Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures. Bioresour Technol 2014;151:361-366.

[62] Park JI, Steen EJ, Burd H, Evans SS, Redding-Johnson A, Batth T, Benke PI, D'haeseleer P, Sun N, Sale KL, Keasling JD, Lee TS, Petzold CJ, Mukhopadhyay A, Singer SW, Simmons BA, Gladden JM. A Thermophilic Ionic Liquid-Tolerant Cellulase Cocktail for the Production of Cellulosic Biofuels. PLoS ONE 2012;7:e37010.

[63] Fu D, Mazza G. Aqueous ionic liquid pretreatment of straw. Bioresour Technol 2011;102:7008-7011.

[64] Bokinsky G, Peralta-Yahya PP, George A, Holmes BM, Steen EJ, Dietrich J, Soon Lee T, Tullman-Ercek D, Voigt CA, Simmons BA, Keasling JD. Synthesis of three advanced biofuels from ionic liquid-pretreated switchgrass using engineered Escherichia coli. Proc Natl Acad Sci U S A 2011;108:19949-19954.

[65] Cheng G, Varanasi P, Li C, Liu H, Melnichenko YB, Simmons BA, Kent MS, Singh S. Transition of Cellulose Crystalline Structure and Surface Morphology of Biomass as a Function of Ionic Liquid Pretreatment and Its Relation to Enzymatic Hydrolysis. Biomacromolecules 2011;12:933-941.

[66] Samayam IP, Hanson BL, Langan P, Schall CA. Ionic-Liquid Induced Changes in Cellulose Structure Associated with Enhanced Biomass Hydrolysis. Biomacromolecules 2011;12:3091-3098.

[67] Dadi AP, Schall CA, Varanasi S. Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. Appl Biochem Biotechnol 2007;137:407-421.

[68] Shafiei M, Zilouei H, Zamani A, Taherzadeh MJ, Karimi K. Enhancement of ethanol production from spruce wood chips by ionic liquid pretreatment. Appl Energy 2013;102:163-169.

[69] Zavrel M, Bross D, Funke M, Büchs J, Spiess AC. High-throughput screening for ionic liquids dissolving (ligno-)cellulose. Bioresour Technol 2009;100:2580-2587.

[70] Vitz J, Erdmenger T, Haensch C, Schubert US. Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chem 2009;11:417-424.

[71] Zhang J, Zhang H, Wu J, Zhang J, He J, Xiang J. NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids. Phys Chem Chem Phys 2010;12:1941-1947.

[72] Toth T, Borsa J, Reicher J, Sallay P, Sajo I, Tanczos I. Mercerization of cotton with tetramethylammonium hydroxide. Text Res J 2003;73:273-278.

[73] Abe M, Kuroda K, Ohno H. Maintenance-Free Cellulose Solvents Based on Onium Hydroxides. ACS Sustainable Chem Eng 2015;3:1771-1776.

[74] Behrens MA, Holdaway JA, Nosrati P, Olsson U. On the dissolution state of cellulose in aqueous tetrabutylammonium hydroxide solutions. RSC Adv 2016;6:30199-30204.

[75] Wei W, Wei X, Gou G, Jiang M, Xu X, Wang Y, Hui D, Zhou Z. Improved dissolution of cellulose in quaternary ammonium hydroxide by adjusting temperature. RSC Adv 2015;5:39080-39083.

[76] Jia X, Chen Y, Shi C, Ye Y, Wang P, Zeng X, Wu T. Preparation and Characterization of Cellulose Regenerated from Phosphoric Acid. J Agric Food Chem 2013;61:12405-12414.

[77] Zhao H, Holladay JE, Kwak JH, Zhang ZC. Inverse Temperature-Dependent Pathway of Cellulose Decrystallization in Trifluoroacetic Acid. J Phys Chem B 2007;111:5295-5300.

[78] Sasaki M, Adschiri T, Arai K. Production of Cellulose II from Native Cellulose by Near- and Supercritical Water Solubilization. J Agric Food Chem 2003;51:5376-5381.

[79] Ma H, Zhang B, Zhang P, Li S, Gao Y, Hu X. An efficient process for lignin extraction and enzymatic hydrolysis of corn stalk by pyrrolidonium ionic liquids. Fuel Process Technol 2016;148:138-145.

[80] Klein-Marcuschamer D, Simmons BA, Blanch HW. Techno-economic analysis of a lignocellulosic ethanol biorefinery with ionic liquid pre-treatment. Biofuels, Bioprod Bioref 2011;5:562-569.

[81] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 2002;83:1-11.

[82] Demirbas A. Bioethanol from Cellulosic Materials: A Renewable Motor Fuel from Biomass. Energy Sources 2005;27:327-337.

[83] Nasri-Nasrabadi B, Behzad T, Bagheri R. Extraction and characterization of rice straw cellulose nanofibers by an optimized chemomechanical method. J Appl Polym Sci 2014;131.

[84] Lindedam J, Bruun S, Jørgensen H, Felby C, Magid J. Cellulosic ethanol: interactions between cultivar and enzyme loading in wheat straw processing. Biotechnol Biofuels 2010;3:1-10.

[85] Mansaray KG, Ghaly AE. Thermal degradation of rice husks in nitrogen atmosphere. Bioresour Technol 1998;65:13-20.

[86] Jústiz-Smith NG, Virgo GJ, Buchanan VE. Potential of Jamaican banana, coconut coir and bagasse fibres as composite materials. Mater Charact 2008;59:1273-1278.

Captions for figures and tables.

Fig. 1. Cumulative investment in renewables-based power generation, 2013-2035, where OECD stands for Organisation for Economic Co-operation and Development, [2] (Reprinted with permission from “IEA Publishing. OECD/IEA© 2013,”).

