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DEEP EUTECTIC SOLVENT PULPING FROM SORGHUM STALKS

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ABSTRACT

Deep eutectic solvents are characterized as natural, green, biodegradable, non-flammable, non-volatile, non-toxic, odorless, colorless, easy to prepare, and easy to recycle after use. They present an opportunity to introduce new techniques for the pulping process. This study investigated the possibility of using a green deep eutectic solvents from sorghum stalks for pulp and paper production. Choline chloride/ethylene glycol was used in the preparation of eutectic mixtures in molar ratios of 4/10, 5/10, and 6/10. These eutectic mixtures were then applied as cooking liquor to sorghum stalks at two different cooking times (140 and 160 minutes). In addition, the traditional pulping methods of soda and kraft cookings were carried out using sorghum stalks and the pulps were compared with the deep eutectic solvents pulps. The results showed that the pulp production using deep eutectic solvents was accomplished successfully. Some properties of deep eutectic solvents pulps were comparable to those of the soda and kraft pulps. deep eutectic solvents can play an essential role in cleaner pulp production.

Keywords: Choline chloride, deep eutectic solvent, ethylene glycol, green chemistry, pulp, sorghum.

INTRODUCTION

Conventional chemical and semi-chemical pulping processes generate enormous amounts of highly polluting effluent (especially those using sulfur compounds). The lack of effective alternatives to these pulping methods has increased interest in finding more efficient pulping processes using reagents that are less polluting and more easily recyclable (Jiménez *et al*. 2008). In view of this, ethylene glycol has been used as a cooking liquor due to its efficient delignification in various biomasses such as palm oil tree residues (González Alriols *et al*. 2009), olive tree trimmings (Jiménez *et al.* 2004), birch (Gast and Puls 1984, Rutkowski *et al*. 1993), aspen and beech (Rutkowski *et al*. 1993), tagasaste (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 Takauti 1941), and larch (Uraki and Sano 1999).

The growing environmental concern in recent years has greatly emphasized forest preservation and more efficient use of lignocellulosic raw materials. At this point, the pulp and paper industry has begun to focus on using new and unconventional raw materials (Jiménez *et al.* 2008). Unfortunately, wood is still the main raw material for global pulp and paper production. However, some nonwoods are used in China and other Asian countries. Currently, the most common nonwood raw material is straw. Other nonwoods used in manufacturing pulp and paper are bagasse, bamboo, cotton, hemp, sisal, abaca, jute, sorghum, and kenaf (Atchison 1995). The evaluation of sorghum stalks as an alternative raw material for pulping has been reported by several authors (Albert *et al.* 2011, Gençer and Şahin 2015, Saeed *et al.* 2017, Gençer and Hatıl 2019).

Deep eutectic solvents (DESs) emerged at the beginning of this century. They are considered as a non-flammable, non-volatile, much cheaper, readily available, less toxic, biodegradable, and environmentally friendly type of solvent (Zhang *et al.* 2012). These DESs are generally composed of a hydrogen bond acceptor (e.g., quaternary ammonium salts) and hydrogen bond donor(s) (e.g., amines, amides, carboxylic acids, and polyols) (Zdanowicz *et al.* 2018). One of the most common components used in forming a DES is choline chloride (ChCl), a non-toxic and biodegradable quaternary ammonium salt (Zhang *et al.* 2012).

Several studies have used DESs for the treatment of lignocellulosic biomass including wheat straw (Jablonský *et al.* 2015, Škulcová *et al.* 2016, Jablonsky *et al.* 2019), rice straw (Pan *et al.* 2017, Hou *et al.* 2018), poplar (Alvarez-Vasco *et al.* 2016), beech sawdust (Jablonsky *et al.* 2019), bamboo (Liu *et al.* 2019), Douglas fir (Alvarez-Vasco *et al.* 2016), pine (Kilic-Pekgözlü and Ceylan 2019, Kwon *et al.* 2020), birch (Soto-Salcido *et al.* 2020), oil palm biomass (Yiin *et al.* 2016), agave bagasse (Soto-Salcido *et al.* 2020), corncobs (Procentese *et al.* 2015), and switchgrass (Abougor 2014).

Choi et al. (2016a) investigated the effects of DES (lactic acid and betaine) treatment on the properties of thermomechanical pulp (TMP) fibers and their handsheets. In another study (Choi *et al.* 2016b), they investigated the effects of DES (lactic acid and betaine) treatment on bleached chemi-thermomechanical pulp (BCTMP) and bleached kraft pulp (BKP) fibers and their handsheets properties. Majová *et al*. (2017) described the effect of DES on the delignification of hardwood kraft pulps having different lignin contents. Jablonsky *et al*. (2018) delignified hardwood kraft pulp using two different DESs (choline chloride/lactic acid, alanine/lactic acid). They investigated the effects of DES delignification on the physical and chemical properties of the kraft pulp. Lim *et al*. (2019) studied the potential of potassium carbonate/glycerol DES (K_2CO_3/Gly) applied as a green solvent in rice straw pulping. The authors also investigated the effect of reaction time, pulping temperature, and rice straw/DES mass ratio on cellulose content. The effect of choline chloride on the pulping of *Eucalyptus globulus* chips was investigated by Smink *et al*. (2019). Fiskari *et al*. (2020) used low-energy mechanical pulp (Asplund fibers) as starting material for DES pulping. Recently, Suopajärvi *et al*. (2020) treated rapeseed stems, corn stalks, and wheat straw using five acidic (natural organic acid/choline chloride) DES treatments and one alkaline (K_2CO_3/glycerol) DES treatment and investigated the effect of DES type on the properties of nanocelluloses and their nanopapers.

