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Comparison of Soda, Kraft, and DES Pulp Properties of European Black Poplar

Usporedba svojstava natronske, kraft i DES celuloze od drva europske crne topole

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ABSTRACT • Kraft pulping as the dominant pulping method contributes to several environmental problems. To overcome these problems, environmentally friendly pulping methods have been investigated. In the last years, deep eutectic solvents (DESs) have been identified as up-and-coming reagents in the lignocellulosic material processing and they are characterized as environmentally friendly. This study investigated the use of DES in pulp production from European black poplar chips. The DES mixture was prepared from choline chloride (ChCl) and ethylene glycol (EG). In addition, traditional soda and kraft pulping methods were carried out with poplar chips for comparison with the DES pulps. It was found that pulp production from poplar chips using DES was comparable to the soda and kraft pulps in terms of pulp yield, pulp viscosity, and opacity. The DES pulps easily reached target pulp freeness levels. However, the strength properties and brightness of the DES pulps were lower than those of the soda and kraft pulps. The strength properties of DES pulps can be improved with paper strength enhancers such as starch and micro or nanofibrillated cellulose. Also, the utilization of DES in pulp production may have an important role in cleaner production and it represents a greener alternative to traditional pulp production methods.

KEYWORDS: DES; European black poplar; green chemistry; cleaner production; pulp properties

SAŽETAK • Celuloza se najčešće proizvodi kraft postupkom koji je povezan s nekoliko ekoloških problema. Kako bi se ti problemi prevladali, istražene su ekološki prihvatljive metode proizvodnje celuloze. Posljednjih su godina duboka eutektička stupala (DES) prepoznata kao ekološki prihvatljivi reagensi za preradu lignoceluloznih materijala u budućnosti. U ovom je radu istraživana uporaba DES-a u proizvodnji celuloze od sječke drva europske crne topole. DES smjesa pripremljena je od kolin-klorida (ChCl) i etilen-glikola (EG). Osim toga, tradicionalnim je natronskim i kraft postupkom proizvedena celuloza od sječke drva topole radi usporedbе s celulozom proizvedenom s dodatkom DES smjese. Utvrđeno je da je celuloza proizvedena od sječke drva topole uz upotrebu DES-a u smislu prinosa, viskoznosti i neprozirnosti usporediva s celulozom dobivenom natronskim i kraft postupkom. Celuloza proizvedena uz dodatak DES-a lako je dosegla ciljani stupanj slobode celuloze. Međutim, svojstva čvrstoće i svjetlina celuloze proizvedene uz dodatak DES-a bili su lošiji od tih svojstava natronske i kraft celuloze. Svojstva čvrstoće DES celuloze mogu se poboljšati pojačivačima čvrstoće papira kao što su škrob i mikrofibriliranom ili nanofibriliranom celulozom. Osim toga, potreba za DES-a u proizvodnji celuloze može imati važan doprinos čišćoj proizvodnji i čini zelenijom alternativu tradicionalnim metodama proizvodnje celuloze.

KLJUČNE RIJEČI: DES; europska crna topola; zelena kemija; čišća proizvodnja; svojstva celuloze

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1 INTRODUCTION

1. UVOD

Although kraft pulping is the dominant method used in pulp industry, it has some serious disadvantages such as air pollution, water pollution, and high investment costs (Muurinen, 2000). For this reason, a number of new pulp processing methods have been studied. Organosolv (solvent-based) pulping is a chemical pulp method having minimum environmental impact, high pulp yield, and low investment costs (Saberikhah et al., 2011). EG pulping has been carried out with various biomass materials such as palm oil tree residues (Alriols et al., 2009), olive tree trimmings (Jiménez et al., 2004), birch (Gast and Pulz, 1984; Rutkowski et al., 1993), aspen and beech (Rutkowski et al., 1993), tagasaste (Jiménez et al., 2008; Rodríguez et al., 2008), vine shoots (Rodríguez et al., 2008; Jiménez et al., 2009), cotton stalks and leucaena (Rodríguez et al., 2008), pine (Nakamura and Takuati, 1941), and larch (Uraki and Sano, 1999).