Fig. 2. Structure of Cellulose I

Fig. 3. Hydrophilic and hydrophobic sides of Cellulose I: (a) top view of glucopyranose ring plane; (b), front view of glucopyranose ring plane, [20] (Reprinted with permission from “Macmillan Publishers Ltd: Polymer Journal, copyright 2006”).

Fig. 4. Cellulose polymorphs

Fig. 5. Intermolecular and intramolecular hydrogen bonding in cellulose I and cellulose II, [31] (Reprinted with permission from “John Wiley and Sons, copyright 1998”).

Fig. 6. Crystallinity index and cellulose II content of mercerised jute fibres by aqueous NaOH for 4 hours, [54] (Reprinted with permission from “The Royal Society of Chemistry”).

Fig. 7. XRD profiles for cellulose samples treated at 120 ^{O}C [65] (Reprinted with permission from “American Chemical Society, Biomacromolecules, Copyright 2011”)

Fig. 8. Influence of temperature and shaking on the dissolution of 4 wt.% Avicel in EMIM-Ac [69] (Reprinted with permission from “Elsevier, Bioresource Technology, Copyright 2009)

Fig. 9. Cellulose I solubility in various solvents [73] (Reprinted with permission from “American Chemical Society, Sustainable Chemistry and Engineering, Copyright 2015”).

Fig. 10. Cellulose hydrolysis [63] (Reprinted with permission from “Elsevier, Bioresource Technology, Copyright 2011).

Table 1: Cellulose I content of various bioethanol feedstocks [82-86]

Table 2: Cellulose II production methods

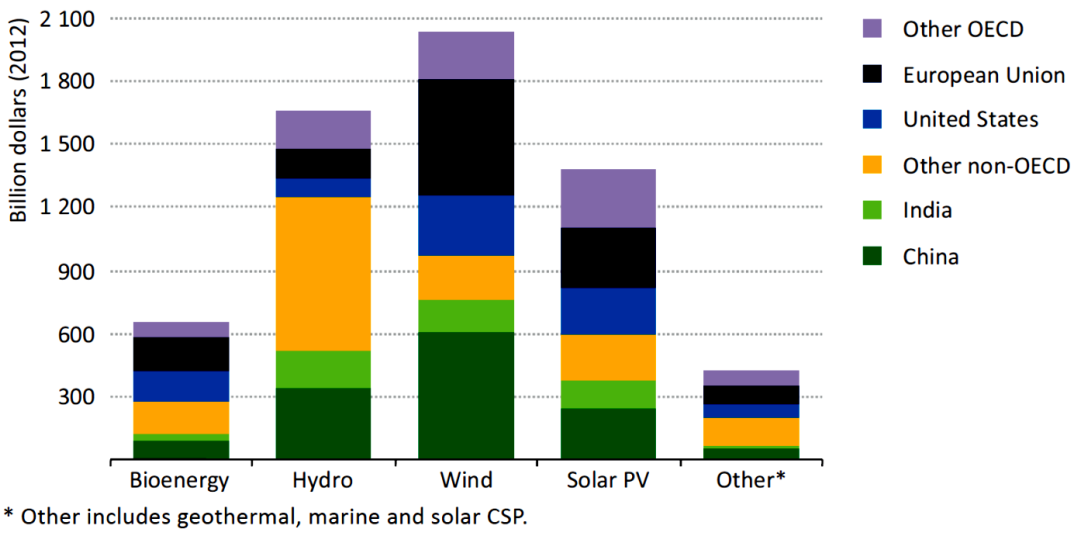
Billion dollars (2012)
2 100
1 800
1 500
1 200
900
600
300
Bioenergy
Hydro
Wind
Solar PV
Other*
Other OECD
European Union
United States
Other non-OECD
India
China
* Other includes geothermal, marine and solar CSP.

Fig. 1.

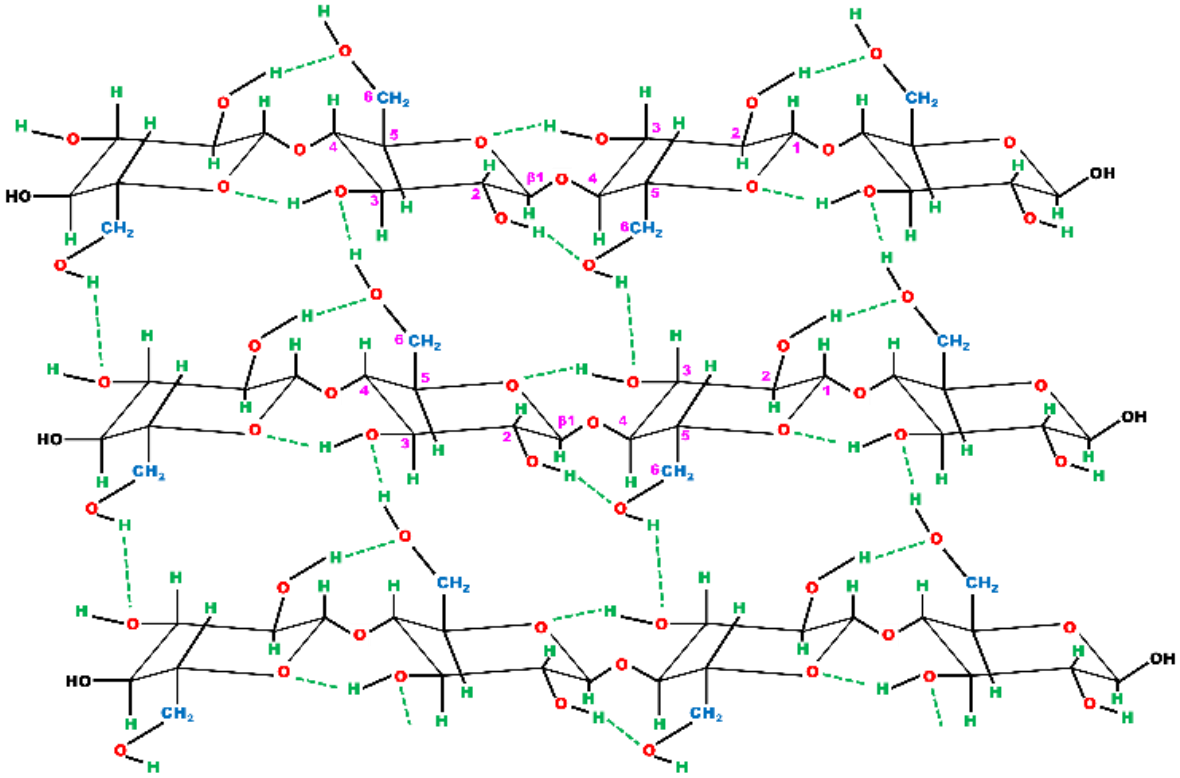

Fig. 2.

