Acidic and alkaline deep eutectic solvents in delignification and nanofibrillation of corn stalk, wheat straw, and rapeseed stem residues

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**ABSTRACT**

In this work, six different deep eutectic solvent (DES) treatments—five acidic (natural organic acid–choline chloride) and one alkaline (K\textsubscript{2}CO\textsubscript{3}–glycerol)—were used and compared in delignification and nanofibrillation of agricultural by-products from wheat straw, corn stalk, and rapeseed stem. The DES treatments were performed at 100 °C for 8 h, at 100 °C for 16 h, and at 80 °C for 24 h. The yield of cellulose and lignin fractions was obtained gravimetrically, and a more detailed composition of fractions was obtained for the 16 h treatment. All the samples were further nanofibrillated, and the properties of nanocelluloses and their nanopapers were measured. Acidic lactic acid–choline chloride and alkaline K\textsubscript{2}CO\textsubscript{3}–glycerol DESs resulted in the highest delignification yields (11.8–5.7 wt-%), nanocellulose viscosity (1360–555 Pa s), and crystallinity index (54–38 %), but the strength properties of nanopapers from alkaline DES treatment (170–132 MPa) were better compared to acidic DESs (132–24 MPa). A plausible explanation for this difference may be that the alkaline DES also dissolved waxes and proteins, which can mitigate the adhesion and network formation between the nanofibers. It was also observed that the separated lignin fractions from acidic and alkaline DES treatments had different characteristics as determined by FTIR.

1. Introduction

Agricultural by-products such as straws, stalks, and stems, which are obtained after harvesting and removing the edible products, make up about half of the yield of agricultural biomass. This means that annually about 875 megatons of wheat straw, 1000 megatons of corn stover, and about half of the yield of agricultural biomass (Lal, 2005; Haberl et al., 2011; Monforti et al., 2015; Hansen et al., 2016; van der Hilst et al., 2018). DESs have previously been used mainly in the dissolution of forest residues in high-value applications typically requires fractionation or isolation processes for the separation of its major and minor constituents. For removal of lignin, i.e., the delignification of biomass, alkaline, organosolv, ionic liquids, ozonolysis, and many other physico-chemical or fungal pretreatments have been harnessed (Balat, 2011; Shirkavand et al., 2016). In recent years, a new class of green chemicals, termed deep eutectic solvents (DES) (Francisco et al., 2012a; Jabłonski et al., 2015; Loow et al., 2017; Lynam et al., 2017; Zhang et al., 2016; Zulkifeli et al., 2017; Tang et al., 2017), has been reported as an alternative, sustainable approach to fractionating and further refining the biomass components into various end-products such as biofuels, furanic derivatives, and other high-value chemicals (Vigier et al., 2015). DESs have previously been used mainly in the dissolution of CO\textsubscript{2}, inorganic salts, organic molecules, and various metal oxides, as well as in metal recovery in electrochemistry (Zhang et al., 2012), since they can be easily prepared from low-cost, bulk chemicals by simply...
mixing them together with heating or even at ambient temperature (Tang et al., 2017). The chemicals used in DES can be biodegradable and sometimes recyclable, which makes them even more attractive in the sustainable processing of various materials (Sirviö et al., 2015; Yang et al., 2019).

Previously, DESs formed from organic acids and choline chloride were found to be able to delignify different biomasses (Francisco et al., 2012b; Kumar et al., 2016; Loow et al., 2017; Zdanowicz et al., 2018). These acidic treatments were used, e.g., as a pretreatment for fermentation of sugars into ethanol, since they selectively dissolved lignin but left cellulose and hemicelluloses intact (Francisco et al., 2012b; Kumar et al., 2016). The cytotoxicity tests have also shown that these natural deep eutectic solvents (NADES) do not reveal any cytotoxicity and they are biodegradable and are considered to be environmental friendly (Haraźna et al., 2019). However, acidic treatments can decrease the degree of polymerization of carbohydrates, which can in turn decrease the material properties of cellulose and hemicelluloses (Mäki-Arvela et al., 2011). On the other hand, the reports of delignification of biomasses by alkaline DES treatments, which can potentially be less harmful to the properties of carbohydrates, are still rare. It has been noted that nontoxic alkaline glycerol cooking (without DES formation) can result in the efficient impregnation of glycerol in the various biomasses and provide an effective reaction medium for delignification (Demirbaş, 1998). Moreover, an alkaline DES of glycerol–potassium carbonate DESs (Ghaedi et al., 2018; Naser et al., 2013) has been reported as potential solvent for industrial applications because of its viscosity, density, surface tension, refractive index, pH, and conductivity in different temperatures, and it has been reported as a promising green medium in the pulping of rice straw (Lim et al., 2019). To the best of our knowledge, a comparison of acidic and alkaline DESs in delignification and further utilization of biomasses has not been reported previously.