Deep eutectic solvents (DESs) consist of a mixture of at least two components: a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD) (Penna-Pereira and Namieśnik, 2014). They are non-toxic, eco-friendly, easily prepared, inexpensive, readily available, biodegradable, and recyclable green solvents. Because of these extraordinary advantages, interest in DESs continues to grow (Zhang et al., 2012). The usage potential for DESs in organic synthesis, electrochemistry, catalysis, and biology has been studied (Škulcová et al., 2016). In addition, DESs have been extensively used in the field of separation technologies (Hou et al., 2018). The solubilizing capacity of DESs on lignocellulosic biomass or its individual components such as lignins was tested by Francisco et al. (2012). Since then, studies related to biomass processing using various DESs have received increasing attention (Alvarez-Vasco et al., 2016; Hou et al., 2018; Chen et al., 2019; Jablonsky et al., 2019; Oh et al., 2020; Soto-Salcido et al., 2020).

A number of studies have focused on DES treatment using several types of lignocellulosic biomass. De Dios (2013) studied lignin isolation from wheat straw and pine sawdust using several deep eutectic mixtures and reported that the lignin solubility was increased with the higher content of lactic acid in DES. Abougour (2014) pretreated switchgrass with ChCl/trifluoroacetamide and lignin content was reduced by 6.66 %. In addition, they noted that pretreatment did not cause a reduction in cellulose and hemicellulose content. The wheat straw was pretreated with ChCl based DESs and containing different HBDs such as urea, lactic acid, malic acid, malonic acid, and oxalic acid hydrate by Jablonský et al. (2015). The highest lignin removal was 57.9 % with ChCl/oxalic acid dihydrate at 60 °C and 24 h. Kumar et al. (2016) investigated solubility of cellulose, xylan, and lignin from rice straw in DESs containing ChCl, betaine, and lactic acid. Their experiments revealed that xylan and cellulose are not soluble in DESs. The lignin solubility in DES consisting of ChCl/lactic acid treatment were 78 % in poplar and 58 % in Douglas-fir. The isolation of willow lignin with the treatment of DESs (ChCl/lactic acid, ChCl/urea, ChCl/glycerol) was evaluated by Li et al. (2017). Optimal DES-lignin yield (91.8 %) was obtained at a ChCl/lactic acid molar ratio of 1:10, extraction time of 12 h, and temperature of 120 °C. Pan et al. (2017) focused on the effects of DES (ChCl/urea) pretreatment on holocellulose, α-cellulose, and acid-insoluble-lignin contents of rice straw. They observed that ChCl/urea had a selective delignification. Lynam et al. (2017) noted that DESs (lactic acid/betaine, lactic acid/ChCl, lactic acid/proline, formic acid/ChCl, and acetic acid/ChCl) were capable of selectively dissolving the lignin at 60 °C. Zulkifeli et al. (2017) noted that the pretreatment of oil palm trunk with ethylammonium chloride/EG had removed 42 % lignin and 83 % hemicellulose. Hou et al. (2018) also reported that DES consisting of ChCl/urea could effectively delignify from the rice straw. Chen and Wan (2018) noted that lignin was recoverable with high purity after microwave-assisted DES pretreatment of Miscanthus, switchgrass, and corn stover. Kılıç-Pekgözlü and Ceylan (2019) extracted the Scots pine wood with several DESs. They found that DESs could be alternative solvents for organic solvents. Recently, the effects of DESs (ChCl/lactic acid and ChCl/glycerin) treatment on the chemical composition of the sapwood and heartwood of red pine were investigated by Kwon et al. (2020). They observed that the solid residue yield after DES treatment decreased with increasing HBD concentration and treatment time. In addition, the solid residue amount in the sapwood was higher compared to the heartwood.

