# Use of green solvents as pre-treatment of dissolving pulp to decrease CS$_2$ consumption from viscose production

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## Abstract

Choline chloride-based deep eutectic solvents are widely used in biomass processing. In this work, four different green solvent mixtures were used as pre-treatment of acid sulphite dissolving pulp with the hypothesis of increasing the possibilities to produce viscose fibres and decreasing the use of the harmful and toxic carbon disulphide in the process. The experiments were performed at two different pulp to solvent mass ratios. Pulp quality parameters were also measured to determine the suitability of the pre-treatment: α-cellulose, viscosity, lignin and pentosan content. In addition, X-ray diffraction analysis of pulps at the best solid to liquid ratio was performed to obtain the influence of the crystallinity index. Best results were obtained with the use of lactic acid, with reactivity values close to 94 %, giving a reduction of CS$_2$ usage of 15.83 %. Furthermore, a linear relationship between the crystallinity index calculated by the XRD and reactivity with a regression factor of 0.87 was found.

*Keywords: Deep eutectic solvents, Reactivity, Dissolving Pulp, Crystallinity*

# Introduction

The growing concern about environmental issues has led researchers to find newer technologies to solve conventional problems. In this sense, the search of greener solvents to be used industrially has become of great importance (Zdanowicz et al. 2018). As a result, Abbott et al. (2003) proposed deep eutectic solvents (DES) as an alternative to traditional solvents. DES systems are a mixture of two or more components with a final melting point much lower than the individual components (Kumar et al. 2016) which makes it liquid at room temperature (Procentese and Rehmann 2018). These solvents are usually composed by a quaternary ammonium, phosphonium or sulfonium cation or a metal chloride (Smith et al. 2014), defined as Hydrogen Bond Acceptor (HBA) and a Hydrogen Bond Donor (HBD).

Depending on the components employed to form the solvent, DES can be classified in four types (Zdanowicz et al. 2018): (1) Organic salts and metal chlorides; (2) Organic salts and metal hydrates; (3) Organic salts and organic compounds (carboxylic acids, alcohols, or amides); and (4) Metal chlorides and organic compounds (amides, alcohols). These solvents have similar properties to Ionic Liquids (IL): low vapour pressure, chemical and thermal stability, non-flammability and can be tailored (Wilpiszewska and Spychaj 2011). However, DES mixtures exhibit some advantages when compared with IL, i.e. easier to prepare, cheaper and have higher biodegradability (Ling et al. 2020). These characteristics make DES to be used in a wide range of research areas: metal processing (Zhang et al. 2012; Smith et al. 2014), biotechnology and bioengineering (Mbous et al. 2017), gas separation (García et al. 2015) or biomass processing (Zdanowicz et al. 2018; Kalhor and Ghandi 2019) among others.

Regarding biomass processing, the use of DES has focused on lignocellulosic materials because of their ability to dissolve lignin with the almost negligible dissolution of cellulose (Francisco et al. 2012), making biomass suitable for further processing. However, lignin is not the only undesirable component in lignocellulosic materials. Hemicelluloses, in the form of pentosan, can hinder the processability of this kind of materials, in this sense, enzymatic treatment (Kaur et al. 2016) or alkali treatment (Kaur et al. 2017) can be used effectively. The application of DES to lignocellulosic biomass covers a wide range of steps during biomass processing: pre-treatment (Fang et al. 2017;

Tommasi et al. 2017; Shen et al. 2019), delignification, (Jablonský et al. 2015; Liu et al. 2017; Chen and Wan 2018), extraction (Huang et al. 2017; Cao et al. 2019; Deng et al. 2019) and reaction media (da Silva Lacerda et al. 2015; Sert et al. 2018; Lou et al. 2019). Researches have tested several DES in biomass: Using different HBD's (Gunny et al. 2015; Ling et al. 2020); different HBA's (Francisco et al. 2012; Abdulmalek et al. 2017) or even a different kind of DES (Biswas et al. 2006; Supeno et al. 2014). For the components of the DES used in this field, Choline Chloride (ChCl) has been extensively used as HBD, due to its availability and biodegradability (Gadilohar and Shankarling 2017). Carboxylic acids such as malic acid (MA), oxalic acid (OxA) and lactic acid (LA) and amides such as urea (Ur) can be used as HBA for treatment of lignocellulosic biomass (Tan et al. 2019).

Cellulose is the most abundant natural polymer on earth, and dissolving pulp is the primary source of high purity cellulose (Li et al. 2018). Dissolving pulp can be used to produce a wide variety of products such as cellulose acetates, cellulose nitrates, cellulose ethers, viscose fibres and lyocell fibres (Miao et al. 2014). Among the end-use products mentioned above, viscose production is the main consumer of dissolving pulp; in fact, 70 % of viscose was produced from dissolving pulp (Kumar and Christopher 2017). Carbon disulphide ($CS_2$) is used in the xanthation phase of the viscose process, to dissolve alkali cellulose formed in the mercerisation phase. This compound is toxic and environmentally harmful (Duan et al. 2015). Therefore, $CS_2$ consumption needs to be reduced as much as possible and as a result, mitigate the adverse effects that this reagent can produce on the process, either economically or environmentally (Li et al. 2018). Cellulose reactivity is the key parameter to improve for reducing the use of $CS_2$ within the viscose process. Therefore, it is crucial to make the viscose process more sustainable with the environment. Cellulose reactivity is defined as the ability of chemicals to dissolve cellulose, and it has a direct relationship with $CS_2$ consumption (the higher the reactivity, the lower the $CS_2$ needed). Such parameter can be determined by several methods such as Iodine sorption, NMR spectroscopy, viscose filterability and Fock's test (Arce et al. 2020).