Nanocelluloses, i.e., cellulose particles that typically have a diameter in nanoscale (< 100 nm) and a length from nanoscale to several micrometers, are considered to be among the most promising future materials because of their high strength, light weight, tailorability, and green origin to enable their use in replacing plastics (Chin et al., 2018; Nechyporchuk et al., 2016). Typically, chemical or enzymatic pretreatments are used to loosen the recalcitrance structure of biomass to unravel elongated and flexible cellulose nanofibrils (CNF) or shorter and rigid cellulose nanocrystals (CNC) from biomass (Lee et al., 2014). DESs also offer a potential medium for the production of nanocelluloses and have been used to form non-derivatized nanofibrils (Li et al., 2017a; Sirviö et al., 2015; Suopajärvi et al., 2017), anionic nanofibrils (Selkälä et al., 2016; Sirviö et al., 2019), and even cellulose nanocrystals (Sirviö et al., 2016).

In this work, six different deep eutectic solvent (DES) treatments—five acidic (natural organic acid – choline chloride) and one alkaline (K2CO3 – glycerol)—were compared in the delignification and nanofibrillation of agricultural by-products from wheat straw, corn stalk, and rapeseed stem. After treatments, the solid fraction, consisting mainly of carbohydrates (i.e. cellulose and hemicellulose), and the liquid fraction, consisting mainly of lignin and hydrolyzed carbohydrates, were separated, the composition of the cellulose-rich fractions was analyzed by gravimetric and analytic methods, and precipitated lignin was investigated with FTIR. The cellulose-rich fractions were further nanofibrillated, and properties of nanocelluloses and their nanopapers were measured.

2. Materials and methods

2.1. Raw materials and chemicals

The wheat straw (Chile), corn stalk (Argentina), and rapeseed stem (Argentina) samples were oven-dried to a constant weight and then milled to a particle size of one millimeter and used as such. The
compositional analysis (glucan, xylan, lignin, and ash) was performed according to the analytical procedure provided by the National Renewable Energy Laboratory (NREL) (NREL/TP-510-42622 and NREL/TP-510-42618) (Sluiter, 2008; Sluiter et al., 2008) on the raw biomass previously dried at 105 °C overnight. The analyses were performed in triplicate. Quantification of monomeric sugars was carried out by HPLC using the ROA column Phenomenex (USA) at 85 °C and the evaporative light-scattering ELS-2041 detector Jasco (Japan). The mobile phase was ultrapure H2O with a flow rate of 0.6 mL min⁻¹. All the experiments were conducted in triplicate. The raw materials and their compositions are shown in Fig. 1. The chemicals used in the preparation of DES solutions are shown in Table 1. The molar ratio of the hydrogen bond donor (HBD) (acids and glycerol) and hydrogen bond acceptor (HBA) (choline chloride and K2CO3) were chosen according to the literature (Francisco et al., 2013, 2012a; Kumar et al., 2016) (acidic DES) and by knowing that the solubility of lignin compounds increases by increasing the molar ratio of HBD (Soares et al., 2017). However, in the case of glycerol, the viscosity of formed DES limited the used molar ratio, which was thus chosen to be 5:1. Choline chloride (99 %) was obtained from Algry Quimica, S.L. (Spain) and glycerol (98 %), glutaric acid (98 %), lactic acid (90 %), levulinic acid (98 %), DL-malic acid (99 %), and ethanol (96 %) from VWR (Finland). K2CO3 (99 %) was obtained from Honeywell (Germany). Sulfuric acid (72 % w/w), CaCO3, D (+) glucose and D (+) xylose were used as received and were of analytical grade (Merk). For the fabrication of the nanopapers, Durapore polyvinylidene fluoride membranes with pore size of 0.65 μm were used, and for the preparation of the FESEM samples, track-etched Nuclepore membranes with pore size of 0.20 μm from Millipore (France) were used. Deionized water was used throughout the experiments.

### 2.2. DES pretreatments

Acidic DES solutions were prepared by mixing choline chloride and a natural organic acid together, and the alkaline DES solution, by mixing glycerol and potassium carbonate together, at a chosen molar ratio (Table 1). Mixtures were heated in an oil bath at 100 °C under stirring until a clear solution formed. 3 g of wheat, corn, or rapeseed was added to the suspension with 5 g of water, and the suspension (3 wt%) was allowed to stir at 100 °C for 8 or 16 h or at 80 °C for 24 h. The reaction was stopped with the addition of 100 mL of ethanol, after which the warm mixture was filtered and the solid residue washed twice with warm water, dried at 50 °C for 48 h, and weighed. Around 200 mL of water was added to the ethanol-DES filtrate, and lignin was allowed to precipitate overnight. The alkaline-DES solution was acidified with 1 M HCl solution before lignin precipitation. Precipitated lignin was separated from the solution by centrifugation and washed twice with a water-ethanol (9:1) solution. Washed lignin was dried at 50 °C for 48 h and weighed.