DESs have potential applications in the pulp and paper industry. Choi et al. (2016a and 2016b, respectively) investigated the effects of DES treatment of thermomechanical pulp (TMP) and bleached chemithermomechanical pulp (BCTMP) on handsheet properties. Majová et al. (2017a) reported the effect of initial kappa number of kraft pulp on the DES pulp delignification efficiency, and determined that kraft pulp having higher kappa number was more easily delignified with DES. A recent study found that DES could be replaced by oxygen in kraft pulp delignifica-
The hardwood kraft pulp was delignified using two different DESs (ChCl/lactic acid and alanine/lactic acid) and the effects of DES delignification on the chemical and physical properties of the kraft pulp were investigated (Jablonsky et al., 2018). The potential of potassium carbonate/glycerol (K₂CO₃/Gly) DES applied as a green solvent in rice straw pulping was evaluated by Lim et al. (2019).

Smink et al. (2019) investigated the effect of ChCl on the pulping of *Eucalyptus globulus* chips. Rapseed stems, corn stalks, and wheat straw were treated with acidic and alkaline DESs and the effect of DES type on nanocelluloses properties and on the resulting nanoparticles was investigated by Suopajärvi et al. (2020). Recently, the effect of ChCl based DES treatment on the chemical composition of the low-energy mechanical pulp was reported by Fiskari et al. (2020).

Although several DESs have been extensively studied for pretreating biomass, the literature available regarding the use of DESs in pulp production is limited. To the best of our knowledge, to date, no investigation has been carried out comparing DES pulp production with traditional pulping methods. Therefore, the aim of this study was to evaluate the usage possibilities of a DES (ChCl:EG) in pulp production from poplar wood and to compare DES pulping with traditional pulping methods. The effects of different ChCl:EG molar ratios (4:10, 5:10, 6:10) were also investigated in this study.

### Materials and Methods

#### 2.1 Material

European black poplar (*Populus nigra* L.) was chosen as the wood material because it has a rapid growth rate and provides easier delignification compared to softwoods. A 10 cm-thick wood disc was taken at breast height from a poplar log originating from Bartın Province (Turkey). This disc was debarked and subdivided into four discs (25 mm-thick). These were manually chipped, using a chisel, as homogeneously as possible to 25 mm × 15 mm × 5 mm in size for pulping.

#### 2.2 Chemical composition and fiber morphology of poplar wood

The chemical analysis of poplar wood was carried out according to TAPPI T 257 cm-99, TAPPI T 204 cm-97, and TAPPI T 212 om-02, respectively. In addition, poplar wood chips were macerated with the chlorite method (Spearin and Isenberg, 1947). After maceration, the fiber length (*L*) and width (*D*), lumen width (*d*), and cell wall thickness (*w*) of fibers were measured. The slenderness ratio (*L/D*), flexibility ratio ([(*d/D*) × 100]), and Runkel ratio ([2 × *w*/(*d* + *w*)) were calculated from the dimensional measurements of fibers.

### 2.3 DES preparation

#### 2.3.1 Priprema DES-a

DES was prepared by mixing ChCl with EG. All chemicals were acquired commercially (Merck) and used as received. The ChCl and EG were mixed in different molar ratios (4:10, 5:10, and 6:10) and used as DES. The solution was heated at 100 °C for 60 min until a transparent liquid retaining no solid particles was formed. The mixture was stored in a desiccator until use after being cooled to room temperature.

### 2.4 DES and traditional pulping

#### 2.4.1 DES i tradicionalna proizvodnja celuloze

DES and traditional pulping conditions are shown in Table 1. In DES cookings, the oven-dried (o.d.) poplar chip weight was calculated for each cooking experiment using the ChCl/EG molar ratio and cooking liquor/chip ratio. In DES-1 (4ChCl/10EG), 558.48 g ChCl (ChCl molecular weight × 4) and 620.7 g EG (EG molecular weight × 10) were used. The total weight of ChCl and EG was 1179.18 g. The o.d. poplar chip weight in the 2.5/1 cooking liquor/chip was 471.73 g (1179.18/2.5). According to the same calculation, 527.52 g and 583.37 g o.d. poplar chips were used in DES-2 (5ChCl/10EG) and DES-3 (6ChCl/10EG) cooking experiments, respectively (Table 1).