Treatments of different nature can improve cellulose reactivity: (1) mechanically, breaking or removing the primary cell wall and shortening cellulose chains (Tian et al. 2014); (2) chemically, eliminating undesired components or hydrolysing cellulose chain

84    (Arnoul-Jarriault et al. 2015; Wang et al. 2018); (3) enzymatic processes, removing

85    hemicelluloses (pentosan content) and adjusting viscosity (Ibarra et al. 2010; Gehmayr et

86    al. 2011; Sango et al. 2018); (4) IL extraction, removing pentosan with nearly no effect

87    on cellulose (Li et al. 2012); (5) or using combinations of them (Yang et al. 2018). The

88    methods mentioned before, either use energy or reagents that increase the environmental

89    impacts of the pulping and the viscose process. For this reason, authors selected DES as

90    the best technique able to reduce the environmental impacts of the pulping and viscose

91    sectors. Due to the similarity between IL and DES, this work has the hypothesis that DES

92    can be used as pre-treatment for dissolving pulp to increase its reactivity. DES green

93    solvents have been successfully used to increase the hydrolysis of cellulose (Xia et al.

94    2014) or to improve the production of hydroxymethylfurfural (HMF) and furfural (da

95    Silva Lacerda et al. 2015). DES have also been used in pulp to observe the effect that this

96    treatment would have on it (Jablonsky et al. 2018). However, DES have never been used

97    as pre-treatment to increase pulp reactivity, reducing the $CS_2$ used in the viscose process.

98    Therefore, this work aims to assess the enhancement of reactivity of dissolving pulp

99    towards viscose and quantify the theoretical reduction of $CS_2$ usage, employing ChCl-

100   based DES mixtures. The properties α-cellulose content, pentosan content, lignin content

101   and intrinsic viscosity are also analysed to check that the resulting pulp meets the

102   requirements to be transformed into viscose. The reduction of the quantity of $CS_2$ used in

103   the viscose process, as a result of the reactivity increase, is also determined together with

104   the correlation between reactivity and cellulose crystallinity.

# MATERIALS AND METHODS

105

## DES preparation and pulp treatment

106

107   Dissolving pulp used in this work was provided by a pulp mill, Sniace S.A. located in

108   Northern Spain (Cantabria). This company produces dissolving pulp through the acid

109   sulphite cooking coupled with total chlorine-free (TCF) bleaching.

110   DES treatment of pulp was performed based on the methodology of Majová et al. (2017).

111   Initially, the pulp was soaked and stirred in water to obtain a consistency of 4 %. The

112   mole ratio for each DES system was 1:9 ChCl:LA, 1:1 ChCl:MA, 1:3 ChCl:OxA and 1:2

113   ChCl:Ur as recommended in the bibliography (Jablonský et al. 2015; Pan et al. 2017).

These DES are widely used with lignocellulosic materials because of their ability to delignify (Zdanowicz et al. 2018). Reactants were weighed and mixed. The mixture was heated at 80 ℃ and magnetically stirred, until a clear liquid was formed. Finally, pulp and DES are put together in a flask and placed in a water bath at 60℃ for one hour. When the treatment finishes, the pulp is washed with tap water, until the pH of washing wastewater is around 7.

Reactivity and intrinsic viscosity analyses were performed in triplicates; error bars were calculated as standard deviation. Pentosan, α-cellulose and kappa number error bars were calculated in duplicates, because of the scarce in pulp quantity and results were confirmed with quality pulp parameters from the industry. These analyses are based on the methodology used by a previous work of the authors (Llano et al. 2018). Table 1 shows the characteristics of the untreated dissolving pulp.

**Table 1** Untreated pulp quality values

| Sample | Pentosan (%) | Fock's reactivity (%) | α-cellulose (%) | Viscosity (mL/g) | Kappa |
|---|---|---|---|---|---|
| **Raw pulp** | 2.89 ± 0.169 | 80.58 ± 2.437 | 91.05±0.045 | 465.90±14.46 | 1.04±0.179 |

## Fock reactivity

Reactivity of pulp samples was measured by the method described by Tian et al. (2013) which is based on Fock (1959). First, 0.5 g of pulp calculated as oven-dried (o.d.) was weighed and put into a 250 mL Erlenmeyer flask. Then, 50 mL of 9 % (w/w) NaOH was added and stirred for 10 min at 19 ℃. 1.3 mL of $CS_2$ was added, sealed with plastic parafilm and stirred at 250 rpm for 3 h at 19 ℃; this is the xanthation phase in which cellulose-xanthate is formed. When reaction time finishes, water was added until a total mass of 100 g, the solution was then agitated and centrifuged at 5000 rpm for 15 min. Afterwards, 10 mL of the supernatant was poured in a 100 mL flask, and 3 mL of sulphuric acid 20% (w/w) was added to regenerate the dissolved cellulose. The flasks were left in a fume hood for 15 h-20 h for the $CS_2$ excess to be removed.

Dissolved cellulose was measured by oxidation with $K_2Cr_2O_7$. Firstly, 20 mL of 68 % (w/w) sulphuric acid was added and stirred at 250 rpm for 1 h. When the stirring time was set, 10 mL of 1/6 M $K_2Cr_2O_7$ was added, and the mixture was reflux-boiled for 1 h.