### 2.3. Composition of DES-treated solid fractions

The compositional analysis of DES-treated solid fractions (glucan, xylan, lignin, and ash) was performed according to the analytical procedure provided by the National Renewable Energy Laboratory (NREL) (NREL/TP-510-42622 and NREL/TP-510-42618) (Sluiter, 2008; Sluiter et al., 2008), after having dried at 105 °C overnight. The analyses were performed in triplicate. Quantification of monomeric sugars was carried out by HPLC using the ROA column Phenomenex (USA) at 85 °C and the evaporative light-scattering ELS-2041 detector Jasco (Japan). The mobile phase was ultrapure H2O with a flow rate of 0.6 mL min⁻¹. All the experiments were conducted in triplicate.

### 2.4. Nanofibrillation of solid fractions

DES-treated wheat, corn, and rapeseed samples were soaked in water overnight at a consistency of 0.5 % and treated with an Ultra Turrax mixer (IKA T25, Germany) for 20 min at 10,000 rpm before nanofibrillation with a microfluidizer (Microfluidics M-110EH-30, USA). Three passes through a 400 μm chamber without pressure, three passes through 400 and 200 μm chambers at a pressure of 1000 bar, and then three passes through 200 and 100 μm chambers at a pressure of 1500 bar were used to obtain gel-like nanocelluloses suspensions, which are shown in Fig. 1.

### 2.5. Analysis of nanofibrillated samples

#### 2.5.1. Rotational viscosity

The rotational viscosity of nanocellulose suspensions was measured with the Brookfield DV-II + Pro EXTRA (USA) rotational viscometer using vane-shaped spindle (V-73). Measurements were performed at constant temperature (20 °C) with the sample consistency at 0.35 %. Rotational speeds of 10, 20, 50, and 100 rpm and measurement time of 2–5 min were used.

#### 2.5.2. X-ray diffraction

The crystallinity of the CNFs from acidic-DES (Lac5-Ch) and alkaline-DES (Gly–K2CO3) treatments were measured from freeze-dried samples, which were pressed into around 1 mm thick tablets. Wide-angle X-ray diffraction (WAXD) measurements were conducted with a Rigaku SmartLab 9 kW rotating anode diffractometer (Japan) by using a Co Kα radiation (40 kV, 135 mA) (λ = 1.79030 nm). Scans were taken over a 2θ (Bragg angle) range from 5° to 50° at a scanning speed of 10°/s, using a step of 0.5°. The degree of crystallinity in terms of the crystallinity index (CrI) was calculated from the peak intensity of the main crystalline plane (200) diffraction (I_{200}) at 26.2° and from the peak intensity at 22.0° associated with the amorphous fraction of cellulose (I_{am}) by using the Segal empirical Eq. (1) (Segal et al., 1959):

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CrI = \left( \frac{I_{200} - I_{am}}{I_{200}} \right) \times 100\%
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2.5.3. TEM and FESEM imaging

An energy filtered transmission electron microscope (EFTEM), LEO 912 OMEGA (Germany), was used to observe the morphology of the produced nanofibrils. TEM samples were prepared by dropping the diluted nanocellulose suspension on a carbon-coated copper grid. Uranyl acetate (2 % w/v) was used in the negative staining of the samples, after which the samples were dried at room temperature. The TEM images were captured with a Quemesa CCD camera (Japan), using 100 kV as an accelerating voltage. The widths of individual nanofibrils were measured from images with ImageJ processing software. As a pretreatment to FESEM imaging, nanofibrillated samples were filtered on the polycarbonate membrane (pore size of 0.2 µm), rapidly frozen in liquid nitrogen, and freeze-dried in a vacuum overnight. Samples were sputter-coated with platinum and imaged using an accelerating voltage of 5 kV and a working distance of 5 mm.

2.6. Preparation and characterisation of nanopapers from nanofibrillated samples

Nanopapers were produced by filtering 300 mg (abs.) nanofibrillated samples on a polyvinylidene fluoride membrane (pore size 0.65 µm). After filtration, the moist nanopaper was covered with another membrane, placed between two blotting boards, and dried with a Rapid-Köthen sheet dryer (Karl Schröder KG, Germany) at 94 °C under 900 mbar vacuum for 10 min. The samples were stored at standard conditions of 23 °C and 50 % relative humidity. After preconditioning in the standard environment for at least 48 h, the sample thickness was measured in five different locations using a precision thickness gauge (Hanatek FT3, UK), and the results were averaged. The nanopaper was cut into 6 strips with a width of 5 mm prior to the strength measurements. The tensile tests were performed with a Zwick 50724587 (Switzerland) universal material testing machine equipped with a 100 N load cell. For the tensile tests, the gauge length was set to 40 mm, and six replicates of each sample were tested at a strain rate of 4 mm min⁻¹ using a pre-strain of 0.1 N at the standard conditions of 23 °C temperature and 50 % relative humidity.