The air-dried poplar wood chips were cooked in a rotary digester. After cooking, the DES pulps and traditional pulps were washed to remove the black liquor with tap water. The DES pulps were also washed in ethanol. All pulps were disintegrated in a laboratory-type pulp mixer with 2-L capacity. The pulps were screened with a Somerville-type pulp screen according to TAPPI T 275 sp-02. After screening, all the pulp samples were beaten to 25 °SR and 35 °SR in a Valley Beater according to TAPPI T 200 sp-15.

#### 2.5 Pulp and paper properties

#### 2.5.1 Svojstva celuloze i papira

The screened yield (TAPPI T 210 cm-02), kappa number (TAPPI T 236 om-99), viscosity (SCAN-CM 15-62), and freeness of the pulps (ISO 5267-1) were determined. The handsheets (75 g/m²) were made by a Rapid-Kothen Sheet Former (ISO 5269-2) at three different freeness levels (unbeaten, 25 °SR, and 35 °SR).
After conditioning in accordance with TAPPI T 402 sp-03, the tensile index, stretch, and tensile energy absorption (TEA) (ISO 1924-3), tear index (TAPPI T 414 om-98), burst index (TAPPI T 403 om-02), opacity (TAPPI T 519 om-02), and brightness (TAPPI T 525 om-02) of the handsheets were determined.

### 2.6 Statistical analysis

#### 2.6.1 Statistička analiza

The data related to properties of the DES, kraft, and soda pulps from poplar chips were analyzed using analysis of variance (ANOVA) and the Duncan test at a 95% confidence level ($p < 0.05$). The effects of the methods and conditions of pulping on the paper properties were evaluated statistically using SPSS software. In Figures 2-8, the same letters on the columns denote no statistically significant differences between the groups. In addition, there were no significant differences among the values with the same letters in the same column of Table 3 and Table 4.

### 3 RESULTS AND DISCUSSION

#### 3.1 REZULTATI I RASPRAVA

The results of the chemical composition analysis and fiber morphology of the *Populus nigra* wood are presented in Table 2. These results are similar to those of *Populus tremula*.

The pulp properties of DES, soda, and kraft pulps are presented in Table 3. The screened yield of the DES pulps was higher than that of the soda and kraft pulps. The highest screened yield was obtained from DES-3 pulp. The screened yields of the DES pulps after washing with ethanol were similar to those of the traditional pulps (Table 3).

The effect of ChCl molar ratio on kappa number of DES pulp was insignificant ($p > 0.05$). The kappa numbers of DES pulps were higher than for the traditional pulps ($p < 0.05$). This result can be ascribed to the insufficient delignification of DES pulping compared to the traditional pulping methods. Alvarez-Vas-

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### Table 1 DES and traditional pulping conditions

| Pulps | ChCl/EG mole ratios in cooking | Active alkali | Sulfidity | Wood weight in cooking, o.d. | Liquor/wood ratio | Cooking time to max. temp., min | Cooking time at max. temp., min | Cooking temp., °C | Temperature kuhanja, °C |
|-------|-----------------------------|--------------|-----------|-----------------------------|------------------|-------------------------------|-------------------------------|-----------------|----------------------|
| DES-1 | 4ChCl/10EG                  | -            | -         | 471.67                      | 2.5/1            | 60                            | 150                          | 190             | 190                  |
| DES-2 | 5ChCl/10EG                  | -            | -         | 527.52                      | 2.5/1            | 60                            | 150                          | 190             | 190                  |
| DES-3 | 6ChCl/10EG                  | -            | -         | 583.37                      | 2.5/1            | 60                            | 150                          | 190             | 190                  |
| Soda  | -                           | 18           | -         | 700                          | 4/1              | 60                            | 60                           | 170             | 170                  |
| Kraft | -                           | 16           | 20        | 700                          | 4/1              | 60                            | 60                           | 170             | 170                  |