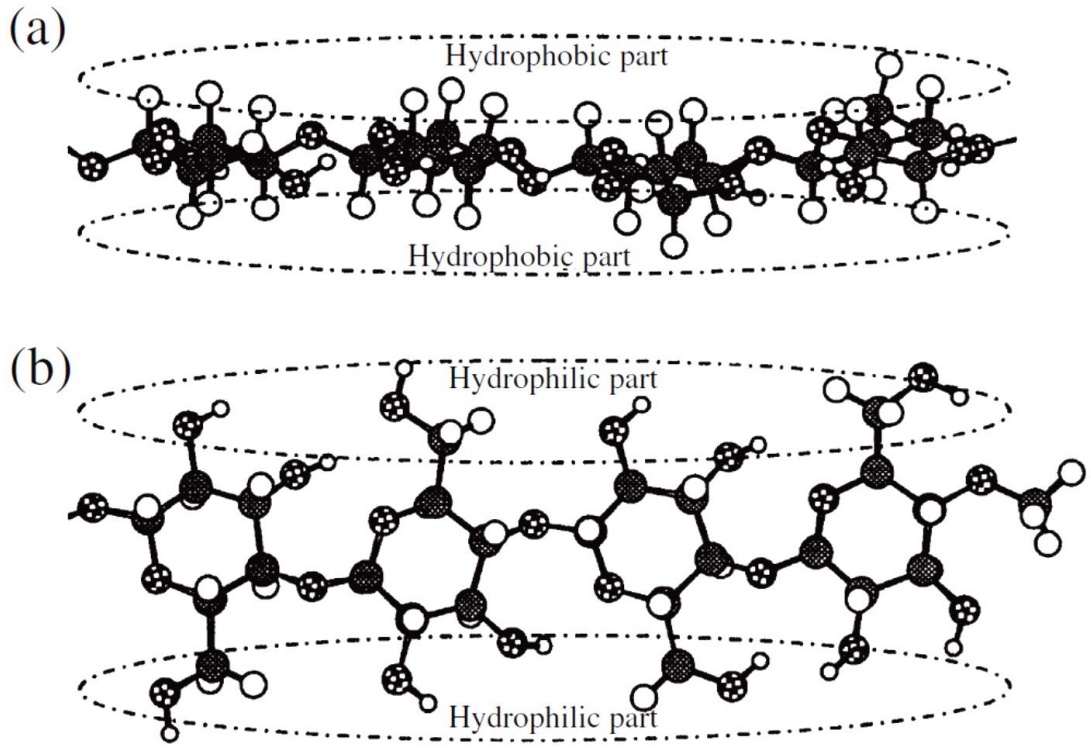
(a)
Hydrophobic part
Hydrophobic part
(b)
Hydrophilic part
Hydrophilic part

Fig. 3.

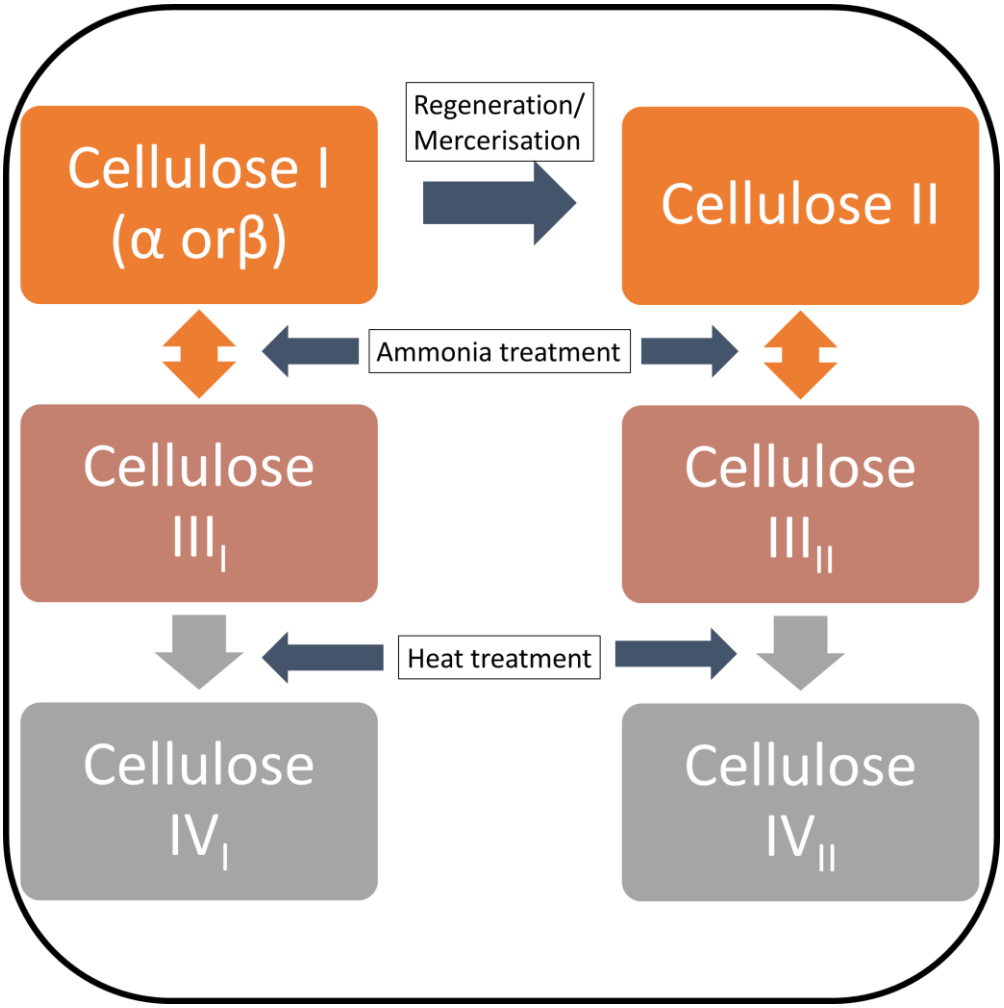
Cellulose I
(α orβ)
Regeneration/
Mercerisation
Cellulose II
Ammonia treatment
Cellulose
III$_I$
Cellulose
III$_{II}$
Heat treatment
Cellulose
IV$_I$
Cellulose
IV$_{II}$