143    Finally, the flasks were left to cool at room temperature and then diluted to a total volume

144    of 100 mL. 40 mL of the solution was pipetted into a 250 mL Erlenmeyer flask and 5 mL

145    of 10 % (w/w) KI was added and titrated with 0.1 N $Na_2S_2O_3$ using starch as an indicator.

146    The volume of $Na_2S_2O_3$ was used for the calculation of the dissolved cellulose (DC) using

147    equation 1:

148

$$DC(\%) = \frac{\left[v_1 \cdot c_1 - \left(v_2 \cdot c_2 \cdot \frac{100}{40}\right) \cdot \frac{1}{6}\right] \cdot M \cdot \frac{1}{4} \cdot \frac{100}{10.4}}{m} \cdot 100 \quad (1)$$

149    Where M is the molecular weight of a glucose unit, m is the o.d. weight of the pulp sample

150    (g), $v_1$ and $c_1$ are the volume and the concentration of $K_2Cr_2O_7$, respectively. $v_2$ and $c_2$ are

151    the volume and the concentration of $Na_2S_2O_3$, respectively.

## Pentosans

153    The moisture content of the pulp was measured, and 1.6 g of pulp was weighed, and 100

154    mL of NaOH 5% (w/w) was added. Then, it was stirred for 3 min and left in a water bath

155    for 1 hour, the suspension was filtered, and 15 mL of the filtrate was added to a 250 mL

156    Erlenmeyer flask and mixed with 10 mL of $K_2Cr_2O_7$ 1/6 M and 35 mL of commercial

157    $H_2SO_4$. It was left to cool for 15 min, and 50 mL of distilled was were added. The solution

158    was titrated with 0.1 N $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin as an indicator.

## Intrinsic viscosity

160    Intrinsic viscosity was determined by the standard ISO 5351(2010). 0.25 g. oven-dried

161    pulp was dissolved in cupriethylendiamine solution for half an hour. After this, the sample

162    was left in a water bath at 25 ºC for 15 minutes and passed through Cannon-Fenske 150

163    viscometer at 25 ºC.

## α-cellulose

165    α-cellulose was determined according to TAPPI T203 cm-99 (1999). Oven-dried pulp

166    samples were weighed to an equal of 1.6±0.1 g. Pulp was consecutively extracted with

167    17.5 % NaOH solutions at 25±0.2 ºC for a total extraction time of 60±5 min. Then, pulp

168    samples were stirred and filtered. 25 mL of the filtrate were taken and mixed with 10 mL

169    of 0.5 N $K_2Cr_2O_7$ and 50 mL of 96 % $H_2SO_4$. After 15 minutes, samples were cooled by

170    adding 50 mL of water and titrated with 0.1 N $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin

171    indicator.

## Kappa

173    Kappa is an index that estimates the amount of residual lignin and hexenuronic acid by

174    measuring the oxidant demand of the pulp. TAPPI UM 246 (1991) method was

175    implemented to obtain the micro kappa number of high-purity pulp from the final stages

176    of the bleaching process. Micro kappa is used in this work because lignin content at this

177    stage of the production of dissolving pulp is too low, and using traditional kappa method

178    may lead to unprecise values.

## CS$_2$ consumption calculation

180    $CS_2$ consumption was calculated using Fock reactivity, α-cellulose content and the

181    stoichiometric value required for the xanthation phase which is 23.5 % (expressed in g

182    $CS_2$ per 100 g of cellulose) (Arce et al., 2020; Gondhalekar et al., 2019a). Considering

183    Fock's reactivity as a reaction yield of xanthation, and the α-cellulose content of the pulp,

184    the theoretical quantity of fibres (TF) is obtained using equation 2. $CS_2$ consumption is

185    calculated using the stoichiometric value of $CS_2$ and α-cellulose content (equation 3).

186

187    $$\text{TF}(\%)=\frac{\text{α-cellulose }(\%) \cdot \text{Reactivity}(\%)}{100} \quad (2)$$

188    $$\text{CS}_2\text{usage}(\%)=\frac{\text{α-cellulose}(\%) \cdot 23.5}{100} \quad (3)$$

189

190    The $CS_2$ usage needs to be calculated not only to consider the reactivity of the sample but

191    also to assess the ratio of consumption per fibre (RCF), as shown in equation 4. The final

192    reduction of $CS_2$ usage was calculated using as reference the RCF from the inlet pulp.

193

194    $$\text{RCF} = \frac{\text{CS}_2\text{usage}(\%)}{\text{TF}(\%)} \quad (4)$$

195

### X-ray diffraction and crystallinity index

Characterisation of the untreated pulp and DES-treated pulps at 1/20 S/L ratio was carried out by powder-Ray diffraction (XRD); XRD studies were performed in air atmosphere on a Bruker D8 Advance diffractometer, using Cu Kα radiation and a LynxEye detector. Diffraction patterns were collected with an angular 2θ range between 10° and 70° with a 0.03° step size and measurement time of 3 s per step, and a graphite monochromator.

The XRD spectra were used to calculate de crystallinity index (CrI) using equation 5 proposed by Segal (Segal et al. 1959).

$$CrI(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \cdot 100 \quad (5)$$

Where $I_{002}$ is the intensity of the crystalline plane (200) at around 22° and $I_{am}$ is the intensity of the amorphous cellulose at 18°.