### Table 2 Chemical composition and fiber morphology of poplar wood

| Experiments / Eksperimenti | *Populus nigra* | *Populus tremula* (Gülsoy and Tufek, 2013) |
|----------------------------|-----------------|-------------------------------------------|
| Holocellulose, % / Holoceluloza, % | 81.25           | 82.68                                     |
| α-cellulose, %             | 46.30           | 49.03                                     |
| Klason lignin, %           | 18.51           | 16.69                                     |
| Ethanol solubility, % / Topljivost u etanolu, % | 2.22            | 3.22                                      |
| 1 % NaOH solubility, % / Topljivost u 1-postotnom NaOH, % | 14.65          | 15.34                                     |
| Hot water solubility, % / Topljivost u vrućoj vodi, % | 3.59            | 3.04                                      |
| Cold water solubility, % / Topljivost u hladnoj vodi, % | 2.18            | 1.73                                      |
| Fiber length, mm / Duljina vlakana, mm | 1.05           | 1.10                                      |
| Fiber width, µm / Širina vlakana, µm | 27.47           | 23.90                                     |
| Lumen width, µm / Širina lumena, µm | 15.53          | 11.40                                     |
| Cell wall thickness, µm / Debljina stanične stijenke, µm | 5.97           | 6.30                                      |
| Slenderness ratio / Omjer vitkosti | 38.22          | 46.00                                     |
| Flexibility ratio / Omjer fleksibilnosti | 56.53          | 47.70                                     |
| Runkel ratio / Runkelov omjer | 0.77           | 1.10                                      |

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co et al. (2016) reported that DESs can selectively cleave ether bonds without affecting the C-C linkages in lignin and can facilitate lignin extraction from wood fibers. Choi et al. (2016a) treated thermomechanical pulp (TMP) with DES (lactic acid and betaine) and identified a linear correlation between the delignification of the TMP and the molar ratio of lactic acid in DES. Yin et al. (2016) noted that the lignin solubility capacity of DES was improved with the increased molar ratio of HBA. Majová et al. (2017a) noted that the kappa number of kraft pulp decreased from 21.7 to 12.3 with alanine/lactic acid treatment. Jablonsky et al. (2018) reported that the kappa number of untreated hardwood kraft pulp was reduced from 21.7 to 13.5 with ChCl/lactic acid treatment and to 12.3 with alanine/lactic acid treatment. Lim et al. (2019) found that the lignin content in rice straw significantly decreased after DES (K₂CO₃/Gly) pulping. Fiskari et al. (2020) stated that DESs consisting of ChCl/lactic acid, ChCl/urea, and ChCl/oxalic acid reduced the lignin content of Asplund fibers by approximately 50 %. On the other hand, the viscosity of the DES, soda, and kraft pulps had similar values (p >0.05). Majová et al. (2017a) reported that the viscosity of kraft pulp decreased slightly, from 789 to 784 ml/g, with alanine/lactic acid treatment.

Pulp refinability (beatability) is a significant parameter in terms of energy consumption of a pulp mill and usually depends on the chemical composition of the pulps (Gülsoy and Eroglu, 2011). Pulp beating consumes up to 15-18 % of the total electric energy used for paper production (Bajpai et al., 2006; Cui et al., 2015). Therefore, the pulp should reach the desired freeness level as soon as possible. DES pulps easily reached 25 ºSR and 35 ºSR freeness levels despite their higher kappa numbers (Table 3, Figure 1). DES-2 pulp reached 25 ºSR in 240 s., whereas soda pulp reached the same freeness level in 660 s. DES-1 pulp and soda pulp reached 35 ºSR in 420 s and 900 s, respectively.