Fig. 4.

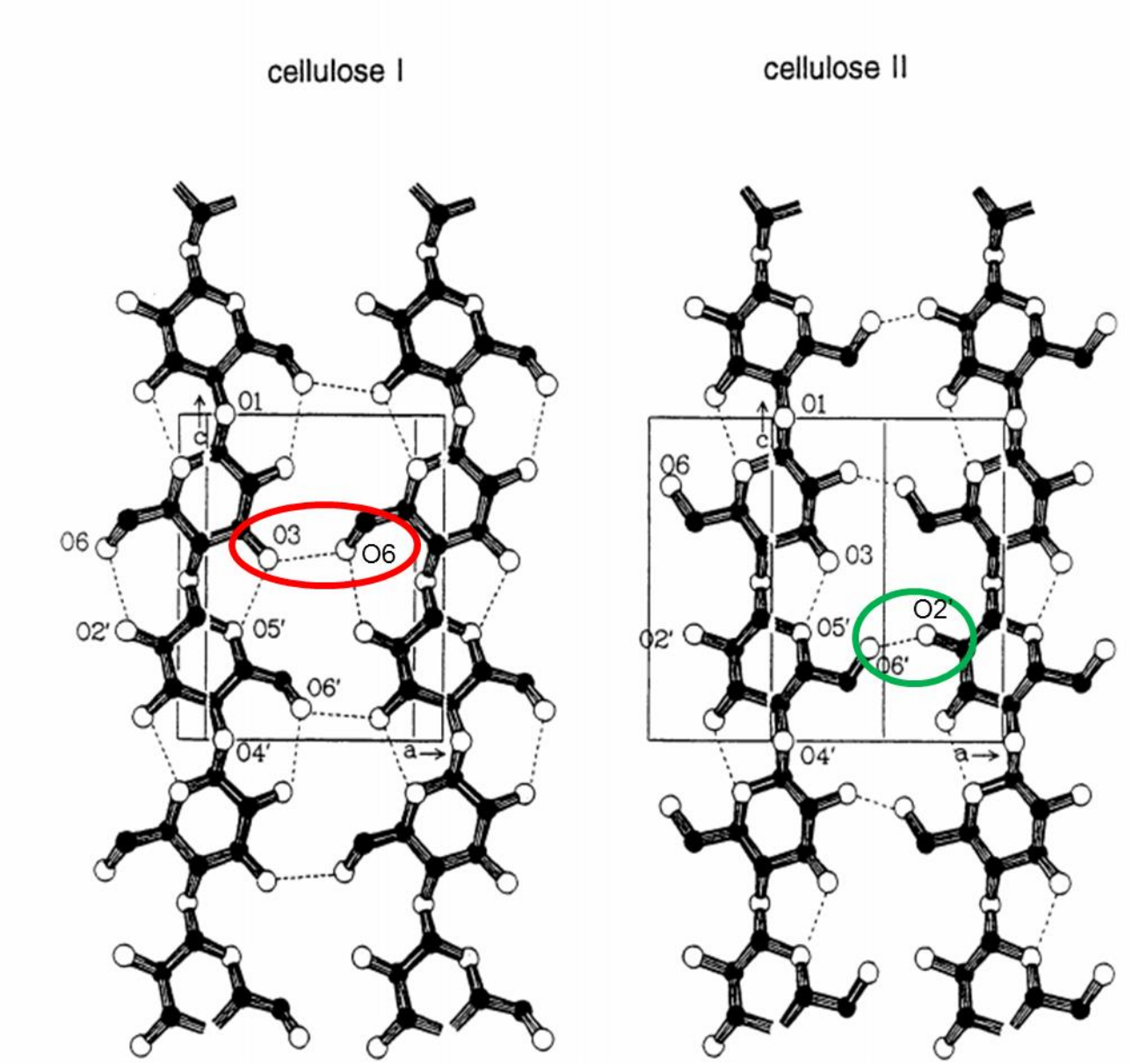
cellulose I
cellulose II
01
c
06
03
O6
02'
05'
06'
04'
a
01
c
06
03
O2'
02'
05'
06'
04'
a

Fig. 5.