# Results

### Effect of DES pre-treatment on pulp quality parameters

In this work, the pre-treatment of dissolving pulp with DES to increase reactivity has been assessed. Four DES were tested: ChCl:MA, ChCl:LA, ChCl:OxA and ChCl:Ur at two different S/L ratio, 1/5 and 1/20. Intrinsic viscosity, lignin content (micro-kappa), pentosan content and reactivity of the pulp were analysed to evaluate the effects of the pre-treatment α-cellulose content. The parameters α-cellulose and intrinsic viscosity are shown in figure 1, with both solid to liquid ratios.
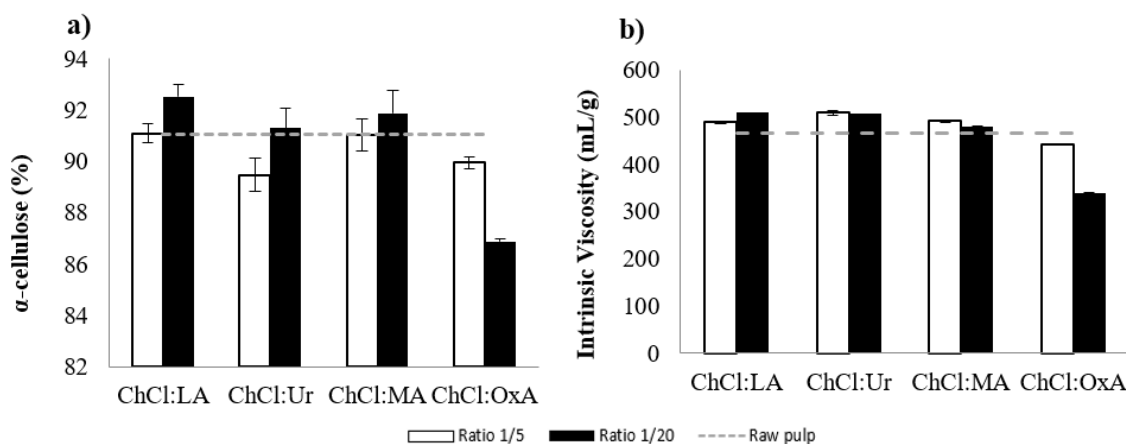
Figure 1 Evolution of a) α-cellulose content and b) intrinsic viscosity after DES treatment

At 1/20 solid to liquid ratio, cellulose content increases slightly when the system is formed by ChCl:LA (1.65 %), ChCl:MA (0.29 %) and ChCl:Ur (0.94 %), showing that the solubility of cellulose in the DES used in this work is almost negligible as stated by Kumar et al. (2016). It should be noted that the increase in cellulose does not mean that it is a product of a chemical reaction; it means that other compounds are eliminated; thus, cellulose content is concentrated.

Viscosity also increases when using the same DES systems, as long fibres of cellulose are released. Higher viscosity values are obtained when the ChCl:LA and ChCL:Ur systems are used, reaching values of 509.25 and 507 mL/g respectively. The system ChCL:MA nearly did not affect viscosity (479.61 mL/g concerning 465.9 mL/g in the raw pulp). However, using the ChCl:OxA DES mixture both α-cellulose content (86.86 %) and viscosity (338.70 mL/g) decrease. These results are in accordance with Škulcová et al. (2016) and Zhang et al. (2020). The later studied the dissolution of cellulose when using many DES systems. It was found that ChCl:OxA lead to the highest dissolution of cellulose, up to 2.5 % of cellulose was dissolved in OxA. In this study the dissolution of cellulose was 4.57 %; however, the system in this study was formed by 1/3 ChCl:OxA and Zhang et al. (2020) used 1/2 ChCl:OxA, therefore it is possible that increasing OxA in the mixture, might lead to higher cellulose dissolution.

Regarding the S/L ratio, also affects the dissolution of OxA significantly, since increasing the quantity of DES results in the higher dissolution of cellulose. The decrease in cellulose, significantly affects viscose, since α-cellulose includes high molecular weight chains. This effect is probably due to the H-bonds formed when using this system. At 1/5

242 solid to liquid ratio, cellulose content remains almost constant for all the systems used

243 with values ranging between 91.09 % for ChCl:LA and 89.46 % for ChCl:Ur. Therefore,

244 using a lower S/L ratio softens the effect that DES has on the pulp, in terms of α-cellulose

245 content.

246 Regarding viscosity changes, the trend is very similar to that shown for a 1/20 ratio. The

247 highest viscosity increase was obtained with ChCl:Ur and the system ChCl:OxA gave the

248 lowest viscosity as well; therefore this system harms pulp viscosity, making it unsuitable

249 for pulp pre-treatment for viscose purposes. Figure 2 shows the influence of DES pre-

250 treatment on lignin content (kappa) and pentosan content.

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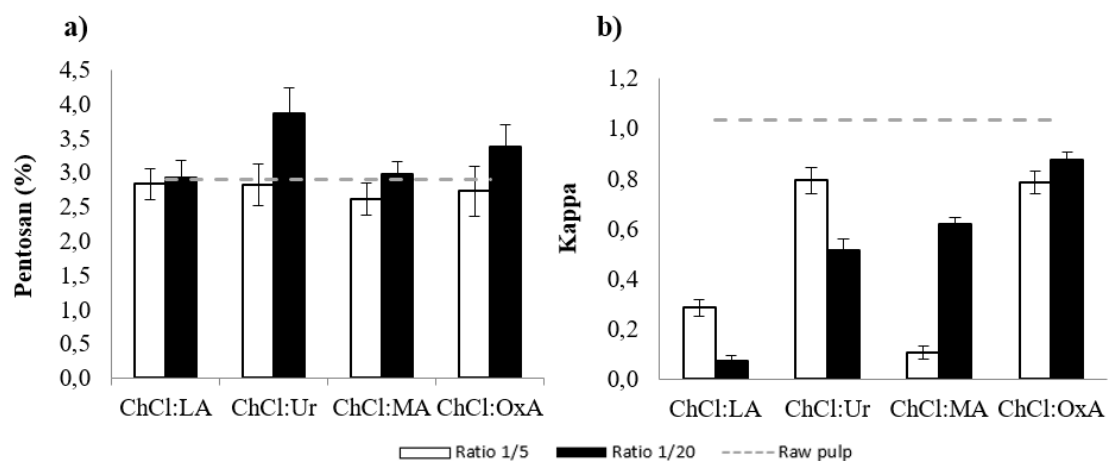