2.7. Analysis of lignin

2.7.1. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)

DRIFT was used for chemical characterization of the separated lignin fractions. Spectra were collected with a Bruker Vertex 80v spectrometer (USA) for precipitated and dried lignin samples. For each sample, 40 scans were taken at a resolution of 2 cm⁻¹, and spectra were obtained in the 400–4000 cm⁻¹ range.

3. Results and discussion

3.1. Characteristics of DES-treated biomass

Five acidic and one alkaline DES treatments were used to delignify wheat straw, corn stalk, and rapeseed stem samples. The samples initially contained 19–24 wt-% lignin, 27–40 wt-% cellulose, and 11–18 wt-% hemicelluloses. The gravimetric yield of lignin from DES treatment varied from 1.0 wt-% to 9.5 wt-% for wheat, 0.8–8.5 wt-% for corn, and 0.8–11.8 wt-% for rapeseed stem (Fig. 2a–c). The results show that acidic Lac5–Ch resulted in the highest lignin yield among the different DESs with all biomasses, and the 16-h reaction at 100 °C was the optimum condition for lignin removal with Lac5–Ch (8.5 wt-% for wheat, 9.5 wt-% for corn, and 11.8 wt-% for rapeseed) and other acidic DES treatments. However, it was noticed that the Lac-Ch and Lac5-Ch DESs evaporated slightly during long treatment times at 100 °C. It is not unusual to see that the characteristics of HBDS affect notably the thermal stability of DESs and they decompose or volatilize first in the DES. (Chen et al., 2018; Harázná et al., 2019). Evaporation was not observed with other acids nor with glycerol. Despite, the evaporation the Lac DESs had the highest delignification efficiency. The lignin yield with the alkaline DES treatment was from 0.8 to 5.7 wt-% and was comparable to acidic DESs with wheat and rapeseed and lower with corn. However, the lignin content measured from solid fractions (Fig. 2d–f) was generally only slightly lower with Gly-K₂CO₃s, thus indicating similar delignification efficiency to that of Lac–Ch and Lac5–Ch. This result may be attributed to incomplete precipitation of lignin from alkaline DES, which is seen as a low lignin recovery.

The gravimetric yield of the cellulose-rich fraction varied from 44.9 wt-% to 70.1 wt-% for wheat, 32.2–53.6 wt-% for corn, and 35.9–57.8 wt-% for rapeseed stem. Both lactic acid DESs gave the lowest yield for cellulose-rich fractions for wheat (45.5 wt-% with Lac–Ch and 44.9 wt-% with Lac5–Ch) and corn (32.2 wt-% [Lac–Ch] and 33.3 wt-% [Lac5–Ch]) samples treated for 16 h at 100 °C, but for rapeseed stem the lowest yield was obtained with Gly–K₂CO₃ DES (35.9 wt-%) at the same conditions. The highest yield in the cellulose-rich fraction was obtained with Lev–Ch samples treated 24 h at 80 °C with all raw materials. On the other hand, the samples having the highest yield in the cellulose-rich fraction had the lowest cellulose content and highest content of lignin and others fraction, thus also showing the poorest delignification performance. The total yield of the cellulose-rich fraction and the lignin fraction varied from 35 to 70 wt-%, indicating that notable amounts of compounds like hemicelluloses, ash, and waxes dissolved in the DES solutions and did not precipitate out of the DES-ethanol/water solutions.

The compositional analyses of original samples and cellulose-rich solid fractions after 16-h reactions at 100 °C in DES are presented in Fig. 2d–f. The carbohydrates are presented as cellulose- and hemicellulose-derived glucans and hemicellulose-derived xylans. The ash, lignin, and other compounds (waxes and proteins) are also presented. The cellulose and hemicellulose contents varied from 62.0 wt-% to 72.3 wt-% for wheat, 53.2–70.7 wt-% for corn, and 50.3–70.7 wt-% for rapeseed stem, while residual lignin contents ranged from 12.1–19 wt-% for wheat, 16.3–26.8 wt-% for corn, and 16.6–22.7 wt-% for rapeseed stem. The highest cellulose contents were reached with acidic Lac–Ch and Lac5–Ch treatments (wheat and corn) as well as with alkaline Gly–K₂CO₃ reaction (rapeseed). In contrast with acidic DES treatments, the alkaline Gly–K₂CO₃ DES did not decrease the hemicellulose content of the biomasses. Overall, the higher solubility of hemicelluloses compared to cellulose is related to shorter chain length (100 ~ 200 with a degree of polymerization) of hemicelluloses compared to that of cellulose (10,000–14,000) (Xiao et al., 2001), different ring structures and hydroxyl configurations, which give the amorphous nature, and a more branched structure for hemicelluloses (Wyman et al., 2004). Therefore, they are generally more reactive than cellulose and can be selectively removed from cellulosic substrates. However, the degree of branching and substitution and composition of hemicelluloses can differ depending on their natural resources (Kishani et al., 2018). The mechanism of chemical hydrolysis is based on the catalytic cleavage of glycosidic bonds in polysaccharides, in which acid acts as a catalyst (Mäki-Arvela et al., 2011). The acid hydrolysis rate of hemicelluloses varies depending on their structure, and both random scission and selective scission mechanisms of the side chain have been reported (Mäki-Arvela et al., 2011). Previously, the solubility of pure lignin, cellulose, and hemicellulose was studied in choline chloride–lactic acid DES, and it was found that only lignin was selectively dissolved into the DES (Kumar et al., 2016). However, our results indicate that all the tested acidic treatments remove hemicellulose as well as lignin, and in the case of Glu–Ch and Malic–Ch DESs (Fig. 2d–f), more hemicelluloses were removed than lignin.