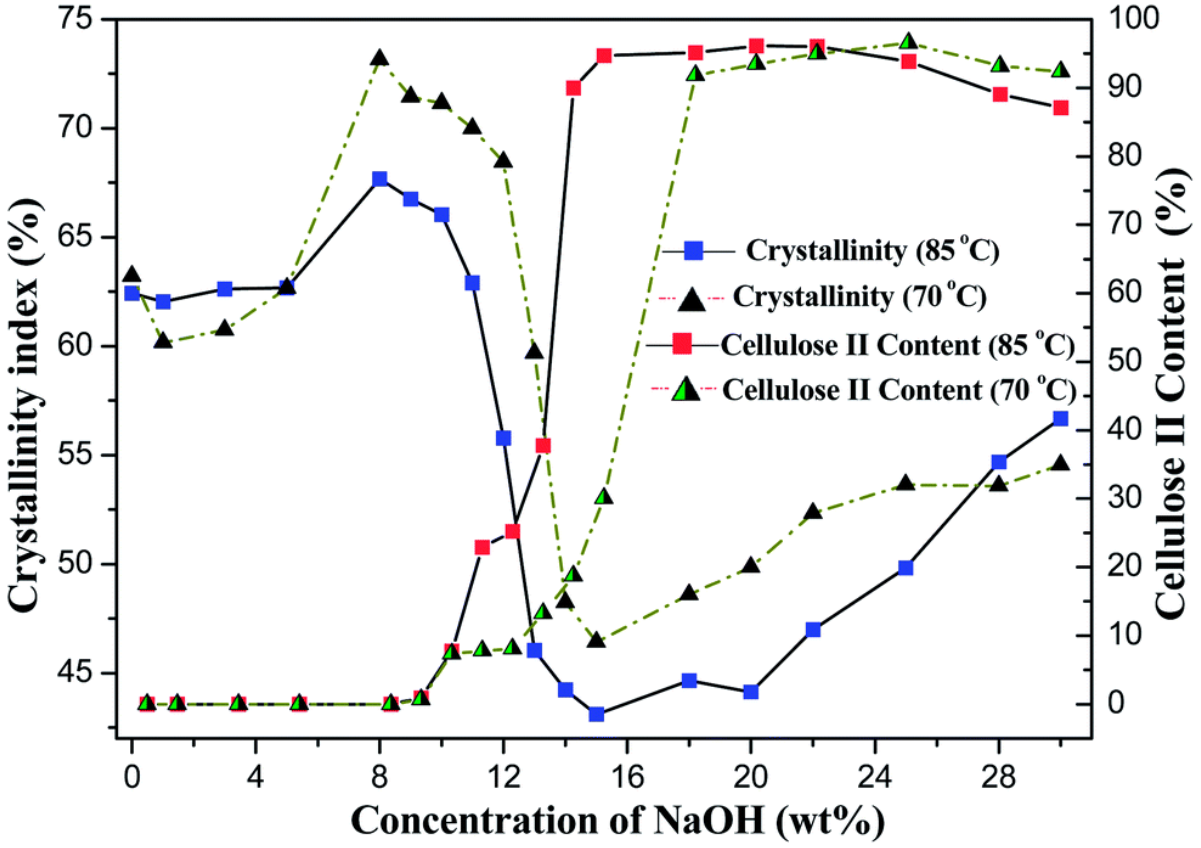
Crystallinity index (%)
Cellulose II Content (%)
Concentration of NaOH (wt%)
Crystallinity (85 °C)
Crystallinity (70 °C)
Cellulose II Content (85 °C)
Cellulose II Content (70 °C)
75
70
65
60
55
50
45
100
90
80
70
60
50
40
30
20
10
0
0
4
8
12
16
20
24
28

Fig. 6.

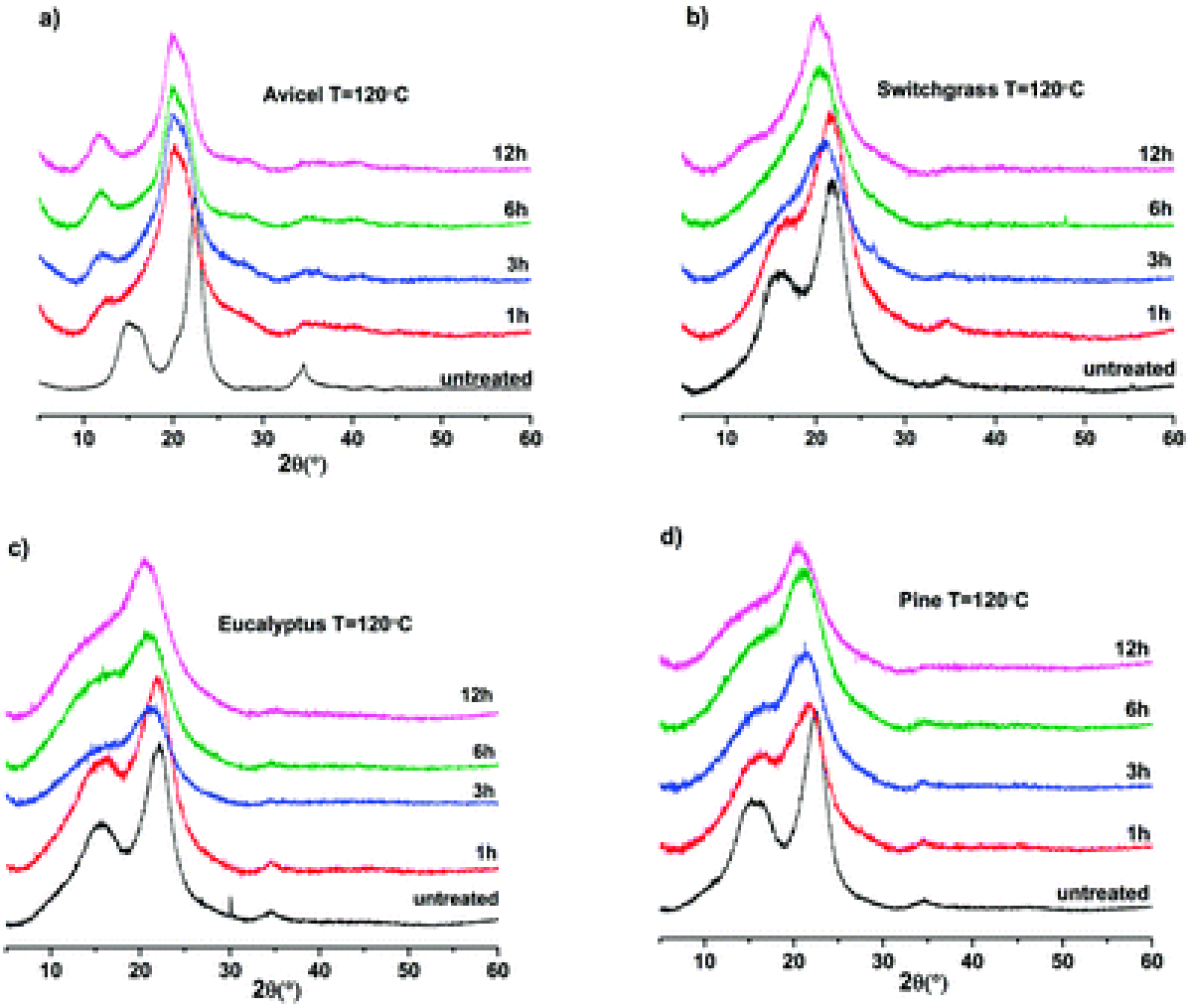
a)
Avicel T=120°C
12h
6h
3h
1h
untreated
10
20
30
40
50
60
2θ(°)
b)
Switchgrass T=120°C
12h
6h
3h
1h
untreated
10
20
30
40
50
60
c)
Eucalyptus T=120°C
12h
6h
3h
1h
untreated
10
20
30
40
50
60
2θ(°)
d)
Pine T=120°C
12h
6h
3h
1h
untreated
10
20
30
40
50
60
2θ(°)