253 Figure 2 Evolution of a) pentosan content and b) kappa number after DES treatment

254

255 As can be seen from figure 2.b lignin content decreases for all the DES systems and ratios

256 tested. When a 1/20 ratio is used, the higher lignin reduction is achieved with ChCl:LA,

257 reducing kappa number until 0.07 (91.83 % reduction). On the other hand, the lowest

258 lignin reduction is obtained using ChCl:OxA with a final kappa value of 0.87 (3.71 %

259 reduction). Recent studies obtained the highest delignification with ChCl:OxA showing

260 a kappa reduction of 38.7 % (Majová et al. 2017). However, initial lignin content had a

261 strong influence on delignification, the lower the initial lignin, the lower the

262 delignification. In fact, Majová et al. (2017) had a 0.8 % kappa reduction when initial

263 kappa was 11.8. This trend is also shown in this work, with an initial kappa value of 1.16,

264 the lignin reduction was 32.5 %. Nevertheless, initial kappa of 0.91 results in a 3.71 %

265 lignin reduction. This trend is the same when using ChCl:MA, achieving up to 90.9 %

266　lignin elimination when initial lignin content was higher. Taking into account the fact that

267　the raw material of this work is dissolving pulp, ChCl:OxA is not recommended because

268　it gives low delignifying properties, a reduction of α-cellulose and a decrease of viscosity

269　in relation to the raw pulp. Zhang et al. (2016) used ChCl:LA, ChCl:OxA and ChCl:MA

270　to increase the saccharification rate of corncob, achieving 86.1 %, 98.5 % and 22.4 % of

271　lignin reduction, respectively. Procentese et al. (2015) employed ChCl:Ur in agricultural

272　biomass giving total lignin reduction of 7.1 %. In this work, the reduction of lignin when

273　using ChCl:Ur was in the range of 31.75 % and 43.17 % when the S/L ratio was 1/5 and

274　1/20, respectively.

275　Most of the studies focus on delignification of untreated biomass residues with higher

276　lignin content than high-cellulose dissolving pulps such as rice residues (Kandanelli et al.

277　2018), corn stover (Xu et al. 2016) or potato peels (Procentese et al. 2018). Based on

278　results obtained in this study, and comparing with the literature working with oxalic-

279　based DES mixtures, it can be concluded that ChCl:OxA is more effective when used

280　with high-lignin content samples than with dissolving pulps.

281　Pentosan content in the pulp, showed in figure 2.a, increases when a higher ratio is used.

282　The highest increase is produced when using ChCl:Ur at a 1/20 S/L ratio, up to 3.9 %. In

283　the bibliography studied, Zhao et al. (2018) achieved a 6 % xylan removal at a 1/5 S/L

284　ratio whereas Tan et al. (2019) obtained 20% xylan removal when using ChCl:Ur at 1/10

285　S/L ratio in the same study the authors reached a 100 % xylan removal with ChCl:LA at

286　1/10. As happened with lignin content, pentosan content seems to be affected by the initial

287　content. The studies mentioned before use wheat straw (21.8 % xylan content) and oil

288　palm empty fruit bunch respectively, which have a higher amount of pentosan content

289　than dissolving pulp. Therefore, pentosan elimination reduces as the initial pentosan

290　content decreases. The evolution of pentosan content is not linear, since increasing the

291　quantity of DES in the system, does not always translate on higher pentosan elimination.

292　Morais et al. (2018) studied the effect solubilisation of xylans, similar to pentosan, using

293　DES, specifically ChCl:Ur, at different ratios and concentrations, and found out that

294　increasing DES quantity in the system does not lead to the same increase on xylan

295　dissolution, the maximum extraction was obtained at 50 % DES/water concentration

296　whereas increasing DES content to a 75 %, xylan extraction did not improve. From table

297　2, reducing DES quantity leads to a reduction in pentosan. Morais et al. (2018), employed

298 temperatures from 70 to 90 ºC, thus reducing the viscosity of DES. In this work, the

299 temperature was kept at 60 ºC; therefore, viscosity is higher. This fact might explain why

300 1/5 S/L ratio can extract more pentosan than 1/20 S/L ratio.

301 It should be noted that the raw material used in this work, has already been through several

302 processes (cooking and bleaching) which makes pulp more accessible to reactants than

303 the untreated material, by increasing the porosity and thus, the specific surface area (Li et

304 al. 2018).