The ash content in the wheat and corn samples was clearly lower after alkaline Gly–K₂CO₃ treatment than with the acidic treatments (0.9–2.5 % vs. 4.5–7.8 %), indicating high solubility of inorganic compounds in alkaline DES. However, a higher content of inorganics was noted with the rapeseed. The ash in the corn and wheat consisted mainly of silicates (Adebisi et al., 2017; Kraszkiewicz et al., 2017; Li et al., 2018).
et al., 2017), but in the rapeseed stem the primary inorganics are calcium (CaO); potassium (K₂O), phosphorus (P₂O₅), and magnesium (MgO) oxides; and metals such as Fe, Mo, Mn, Cu, Zn, and Co (Kraszkiewicz et al., 2017; Paleckienė et al., 2012), which have a poor solubility in alkaline media. The remaining part of the solid fractions (others in the diagrams Fig. 2d–f) consists of waxes and proteins and was not analyzed further. Those compounds are more soluble in alkaline conditions than in acidic conditions. Thus, Gly–K₂CO₃ samples have a clearly lower fraction of these compounds than acidic ones, especially for the rapeseed sample.

### 3.2. Nanocelluloses from DES-treated biomasses

Solid fractions from DES treatments were further nanofibrillated using a microfluidizer to test their feasibility in nanocellulose production. All specimens were successfully disintegrated into viscous gels except those from rapeseed treated with Glu–Ch and Malic–Ch DESs for 24 h at 80 °C. Based on the compositional analysis (Fig. 2f), these samples also had the highest lignin content. In acidic DESs second carboxylic group in the HBD may lower the solubility of lignin (Soares et al., 2017), which explains the poor delignification of the lignocellulose structure more stiffer, affects the surface charge, and reduces water uptake and swelling (Lê et al., 2018). The lignin removal was promoted by the higher temperature during DES treatment (Fig. 2a–c); i.e., more efficient delignification was observed at 100 °C than at 80 °C, despite the longer treatment time. The same trend was also noted during the nanofibrillation; the samples from DES treatment at 100 °C for 16 h were nanofibrillated most easily without clogging of the microfluidizer, while the samples treated at 80 °C for 24 h were most difficult to disintegrate into homogenous nanocellulose suspensions because of clogging of the microfluidizer. However, harsh acidic conditions were observed to darken the samples, which can clearly be seen especially with rapeseed samples (Fig. 1). This darkening was probably because of the coating of the cellulose. Lignin may also degrade to acid-soluble form in acidic conditions and further depolymerize to smaller Mw products, which may condense or repolymerize into the insoluble residual lignin during long reactions (Mäki-Arvela et al., 2011). In addition, a high content of calcium ions, which are present especially in the rapeseed stem samples, increases the precipitation of lignin onto the fibers (Gellerstedt and Al-Dajani, 2003) and can cause a dark color in the acidic DES-treated cellulose-rich fractions.

Based on solid fraction analysis (highest cellulose content) and on visual evaluation of the quality of nanocellulose samples, the specimens from acidic Lac5-Ch and alkaline Gly–K₂CO₃ DES treatments were selected for further analysis. Rotational viscosity was used to indicate the homogeneity, dimensions, and aggregation of the samples, which are shown in Fig. 3. Low share rate viscosities are reported to correlate especially with the morphology of the cellulose particles (Besbes et al., 2011; Iotti et al., 2011), and thinner and longer nanofibrils possess higher viscosities in the given concentration (Lasseuguette et al., 2008). Acidic-DES samples treated at 100 °C for 16 h (Fig. 3) had the highest viscosities, even though viscosities varied significantly between the raw materials. The highest viscosity was obtained with corn, and the lowest, with the rapeseed sample. The differences in pH of DES treatments may affect the viscosities, since acidic treatments leave the samples in protonated form, which increases the viscosity of the nanocellulose suspension by decreasing the interfibrillar charge repulsions. The highest differences in viscosities with alkaline treatment are seen in the

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**Fig. 2.** The yield of solid and lignin fractions after different DES treatments for (a) wheat, (b) corn, and (c) rapeseed, and compositions of solid fractions of (d) wheat, (e) corn, and (f) rapeseed samples without treatment and after DES treatments at 100 °C for 16 h.
rapeseed stem samples, which also had largest differences in the yield of lignin and cellulose-rich fractions (Fig. 2c).