Fig. 7.

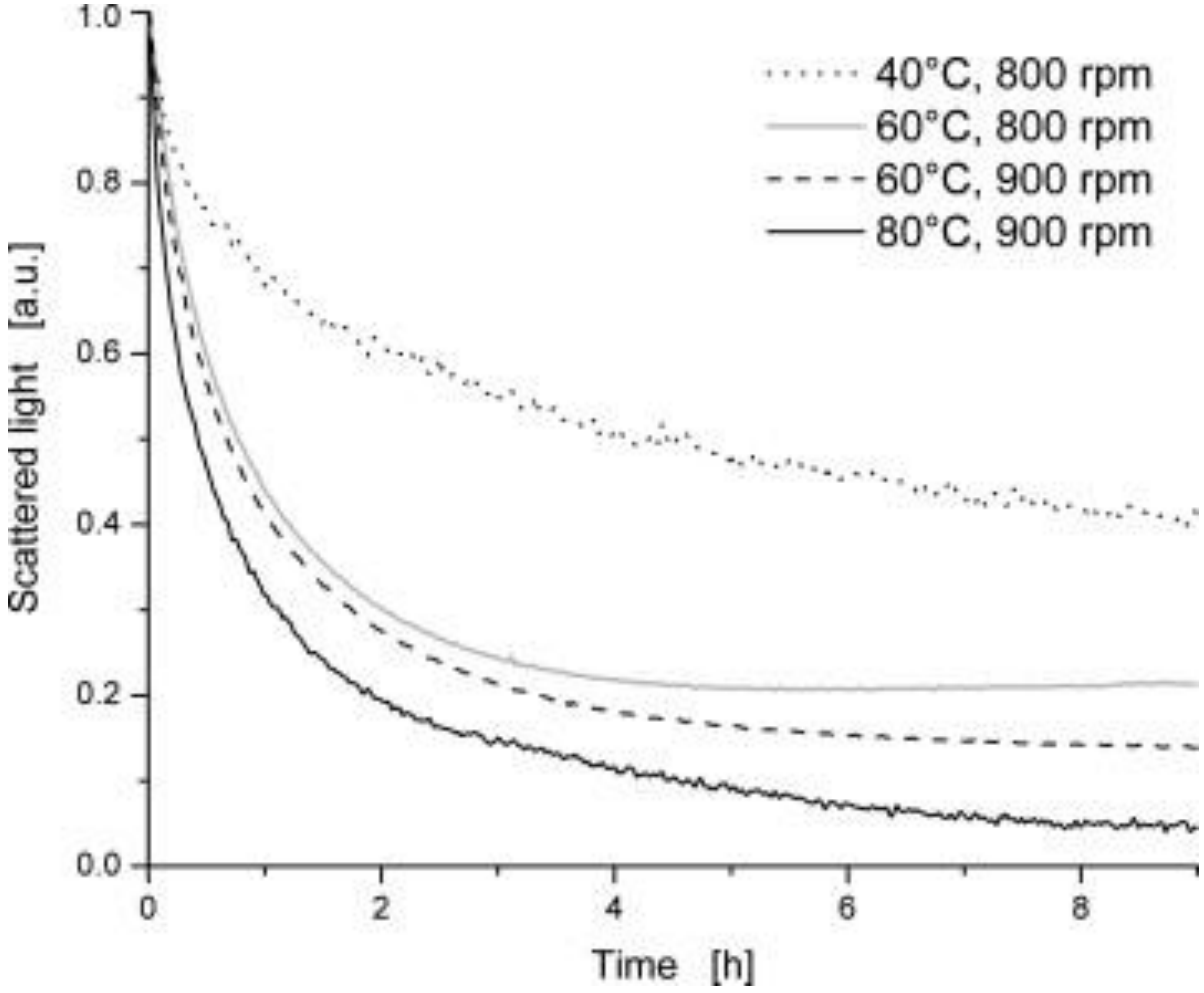
40°C, 800 rpm
60°C, 800 rpm
60°C, 900 rpm
80°C, 900 rpm
Scattered light [a.u.]
Time [h]
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8

Fig. 8.