305 The selectivity of the DES treatment towards delignification can be seen comparing

306 Figures 1.a and 2.b. While α-cellulose content remained constant or even increased, lignin

307 content decreased for all the DES employed. Alvarez-Vasco et al. (2016) explained this

308 effect by the ability of DES to cleave ether bonds present in lignin. They also observed

309 no carbohydrates dissolved in the DES. Tang et al. (2017) showed that DES systems

310 exhibit strong interactions with lignin; in fact, some of the DES precipitated with the

311 lignin extracted. Therefore, the results showed in this work, regarding lignin and cellulose

312 content, agree with the bibliography studied.

313 Table 2 shows the yields obtained when compared with the raw pulp; negatives values

314 imply the property decreased.

315

316
**Table 2** Yields, in %, obtained referred to the raw pulp

| | α-cellulose | | Intrinsic Viscosity | | Pentosan | | Kappa | |
|---|---|---|---|---|---|---|---|---|
| **S/L ratio** | 1/20 | 1/5 | 1/20 | 1/5 | 1/20 | 1/5 | 1/20 | 1/5 |
| **ChCl:LA** | 1.65 | 0.01 | 6.95 | 7.17 | 5.55 | -6.08 | -91.83 | -75.47 |
| **ChCl:Ur** | 0.29 | -1.78 | 6.47 | 11.63 | 38.99 | -6.28 | -43.17 | -31.75 |
| **ChCl:MA** | 0.94 | -0.08 | 0.72 | 7.81 | 7.42 | -13.56 | -31.78 | -90.87 |
| **ChCl:OxA** | -4.57 | -1.25 | -28.87 | -3.14 | 21.66 | -9.38 | -3.71 | -32.45 |

317

318 From table 2, some conclusions can be drawn. Regarding α-cellulose content, some DES

319 lead to a low quantity (DES:Ur and DES:OxA), undesirable for viscose purposes. The

320 reference values for pulp quality were obtained from the standard FZ/T 51001-2009.

321 Regarding pentosan content, even though it increases for some systems, pentosan content

322 never reaches 4 %, which is the maximum value that the standard considers. Kappa is

323 always below 1 %, and viscosity barely changes, except for DES:OxA, which leads to a

324    28.87 % viscosity reduction and a 4.57 % α-cellulose reduction. These results make

325    DES:OxA unsuitable to be used as pre-treatment for viscose purposes.

326    Figure 3 represents the changes in reactivity with each DES and at each S/L ratio. Effects

327    of DES mixtures over this parameter have never been studied before and is crucial for

328    improving the viscose process and decrease the use of non-environmentally friendly

329    reagents, i.e. $CS_2$ and NaOH. Error bars have been added in the figure. These errors are

330    based on standard deviation and are lower than 10 for every analysis.
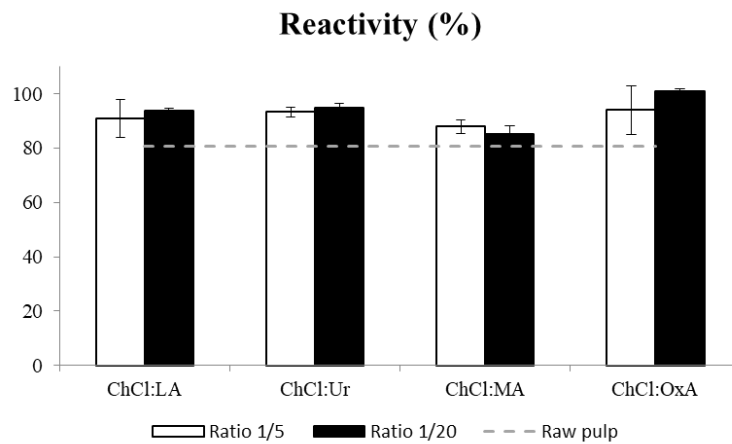
**Reactivity (%)**



331

332    Figure 3 Evolution of reactivity after DES treatment

333

334    Reactivity increases for all the DES employed. The best results were obtained using an

335    S/L ratio of 1/20, except for ChCl:MA. The highest increase of reactivity was produced

336    using ChCl:OxA at a 1/20 ratio, however, as stated before, this DES will not be

337    considered as the best, because pulp after the treatment does not have enough quality to

338    be considered suitable for viscose purposes. Tian et al. (2020), stated that the hydrogen

339    bonding abilities of DES could swell cellulose and as a result, increase reactivity, which

340    agrees with this work. No literature has been found about the use of DES to increase

341    reactivity. This paper is the first research analysing the effect of DES over cellulose

342    reactivity. Previous works have used different lignocellulosic materials to increase their

343    accessibility to chemicals, i.e. several authors used DES for glucose release from cellulose

344    (Nor et al. 2016; Xu et al. 2016; Xing et al. 2018). This behaviour can be related to

345    reactivity.

346 Nevertheless, such behaviour had not been determined. Regarding reactivity towards
347 viscose, several authors have used different methods to upgrade cellulose pulp, recently.
348 Duan et al. (2019) used mechanical and chemical treatments simultaneously to increase
349 reactivity up to 83.5 % while reducing viscosity to 411 mL/g. Zhou et al. (2019)
350 performed an ultrasonic pre-treatment to increase Fock's reactivity by breaking H-bonds
351 through cavitation. This treatment leads to a reactivity value of 73.2 % with nearly no
352 changes on viscosity. Similar effects occurred in this study, since DES barely changed
353 viscosity, except for ChCl:OxA. Sango et al. (2018) used an enzymatic treatment and
354 obtained a resulting pulp with a Fock's reactivity of 77.4 % with a small decrease in
355 viscosity. As an alternative, Arce et al. (2020) studied the possibility of increasing Fock's
356 reactivity through bleaching, instead of using pre-treatments. As a result, bleaching
357 operating conditions were adjusted, and Fock's reactivity was improved to 95.3 % with a
358 viscosity of 448 mL/g. In this study, DES pre-treatment was proved to be an exciting
359 alternative, since Fock's reactivity was increased up to 93.7 % when using ChCl:LA with
360 minor changes on viscosity.