The tensile index of the unbeaten and beaten DES pulps was significantly lower (p <0.05) than that of the traditional pulps (Figure 2). In the unbeaten, 25

**Table 3** Pulp properties of DES, soda, and kraft pulps

| Pulps Celuloza | Screened yield, % | Reject, % | Total yield, % | Weight loss at washing, % | Screened yield after washing, % | Total yield after washing, % | Kappa number | Viscosity, cm³/g |
|----------------|-------------------|-----------|----------------|---------------------------|-------------------------------|-------------------------------|--------------|-----------------|
| DES-1          | 52.02             | 9.27      | 61.29          | 14.29                     | 44.59                         | 53.86                         | 72.55        | 1154           |
| DES-2          | 49.07             | 2.47      | 51.54          | 14.65                     | 41.88                         | 44.35                         | 69.52        | 1170           |
| DES-3          | 52.78             | 5.46      | 58.24          | 17.22                     | 43.69                         | 49.15                         | 70.47        | 1199           |
| Soda           | 40.65             | 7.81      | 48.46          | -                         | -                             | -                             | 37.40        | 1126           |
| Kraft          | 46.42             | 17.31     | 63.73          | -                         | -                             | -                             | 41.08        | 1185           |

*There were no significant differences among the values with the same letters in the same column. / Nema značajnih razlika između vrijednosti s istim slovom unutar istog stupca.

**Figure 1** Beating time required for a given freeness level of DES, soda, and kraft pulps

**Slika 1.** Vrijeme mljevenja potrebno za dani stupanj slobode DES celuloze, natronske i kraft celuloze
°SR and 35 °SR DES pulps, the highest tensile index was determined in DES-2, DES-1, and DES-1 pulps as 39.94, 59.24, and 68.02 N·m/g, respectively. The highest tensile index values in the unbeaten, 25 °SR and 35 °SR DES pulps compared to the soda and kraft pulps, respectively, were lower by 15.42 % and 26.17% (unbeaten pulp), 30.98 % and 36.72 % (25 °SR pulp), and 25.47 % and 33.12 % (35 °SR pulp). At all pulp freeness levels, the highest tensile index values were obtained with kraft pulp. Moreover, the tensile index of the DES pulps was irregularly affected by the ChCl amount in the DES cooking liquor. The tensile index of the DES pulps was significantly increased with beating (p <0.05) (Table 4). However, the tensile index increases due to beating were a little more obvious in the traditional pulps. For example, the tensile index of DES-1 pulp was increased by 66.26 % and 90.91 % with beating to 25 °SR and 35 °SR, respectively. In the soda and kraft pulps, these values were 81.77 % & 93.29 % and 73.03 % & 87.99 %, respectively.

The stretch values of the unbeaten DES pulps were higher than those of the traditional pulps, whereas the stretch values of the beaten DES pulps were lower than those of the traditional pulps (Figure 3, p <0.05). In the unbeaten pulps, the highest and the lowest stretch values were obtained from DES-2 pulp and soda pulp as 1.37 % and 0.85 %, respectively. On the other hand, the stretch values of the unbeaten and 25 °SR DES pulps were irregularly affected by the ChCl amount in the DES cooking liquor. In the 35 °SR pulps, the effect on stretch of the ChCl amount in the DES cooking liquor was statistically insignificant (p >0.05). Stretch values of the DES pulps, as for the traditional pulps, were significantly increased with beating (p <0.05) (Table 4).

In the unbeaten pulps, the highest TEA value was 28.86 J/m² (DES-2 pulp). In the 25 °SR and 35 °SR
pulps, the stretch values of DES pulps were lower than those of soda and kraft pulps (Figure 4, \( p < 0.05 \)). Moreover, the TEA of DES pulps changed irregularly with the rising ChCl amount in the DES cooking liquor. The pulp beating had a positive effect on the TEA values of DES and traditional pulps (Table 4). However, the effect of beating on TEA was more pronounced in the traditional pulps.

In the unbeaten and beaten pulps, the tear index values of the DES pulps were lower than those of the soda and kraft pulps (\( p < 0.05 \)). The highest tear index values of the DES pulps were determined in DES-3 pulp samples. At all pulp freeness levels, the effect on the tear index of the ChCl amount in the DES cooking liquor was statistically insignificant (Figure 5, \( p > 0.05 \)). In terms of the tear index, the response of DES pulps to beating was different from that of traditional pulps. The tear index increased when the traditional pulps were beaten up to 25 °SR. With increasing beating levels, their tear index values decreased. In contrast, the tear index values of the DES pulps regularly decreased with increasing beating levels (Table 4).