TEM images (Fig. 3) of nanofibrils from Glu–Ch and Lac–Ch treatments showed the typical elongated structure of nanofibrils and their continuous network. The average width of nanofibrils ranged from 3 to 12 nm for all raw materials. FESEM imaging (Fig. 3) confirmed that...
Fig. 4. X-ray diffractograms and the crystallinity indexes of cellulose-rich fractions after acidic (Lac5-Ch) and alkaline (Gly–K2CO3) DES treatments for (a) wheat, (b) corn, and (c) rapeseed samples.

Fig. 5. Tested visual appearance of nanopapers (left), tensile strength (top row) of (a) wheat, (b) corn, and (c) rapeseed nanopapers, and force-strain curves (bottom row) of the (d) wheat, (e) corn, and (f) rapeseed nanopapers prepared from the nanofibrillated samples after DES treatments of 16 h at 100 °C.

Table 2
Tensile strength, strain, Young’s modulus, and thickness of the nanopapers prepared from the samples after DES treatments of 16 h at 100 °C.

| Sample  | Tensile strength [MPa] | Strain [%] | Young’s modulus [GPa] | Thickness of the film [μm] |
|---------|------------------------|------------|-----------------------|---------------------------|
| Wheat   |                        |            |                       |                           |
| Glu-Ch  | 62 ± 6                 | 2.1 ± 0.5  | 4.4                   | 77.8                      |
| Gly-K2CO3| 132 ± 7               | 4.9 ± 0.5  | 5.8                   | 60.1                      |
| Lac-Ch  | 114 ± 9                | 4.8 ± 0.9  | 6.5                   | 64.3                      |
| Lac5-Ch | 132 ± 6                | 4.8 ± 0.5  | 6.6                   | 55.5                      |
| Lev-Ch  | 52 ± 4                 | 2.0 ± 0.4  | 3.8                   | 74.0                      |
| Malic-Ch| 57 ± 2                 | 2.9 ± 0.3  | 4.0                   | 71.9                      |
| Corn    |                        |            |                       |                           |
| Glu-Ch  | 50 ± 3                 | 1.6 ± 0.4  | 4.1                   | 60.3                      |
| Gly-K2CO3| 163 ± 11              | 4.9 ± 0.6  | 7.6                   | 89.1                      |
| Lac-Ch  | 99 ± 9                 | 4.8 ± 0.5  | 5.4                   | 71.4                      |
| Lac5-Ch | 95 ± 3                 | 3.6 ± 0.7  | 4.9                   | 75.3                      |
| Lev-Ch  | 68 ± 4                 | 2.3 ± 0.2  | 4.9                   | 77.4                      |
| Malic-Ch| 52 ± 4                 | 2.4 ± 0.3  | 3.3                   | 91.0                      |
| Rapseseed|                    |            |                       |                           |
| Glu-Ch  | 80 ± 6                 | 1.8 ± 0.3  | 6.0                   | 68.7                      |
| Gly-K2CO3| 161 ± 11              | 4.2 ± 0.7  | 7.5                   | 53.2                      |
| Lac-Ch  | 90 ± 5                 | 1.9 ± 0.1  | 5.9                   | 60.4                      |
| Lac5-Ch | 86 ± 4                 | 1.5 ± 0.1  | 6.2                   | 62.4                      |
| Lev-Ch  | 70 ± 6                 | 1.7 ± 0.2  | 5.2                   | 65.4                      |
| Malic-Ch| 57 ± 4                 | 1.2 ± 0.1  | 5.5                   | 81.7                      |

Table 3
Tensile strength, strain, Young’s modulus, and thickness of the nanopapers prepared from the samples after DES treatments of 8 h at 100 °C.