361 **XRD spectra and effect on crystallinity index**

362 Since the best results were obtained when using a 1/20 S/L ratio, XRD of the resulting
363 and untreated pulps were performed to explain this modification in cellulose reactivity.
364 Figure 4 shows the XRD for treated and untreated pulp using 1/20 pulp to DES ratio.
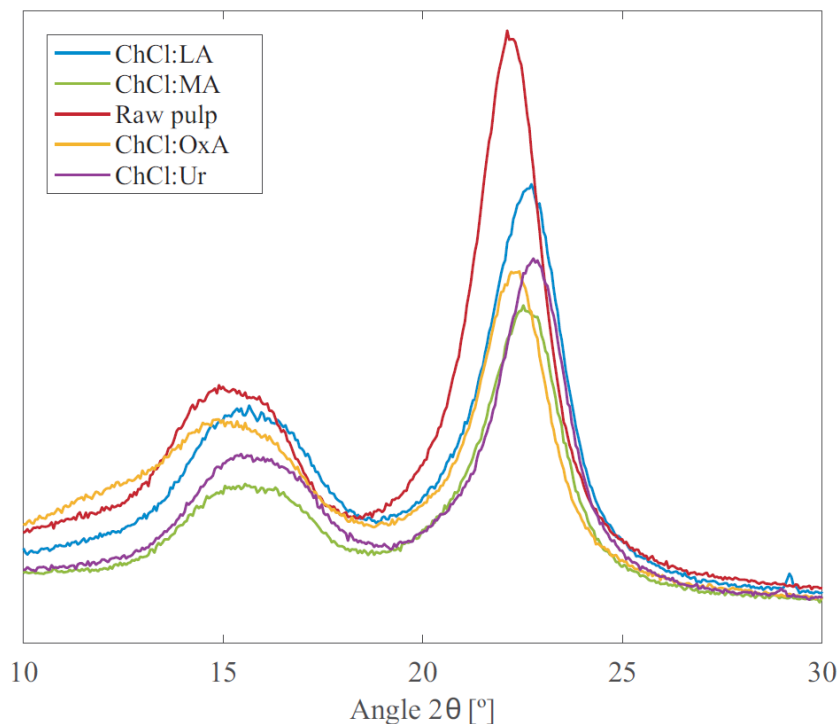
365



366    Figure 4 XRD spectra of pulp before and after DES treatment

367

368    XRD spectra show the typical shape associated to cellulose I, with a broad peak at $2\theta$

369    between 12° and 18° and a maximum at around 22° (Li et al. 2012), which correspond to

370    the planes $\bar{1}10$, 110 and 200 (Sirviö et al. 2015). After DES treatment, the structure of

371    cellulose remains intact, and the intensity of both peaks is reduced after the treatment. No

372    cellulose II is formed because there are no peaks at 20º and 22º, which are characteristic

373    of cellulose II (Hori and Wada 2006). To assess the influence of the intensity reduction,

374    a crystallinity index (CrI) for each pulp was calculated following the Segal method. This

375    method was chosen because it gave results easily comparable with other samples (Segal

376    et al. 1959; Park et al. 2010). Table 3 shows the results obtained.

377

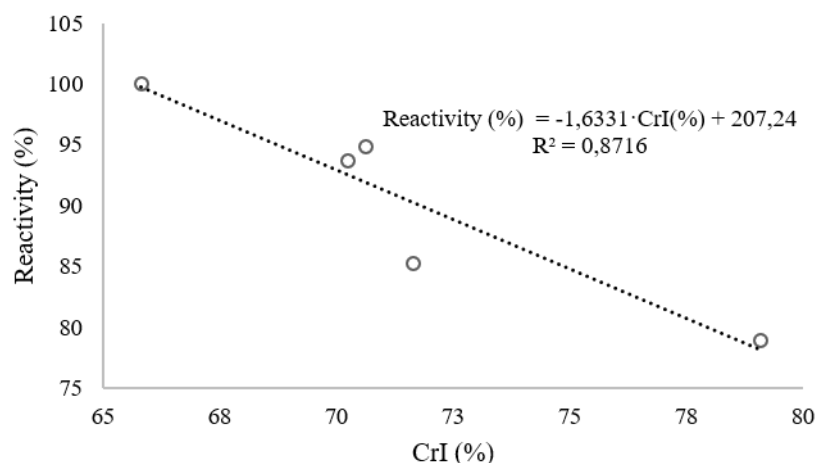378    **Table 3** Crystallinity indexes for untreated and DES-treated pulps

|           | Raw pulp | ChCl:MA | ChCl:LA | ChCl:OxA | ChCl:Ur |
|-----------|----------|---------|---------|----------|---------|
| **CrI (%)** | 79.09 | 71.63 | 70.23 | 65.8 | 70.63 |

379

380   The CrI of the pulps were calculated using equation 5. As can be seen from table 3, CrI
381   of pulp decreases after treatment with DES, making pulps more accessible for subsequent
382   reagent or enzymatic attacks and therefore more reactive. The highest decrease in
383   crystallinity is obtained with ChCl:Ox. Interestingly, the treatment with ChCl:Ox also
384   resulted in the lowest viscosity. This decrease was produced by the diminution of the
385   amorphous and crystalline regions, as proposed by Kumar et al. (2016), who found a
386   decrease in the CrI of rice straw when treated by ChCl:LA system. Gondhalekar et al.
387   (2019a), proposed that the reduction of crystallinity is caused by the weakening of the
388   hydrogen bonding (Gondhalekar et al. 2019a). Procentese et al. (2015) found a slight
389   decrease, as well, in the crystallinity index of corncob when treated with ChCl:Urea
390   system (Procentese et al. 2015). Additionally, a linear relationship between CrI and
391   reactivity was found as represented in figure 5. Looking at figure 5, for reactivity values
392   ranging between 75 and 100 %, the higher the crystallinity, the lower the reactivity.