The burst index values of the unbeaten samples of DES-2, soda, and kraft pulps were 1.54, 1.38, and 1.62 kPa·m²/g. The burst index values of the DES pulps were lower than those of the soda and kraft pulps except for the unbeaten DES-2 pulp (Figure 6). The burst index values of the unbeaten and 35 °SR pulps varied irregularly with increasing ChCl amounts in the cooking liquor. However, the decrease in the burst index with increasing ChCl amount was insignificant (\( p > 0.05 \)). The relationship between the burst index of DES pulps and increasing pulp beating levels was linear (\( p < 0.05 \)) (Table 4). However, the tensile index increases after pulp beating were more pronounced in the traditional pulps. For example, the burst index of DES-1 pulp was increased by 71.09 % and 97.66 % with beating to 25 °SR and 35 °SR, respectively. The burst index increases with beating in the soda and kraft pulps were 152.17 and 181.16 % and 138.27 and 161.11 %, respectively.

**Figure 4** TEA of DES, soda, and kraft pulps
Slika 4. TEA za DES celulozu, natronsku i kraft celulozu

**Figure 5** Tear index of DES, soda, and kraft pulps
Slika 5. Indeks kidanja DES celuloze, natronske i kraft celuloze
Choi et al. (2016a) reported that the burst and tensile indices of TMP pulps increased when a higher molar ratio of lactic acid was used in the DES preparation. The authors also reported that the tear index of TMP pulps was reduced with the increasing molar ratio of lactic acid in the DES. Jablonsky et al. (2018) noted that the burst, tensile, and tear indices of untreated hardwood kraft pulp decreased with ChCl/lactic acid and alanine/lactic acid treatment. Untreated Asplund fiber pulp had a higher or equal tensile index compared to DES-treated pulp at all pulp freeness levels (Fiskari et al., 2020). Suopajärvi et al. (2020) stated that nanopapers from alkaline DES-treated wheat straw, rapeseed stems, and corn stalks had better tensile strength and strain compared with nanopapers from acidic DESs.

At all pulp freeness levels, the DES pulp had lower brightness values compared to soda and kraft pulps (Figure 7) because of the higher kappa numbers and insufficient delignification of the DES pulps (Table 3). Pulp brightness was significantly reduced with the increase of ChCl in the DES (p < 0.05). In addition, the brightness of DES-1 pulp was reduced with beating, whereas for DES-2 and DES-3 pulps, the changes were irregular (Table 4). As expected, the brightness of kraft and soda pulps was reduced with beating. This result can be explained by the homogeneous lignin distribution of the DES fibers in the cell walls.

In the unbeaten and beaten samples, the DES pulp exhibited higher opacity values compared to the soda and kraft pulps (Figure 8). The effect of the amount of ChCl in DES on pulp opacity was statistically insignificant (p > 0.05). Although the opacity of the traditional pulps changed with beating (p < 0.05), the opacity of the DES pulps did not change (p > 0.05) (Table 4). This experiment demonstrated that, compared to traditional pulping methods, DES pulping had a negative effect on pulp brightness, although it had a positive effect on pulp opacity. Choi et al. (2016a) noted that lactic acid and betaine DES treatment had no effect on the optical properties of TMP pulp.
crease in the brightness of kraft pulp was observed with DES treatment (Škulcová et al., 2017). Jablonsky et al. (2018) reported that the brightness of untreated hardwood kraft pulp increased from 27.02 to 34.05 with ChCl/lactic acid treatment and to 33.38 with alanine/lactic acid treatment.