| Sample  | Tensile strength [MPa] | Strain [%] | Young’s modulus [GPa] | Thickness of the film [μm] |
|---------|------------------------|------------|-----------------------|---------------------------|
| Wheat   |                        |            |                       |                           |
| Glu-Ch  | 69 ± 2                 | 2.6 ± 0.3  | 4.6                   | 76.9                      |
| Gly-K2CO3| 117 ± 9               | 4.0 ± 0.5  | 6.1                   | 63.9                      |
| Lac-Ch  | 111 ± 8                | 4.2 ± 0.7  | 5.3                   | 63.1                      |
| Lac5-Ch | 127 ± 7                | 4.8 ± 0.6  | 5.5                   | 59.0                      |
| Lev-Ch  | 45 ± 3                 | 1.8 ± 0.2  | 3.7                   | 74.7                      |
| Malic-Ch| 35 ± 3                 | 1.4 ± 0.1  | 3.1                   | 87.0                      |
| Corn    |                        |            |                       |                           |
| Glu-Ch  | 56 ± 4                 | 1.8 ± 0.3  | 4.3                   | 81.6                      |
| Gly-K2CO3| 143 ± 12              | 3.7 ± 0.7  | 7.6                   | 65.9                      |
| Lac-Ch  | 92 ± 9                 | 3.6 ± 0.9  | 5.2                   | 73.5                      |
| Lac5-Ch | 95 ± 4                 | 3.3 ± 0.6  | 5.3                   | 71.5                      |
| Lev-Ch  | 65 ± 2                 | 2.0 ± 0.2  | 4.8                   | 75.9                      |
| Malic-Ch| 54 ± 8                 | 1.5 ± 0.3  | 4.9                   | 79.5                      |
| Rapseseed|                    |            |                       |                           |
| Glu-Ch  | 82 ± 5                 | 1.7 ± 0.1  | 6.4                   | 67.4                      |
| Gly-K2CO3| 160 ± 4               | 4.0 ± 0.3  | 8.3                   | 53.8                      |
| Lac-Ch  | 80 ± 6                 | 1.7 ± 0.2  | 5.5                   | 63.2                      |
| Lac5-Ch | 103 ± 6                | 1.7 ± 0.2  | 6.9                   | 58.1                      |
| Lev-Ch  | 71 ± 4                 | 1.6 ± 0.2  | 5.6                   | 60.5                      |
| Malic-Ch| 67 ± 6                 | 1.3 ± 0.2  | 6.4                   | 70.8                      |
Tensile strength, strain, Young’s modulus, and thickness of the nanopapers prepared from the samples after DES treatments of 24 h at 80 °C.

| Sample      | Tensile strength [MPa] | Strain [%] | Young’s modulus [GPa] | Thickness of the film [μm] |
|-------------|------------------------|------------|-----------------------|---------------------------|
| Wheat       |                        |            |                       |                           |
| Glu-Ch      | 55 ± 4                 | 2.2 ± 0.2  | 3.8 ± 0.3             | 5.2                       | 71.3                      |
| Gly-K₂CO₃   | 101 ± 7                | 2.7 ± 0.1  | 5.6 ± 0.2             | 4.4                       | 66.1                      |
| Lac-Ch      | 84 ± 4                 | 2.7 ± 0.2  | 6.2 ± 0.3             | 6.3                       | 71.3                      |
| Lac₅-Ch     | 75 ± 2                 | 2.7 ± 0.2  | 6.3 ± 0.3             | 6.3                       | 71.3                      |
| Lev-Ch      | 24 ± 4                 | 1.1 ± 0.2  | 2.4 ± 0.3             | 2.4                       | 89                        |
| Malic-Ch    | 39 ± 2                 | 1.9 ± 0.3  | 3.3 ± 0.3             | 3.3                       | 75.8                      |
| Corn        |                        |            |                       |                           |
| Gly-Ch      | 46 ± 5                 | 4.8 ± 0.2  | 7.7 ± 0.3             | 7.7                       | 92.5                      |
| Gly-K₂CO₃   | 146 ± 6                | 6.0 ± 0.4  | 7.7 ± 0.3             | 7.7                       | 64.3                      |
| Lac-Ch      | 71 ± 5                 | 5.3 ± 0.5  | 5.9 ± 0.3             | 5.9                       | 64.3                      |
| Lac₅-Ch     | 74 ± 6                 | 5.8 ± 0.3  | 6.9 ± 0.3             | 6.9                       | 73.9                      |
| Lev-Ch      | 46 ± 4                 | 4.0 ± 0.2  | 4.1 ± 0.3             | 4.1                       | 81.2                      |
| Malic-Ch    | 40 ± 6                 | 5.6 ± 0.2  | 3.8 ± 0.3             | 3.8                       | 90.7                      |
| Rapeseed    |                        |            |                       |                           |
| Gly-K₂CO₃   | 170 ± 17               | 4.2 ± 0.9  | 8.6 ± 0.3             | 8.6                       | 54.3                      |
| Lac-Ch      | 67 ± 7                 | 1.4 ± 0.2  | 3.5 ± 0.3             | 3.5                       | 62.0                      |
| Lac₅-Ch     | 72 ± 6                 | 1.4 ± 0.2  | 6.2 ± 0.3             | 6.2                       | 60.6                      |
| Lev-Ch      | 77 ± 6                 | 1.7 ± 0.2  | 5.1 ± 0.3             | 5.1                       | 61.0                      |