393



The plot shows Reactivity (%) versus CrI (%) with the fitted line:
$$\text{Reactivity (\%)} = -1{,}6331 \cdot \text{CrI(\%)} + 207{,}24$$
$$R^2 = 0{,}8716$$

394

395   **Figure 5** Relationship between reactivity and CrI

396

## CS$_2$ consumption

398   Carbon disulphide is a critical compound in the manufacture of viscose fibre and
399   environmental wise, one of the most concerning. CS$_2$ consumption was calculated, as
400   stated by Arce et al. (2020). This calculation considers the α-cellulose content and Fock's
401   reactivity, to measure the theoretical quantity of fibres, and the stoichiometric quantity of
402   CS$_2$, used in the xanthation phase to calculate the quantity used of this compound,

described by Gondhalekar et al. (2019b). Finally, a ratio between the $CS_2$ usage and the theoretical fibres was obtained. The reduction was assessed using the untreated pulp (raw pulp) as reference. Results are shown in table 4. DES treatment reduces the usage of $CS_2$ for every system.

**Table 4** $CS_2$ consumption after DES treatment at a ratio of 1/20

| Treatment | α-cellulose | Fock's reactivity (%) | $CS_2$ (%) | TF (%) | RCF | $CS_2$ reduction (%) |
|-----------|-------------|------------------------|-----------|--------|-----|----------------------|
| **Raw pulp** | 91.02 | 78.86 | 21.4 | 71.8 | 0.30 | - |
| **ChCl:LA** | 92.52 | 93.70 | 21.7 | 86.7 | 0.25 | 15.83 |
| **ChCl:Ur** | 91.28 | 94.81 | 21.5 | 86.5 | 0.25 | 16.82 |
| **ChCl:MA** | 91.88 | 85.18 | 21.6 | 78.3 | 0.28 | 7.416 |
| **ChCl:OxA** | 86.86 | 100.00 | 20.4 | 86.9 | 0.24 | 21.14 |

The DES that gave the highest reduction of $CS_2$ usage was ChCl:OxA, even though α-content was the lowest, meaning that reactivity has a more substantial influence on $CS_2$ than α-cellulose content.

Arce et al. (2020), obtained lower reductions, with a maximum reduction of 13.74 %, modifying the operating conditions of the bleaching stage of dissolving pulp. So, DES pre-treatment can be an excellent alternative to increase the reactivity of dissolving pulp and decrease the $CS_2$ in the process of viscose fibre manufacturing.

ChCl:LA at a 1/20 S/L ratio was considered as the best pre-treatment among the experiments performed. The authors would like to remark that the best DES treatment depends significantly on the objective of the research, i.e. Zhang et al. (2016) found that ChCl:OxA was the best for butanol fermentation and saccharification Kumar et al. (2016) chose ChCl:Glycerol. Regarding lignin elimination and mechanical properties of pulp, Škulcová et al. (2016) found ChCl:MA as the best, whereas Xu et al. (2016) selected ChCl:Formic acid as the best for lignin elimination and Abdulmalek et al. (2017) determined that Ethylamonium ethylene glycol as the best for both lignin and hemicellulose removal. Even though reactivity is not the highest obtained with ChCl:LA, the results obtained using this configuration are following the pulp quality standards of FZ/T 51001-2009 for viscose purposes. It should be noted that the decrease in crystallinity

428    can affect not only to $CS_2$ consumption but also to NaOH consumption, since accessibility

429    increases when crystallinity decreases (Gondhalekar et al., 2019b).

## Conclusions

431    The use of DES at two different solid/liquid ratios as a pre-treatment of dissolving pulp

432    to increase its reactivity together with other pulp parameters was assessed in this work.

433    As a result, it was concluded that DES used in this research, increase the reactivity of

434    pulp and reduce crystallisation index. Additionally, a relationship between reactivity and

435    this index was obtained. The highest increase of reactivity was obtained with ChCl:OxA,

436    however, other quality parameters of the pulp were not suitable for viscose purposes.

437    Lactic acid with choline chloride at a 1/20 ratio is recommended in this work. At these

438    conditions, reactivity increased up to 93.70 %, reducing the $CS_2$ usage by 15.83 %.

439    Treated pulp had the following characteristics: 92.50 % of α-cellulose, a kappa number

440    of 0.07, an intrinsic viscosity in mL/g equal to 509.25, pentosan content of 2.93 %, with

441    a crystallinity index of 70.20 %.

442    As future work and with the knowledge acquired from this research, an optimisation of

443    the pre-treatment will be performed to find the most suitable operating conditions to

444    obtain the best quality for the pulp. Furthermore, the use of DES pre-treatment on

445    different parts of the bleaching process will also be considered.

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## Conflict of interest

450    The authors declare no conflicts of interest.

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