4 CONCLUSIONS

In this new century, sustainable development challenges pulp and paper industry to develop new and cleaner technological processes. DESs have potential applications in the pulp and paper industry. The novelty of this study is the utilization of DES in pulp production and comparison of traditional pulps and DES pulps. The results of this study showed that the use of DES was an effective method for the pulping of poplar lignocellulosic biomass (Populus nigra L.). The DES formed by ChCl and EG (molar ratios = 4:10, 5:10, 6:10) applied at 190 °C for 3.5 h enabled pulp production from poplar chips. The DES pulps were comparable to those produced by traditional pulping methods in terms of pulp yield, pulp viscosity, and opacity. The DES-1 pulp exhibited the best cooking conditions in terms of total pulp yield. On the other hand, the beata-

Table 4 Effect of beating level on handsheet properties of DES, soda, and kraft pulps

| Pulps Celuloza | Freeness, °SR | Tensile index, N/m² | Stretch, % | TEA, J/m² | Tear index, mN/m² | Burst index, kPa/m² | Brightness, % | Opacity, % Neprozirnost, % |
|----------------|--------------|-------------------|------------|----------|------------------|---------------------|---------------|--------------------------|
| DES-1          | 15           | 35.63a*           | 1.01a      | 17.76a   | 2.02a            | 1.28a               | 9.73a         | 99.99a                   |
|                | 26           | 59.24b            | 1.36b      | 40.79b   | 1.92a            | 2.19b               | 9.72a         | 99.94a                   |
|                | 37           | 68.02c            | 1.43b      | 48.60c   | 1.80b            | 2.53c               | 9.33b         | 99.88a                   |
| DES-2          | 17           | 39.94a            | 1.37a      | 28.86a   | 2.07a            | 1.54a               | 9.51a         | 99.96a                   |
|                | 25           | 50.26b            | 1.39a      | 35.69b   | 1.95a            | 2.05b               | 9.48a         | 99.97a                   |
|                | 35           | 53.28c            | 1.46a      | 40.69c   | 1.74b            | 2.09b               | 9.68b         | 99.91a                   |
| DES-3          | 16           | 35.91a            | 1.20a      | 22.36a   | 2.14a            | 1.27a               | 8.71a         | 99.98a                   |
|                | 25           | 53.33b            | 1.48b      | 41.00b   | 1.97b            | 2.04b               | 8.80a         | 99.96a                   |
|                | 35           | 61.02c            | 1.51b      | 47.47c   | 1.80c            | 2.25c               | 8.64a         | 99.93a                   |
| Soda           | 12           | 47.22a            | 0.85a      | 19.92a   | 2.71a            | 1.38a               | 24.46a        | 99.56a                   |
|                | 25           | 85.33b            | 1.63b      | 69.43b   | 3.54c            | 3.48b               | 22.84b        | 99.46a                   |
|                | 36           | 91.27c            | 1.75b      | 79.66c   | 3.16b            | 3.86c               | 21.61c        | 99.19b                   |
| Kraft          | 12           | 54.10a            | 0.98a      | 25.34a   | 3.05a            | 1.62a               | 23.03a        | 99.21a                   |
|                | 24           | 93.61b            | 1.71b      | 79.70b   | 3.24c            | 3.86b               | 20.73b        | 98.46b                   |
|                | 35           | 101.70c           | 1.79b      | 90.50c   | 2.90b            | 4.23c               | 19.16c        | 97.65c                   |

*There were no significant differences among the values with the same letters in the same column. / Nema značajnih razlika među vrijednostima s istim slovom unutar istog stupca.
bility of the pulp was positively affected by the DES pulping. However, the strength properties and brightness of the DES pulps were lower than those of the traditional pulps. In the unbeaten and beaten DES pulps, the highest strength values were obtained from the DES-2 and DES-1 pulps.

This study demonstrated that DES composed of ChCl and EG can be used as green solvent for pulp production from biomass. It can be readily applicable to pulp production. The DES pulping process is an alternative to traditional pulping due to its low-environmental-impact. Inexpensive and biodegradable DESs, used in pulping, are characterized as economically and environmentally viable solvents. These solvents could offer unique opportunities for cleaner pulp production. Therefore, in order to reveal true potential of DESs and to improve pulp properties, further research is needed on the use of DESs as green solvents in pulping.

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