Flexible and opaque nanopapers (Fig. 5) were successfully prepared using a vacuum filtration method from all DES-treated nanofibers except those from rapeseed treated with Glu–Ch and Malic–Ch DESs for 24 h at 80 °C, which we were not able to nanofibrillate. Tensile strengths of all nanopapers and force-strain curves of nanopapers after DES treatment for 16 h at 100 °C are shown in Fig. 5. In Table 2 are listed the tensile strength, strain, Young’s modulus, and thickness of the prepared nanopapers for wheat, corn, and rapeseed stem samples after 8 h at 100 °C and in the Table 4 after 24 h at 80 °C. The highest strengths at break (132 MPa, 163 MPa, and 170 MPa for wheat, corn, and rapeseed stem, respectively), strain (4.9 %, 4.9 %, and 6.0 %, respectively), and Young’s modulus (6.1 GPa, 7.7 GPa, and 8.6 GPa, respectively) were obtained with the nanopapers prepared from alkaline DES-treated nanofibers for all biomasses, while acidic DES treatments showed notably lower values (132–24 MPa, 4.8–1.1 %, and 6.6–2.4 GPa for wheat; 99–39 MPa, 5.8–1.5 %, and 5.4–3.3 GPa for corn; and 102–57 MPa, 1.8–1.1 %, and 6.9–5.1 GPa for rapeseed stem; see Tables 2–4). Acidic treatments of wood chips in hemicellulose extraction prior to pulping have been previously reported to reduce pulp strength properties even with dilute acid conditions (0.3 % (v/v)) (Vena et al., 2015). For example, the tensile index of handsheets prepared from wood pretreated with diluted H₂SO₄ was reduced by about 15 % (Vena et al., 2015). However, with the wheat samples, differences in the strength of nanopapers between alkaline Gly–K₂CO₃ and acidic Lac–Ch and Lac₅-Ch samples were small (Fig. 5a and Table 2). The only exception is after a 24-h reaction at 80 °C (Table 4), in which case the tensile strength and strain are clearly higher with Gly–K₂CO₃ (101 MPa and 3.8 %) than with lactic acid samples (84–75 MPa and 2.7 %). For the wheat samples, the amount of waxes and proteins (others fraction) (Fig. 2d) was also small with acidic treatments compared to the corn and rapeseed samples (Fig. 2e and f). Presumably, the residual waxes reduced the interfibrillar adhesion and mechanical properties of nanofibers. It can also be seen from Fig. 5f that the strain of all acidic DES nanopapers is low in rapeseed samples whereas Lac–Ch and Lac₅-Ch resulted in high strain values with wheat and corn samples (Fig. 5d and e and Table 2). Those samples also had the highest cellulose content and lowest lignin content of all the samples. Thus, lignin can make the nanofibrills stiffer and result in more fragile nanopapers (Ma et al., 2018).

The strength properties of alkaline Gly–K₂CO₃ nanofibers, e.g., for the corn samples, were high (tensile strength 163 MPa and Young’s modulus 7.6 GPa) (Table 2) and remarkably higher than recently published results for corn nanopapers obtained from alkaline sodium hydroxide treatment, which also included very intense mechanical treatment of 30 passes with a high pressure homogenizer (tensile strength...
3.4. Lignin from DES treatments

Lignin was separated from all DES-treated wheat, corn, and rapeseed stem samples. Fig. 6 shows the visual appearance of Lac-Ch and Gly–K₂CO₃ lignins and DRIFT spectra of wheat and corn samples in different reaction conditions. The amounts of rapped seed lignin were too low to be analyzed. The color of the acidic-DES lignin was black-brown, and the lignin particles were quite small compared with the alkaline-DES lignin, which had a lighter brown color. All lignins show a broad band around 3400 cm⁻¹ attributed to the hydroxyl groups in phenolic and aliphatic structures and bands at 2930 cm⁻¹ and 2860 cm⁻¹ arising from CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains (Kang et al., 2012; Li et al., 2017b), and 1140 cm⁻¹ (C–O stretching in guaiacyl lignin) for Lac–Ch lignin are more visible than the Gly–K₂CO₃ lignin peaks for both wheat and corn. In addition, the peak at 1260–1280 cm⁻¹, which is characteristic for the guaiacyl unit ring (Kang et al., 2012), is broader in the Gly–K₂CO₃ lignin than in the Lac–Ch. Thus, there seem to be differences between the alkaline- and acidic-DES lignin. However, the spectral region below 1400 cm⁻¹ is difficult to analyze, since most bands have contributions from various vibration modes and are specific to the different monolignol units (Boeriu et al., 2004).

4. Conclusions

The performance of acidic lactic acid–choline chloride and alkaline K₂CO₃–glycerol DESs in delignification of wheat straw, corn stalk, and rapped seed was good, and the nanofibrillation of these delignified cellulose-rich fractions was possible without other pretreatments. The average width of prepared individual nanofibrils was 4–6 nm with raw materials. Both acidic lactic acid–choline chloride and alkaline K₂CO₃–glycerol nanocellulose samples had the highest viscosity (1360–555 Pa s) and crystallinity properties (54–38 %), but the nanocelluloses from acidic DES treatment had better tensile strength properties and Young’s modulus (170–132 MPa and 8.6–5.2 GPa) compared with nanocelluloses from acidic lactic acid–choline chloride DESs (132–67 MPa and 6.9–3.9 GPa). The separated lignin fractions also differed between acidic and alkaline DES treatments visually and according to the FTIR results.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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