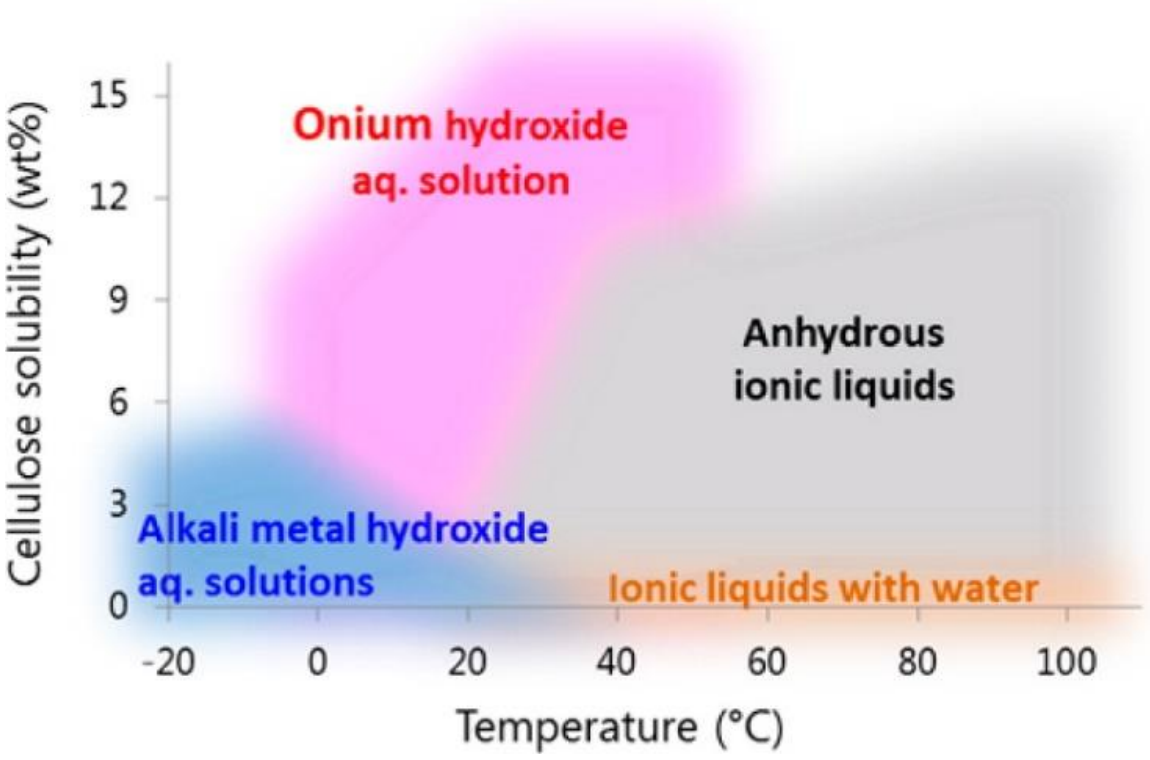
Cellulose solubility (wt%)
15
12
9
6
3
0
Onium hydroxide
aq. solution
Anhydrous
ionic liquids
Alkali metal hydroxide
aq. solutions
Ionic liquids with water
-20
0
20
40
60
80
100
Temperature (°C)

Fig. 9.

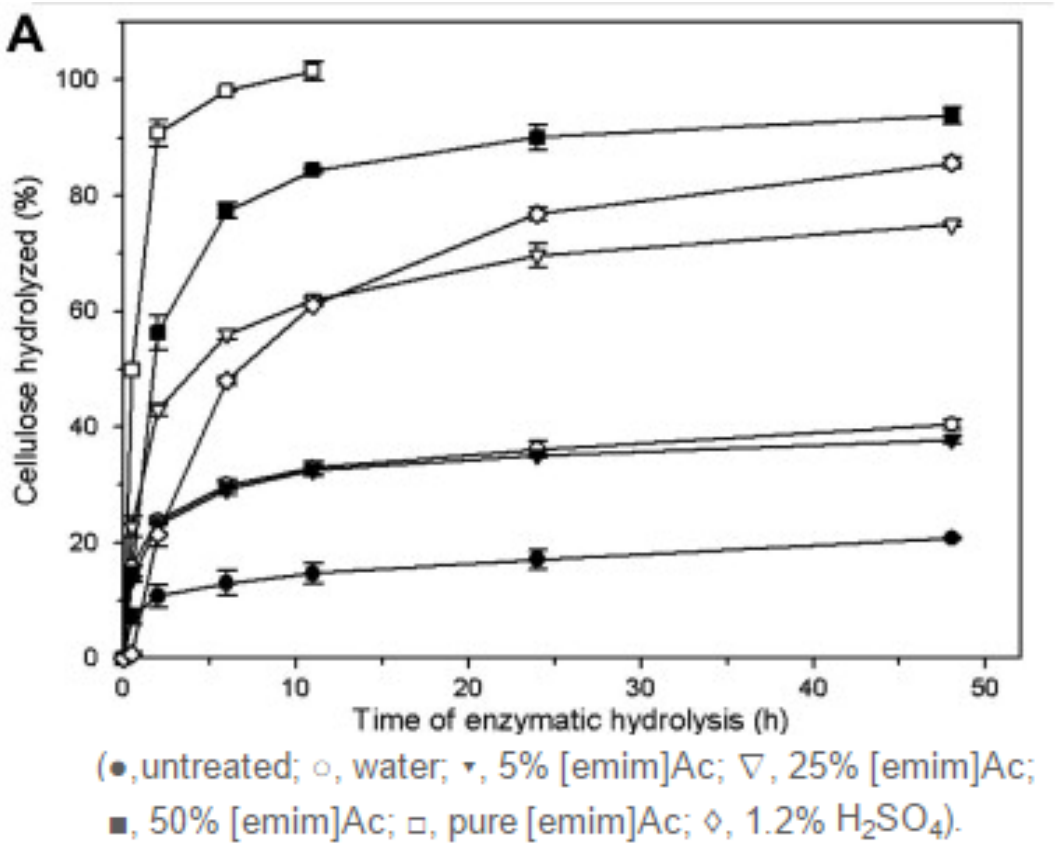
A
Cellulose hydrolyzed (%)
100
80
60
40
20
0
0
10
20
30
40
50
Time of enzymatic hydrolysis (h)
(●,untreated; ○, water; ▾, 5% [emim]Ac; ▽, 25% [emim]Ac;
■, 50% [emim]Ac; □, pure [emim]Ac; ◊, 1.2% H_2SO_4).

Fig. 10.

Table 1

Material	**% cellulose I content (wt./wt.)**
Green algae	20-40
Cotton, flax, etc.	80-95
Grasses	25-40
Hardwoods	45±2
Hardwood barks	22-40
Softwoods	18-38
Softwood barks	42±2
Corn stalks	39-47
Wheat straw	37-41
Newspapers	40-55
Chemical pulps	60-80
Rice straw	46.5±1.5
Wheat straw	35-37
Rice husk	25-35
Bagasse	32-43

Table 2.

Treatment type	Solvent used	Temperature (^{O}C)	Method synopsis	Reference
Alkali	Aqueous NaOH solution	-	Cellulose xanthogenate prepared from pulp is dissolved in aqueous NaOH and precipitated out of solution (viscose process).	[42-44]
	0-30% aqueous NaOH solution	70 ^{O}C/85 ^{O}C	Cellulose I was dissolved in NaOH aqueous solution followed by precipitation and purification (mercerisation). 9 – 15% NaOH aqueous solution was found to produce better cellulose II yields than other concentrations at 85 ^{O}C.	[46,54]
	6% aqueous NaOH solution	-8 ^{O}C to -20 ^{O}C	Cellulose I was dissolved at sub-zero temperatures and after 10 minutes of dissolution at -15 ^{O}C cellulose II started to appear.	[50]
Ionic liquid	1-ethyl-3-methylimidazolium acetate (EMIM-Ac)	120 ^{O}C/160 ^{O}C	Avicel, switchgrass, eucalyptus and pine samples were dissolved in EMIM-Ac at the 120 ^{O}C /160 ^{O}C and upon dissolution, cellulose II was precipitated out using hot water. Higher rate of cellulose II formation was observed with higher temperature.	[65]
	21 different ionic liquids	50 ^{O}C/80 ^{O}C	Avicel, α-cellulose, spruce wood, silver fir, common beech and chestnut wood of 1- 5 wt.% was dissolved in 21 different ionic liquids at 50 ^{O}C and upon dissolution cellulose II was precipitated. EMIM-Ac was found to dissolve standard cellulose I samples and 1-allyl-3-methylimidazolium-	[69]

			chloride (AMIM-Cl) dissolved the wood samples.	
	imidazolium based ionic liquids containing odd or even numbered alkyl side chains in combination with a range of anions	100 ^{O}C	8 wt.% of Avicel PH 101 was dissolved in ionic liquids at 100 ^{O}C. Upon dissolution, excess methanol was used to precipitate cellulose II. It was determined that ionic liquids with shorter even numbered side chains (2 or 4) combined with chloride anions showed good cellulose I dissolving properties.	[70]
Onium hydroxide	Aqueous solutions of tetrabutylammonium hydroxide (TBAH) and tertabutylphosphonium hydroxide (TBPH).	25 ^{O}C	Cellulose I was dissolved in 40 – 70 wt.% aqueous TBAH and TBPH solution. Hot ethanol was added to the solution to precipitate cellulose II. It was determined that a concentration range of 50 – 60% TBAH and 50 – 70% TBPH in water was required for complete cellulose I dissolution at room temperature	[40]
	TBAH	16 ^{O}C – 28 ^{O}C	Cellulose I was dissolved in 40 and 60 wt.% TBAH at different temperatures. Precipitation and regeneration of cellulose II was performed by the addition of hot water. It was determined that cellulose I dissolved better at 16 ^{O}C due to the stable ionic structure of TBAH at lower temperatures.	[75]
	TBPH, tetraethylphosphonium hydroxide (TEPH), tri-n-hexylphosphine tetramethylammonium hydroxide (THTMAH), tetraethylammonium hydroxide (TEAH), TBAH, tri-n-	25 ^{O}C	Cellulose I was dissolved in various 40 wt% onium hydroxide aqueous solutions. A concentration of 15 wt% cellulose I was found to be dissolved in all the onium hydroxides, whereas TBPH and TBAH dissolved 20 wt%	[73]

	butylmethylphosphonium hydroxide and tetra-n-hexylammonium hydroxide		cellulose I. THTMAH and TEAH did not dissolve any cellulose I.	
Phosphoric acid	77 – 85 wt.% phosphoric acid	5 ^{O}C – 75 ^{O}C	0.5 – 3% wt./v cellulose I was dissolved in 77 – 85 wt.% phosphoric acid in the temperature range of 5 – 75 ^{O}C. Regeneration was performed with the addition of water. They determined that a higher concentration of phosphoric acid (≥ 83 wt.%) was required to completely dissolve cellulose I.	[76]
Trifluoroacetic acid	99% Trifluoroacetic acid (TFA)	0 ^{O}C – 65 ^{O}C	Cotton linters were mixed in 99% TFA in mass ratios of 1:15 at different temperatures ranging from 0 – 65 ^{O}C for 3 hours. The swollen samples were washed with water to recover cellulose II. Complete conversion to cellulose II was only observed at 0 ^{O}C.	[77]
Supercritical water solubilisation	Supercritical water	320 ^{O}C – 400 ^{O}C	A 10 wt.% cellulose I was mixed with water in a microreactor and rapidly heated for 0.02 – 0.6 s at 320 – 400 ^{O}C and 25 – 33 MPa pressure to obtain cellulose II. It was determined that at temperatures higher than 380 ^{O}C, cellulose I conversion was constant and was independent of pressure.	[78]