To the best of our knowledge, no comparison of DES, soda, and kraft pulping of lignocellulosic raw material has been reported previously. This study investigated the potential of pulp and paper production with sorghum stalks using a green DES prepared with choline chloride (ChCl) and ethylene glycol (EG). In addition, cooks from traditional soda and kraft pulp production methods were carried out using sorghum stalks and the pulps were compared with the DES pulps.

MATERIAL AND METHODS

The sweet sorghum stalks (*Sorghum bicolor* × *Sorghum bicolor* var. *sudanense*) used in this study were obtained from Bartin Province in the Black Sea Region of Turkey. The leaves and seeds were removed from the stalks, retaining the rind and pith. The average stalk length and thickness were 135 cm and 5,8 mm, respectively. The stalks were cut into 3-cm pieces and then air-dried and stored in polyethylene bags. Since the stalks are used industrially in this form for pulp production, the sorghum stalks were used without milling (grinding) in the current study, thus enhancing the industrial applicability of the results.

The standard methods were used in the main chemical analyses of the sweet sorghum stalks. The sample preparation was carried out according to TAPPI T 257 (TAPPI 2002). Experiments for analysis of α-cellulose, holocellulose, klason lignin, ethanol solubility, 1 % NaOH solubility, and cold and hot water solubility were carried out according to Han and Rowell (1997), Wise and Karl (1962), TAPPI T 222 (TAPPI 2002), TAPPI T 204 (TAPPI 1997), TAPPI T 212 (TAPPI 2002), and TAPPI T 207 (TAPPI 1999), respectively. An average of three repetitions was taken for each experiment.

Sorghum stalks were macerated using the chlorite method (Spearin and Isenberg 1947). The matchstick-size sorghum stalks (3 g) were placed in a 250 mL Erlenmeyer flask. 160 mL of distilled water, 2,5 g of sodium chlorite (CAS No. 7758-19-2, Sigma Aldrich, Steinheim, Baden-Württemberg, Germany), and 1 mL of glacial acetic acid (CAS No. 64-19-7, Merck KGaA, Darmstadt, Germany) were added to Erlenmeyer flask. Erlenmeyer flask was placed in the water bath at 80 °C. Additional 2,5 g of sodium chlorite and 1 mL of glacial acetic acid were added after one hour of heating. This process was continued until the samples turned white. After maceration, the samples were agitated to obtain individual fibers (Berlyn 1976). The fiber length, fiber width, lumen width, and cell wall thickness of 100 randomly selected fibers were measured using a light microscope (Olympus CX21, Tokyo, Japan). The slenderness ratio $\left(\frac{\text{fiber length}}{\text{fiber width}}\right)$, flexibility ratio $\left(\frac{\text{lumen width}}{\text{fiber width}} * 100\right)$, and Runkel ratio $\left(\frac{\text{double cell wall thickness}}{\text{lumen width}}\right)$ were calculated using the measured fiber dimensions.

The DES, kraft, and soda pulps of the sweet sorghum stalks were prepared under the conditions in Table 1. The preparation of DES cooking liquors used three samples of ChCl/EG DESs having different molar ratios as shown in Table 1. The ChCl (CAS No. 67-48-1, Merck KGaA, Darmstadt, Germany) and EG (CAS No. 107-21-1, Merck KGaA, Darmstadt, Germany) were mixed homogeneously on a hot plate at 80 °C for 60 minutes until a transparent colorless mixture was formed. In the DES cookings, oven-dried (o.d.) sweet sorghum stalk weights were calculated for each cooking experiment using the ChCl/EG molar ratio and cooking liquor/stalk ratio. For example, for the DES cookings, the 4ChCl/10EG cooking liquor molar ratio and 2,5/1 cooking liquor/stalk ratio used 558,48 g ChCl (molecular weight of ChCl multiplied by 4) and 620,7 g EG (molecular weight of EG multiplied by 10). The total weight of the ChCl and EG was 1179,18 g. The o.d. sweet sorghum stalk weight in the 2,5/1 cooking liquor/stalk was 471,67 g (1179,32/2,5), whereas 527,52 g and 583,37 g o.d. sweet sorghum stalk were used in the 5ChCl/10EG molar ratio and 6ChCl/10EG molar ratio cooking experiments, respectively (Table 1).

Table 1: Cooking conditions in DES, kraft, and soda cooking experiments.

Cooking	ChCl/EG mol. ratios in cooking	Active alkali	Sulfidity	Cooking Liquor/ stalk ratio (w/w)	Stalk weight in cooking (o.d.)	Cooking time to max. temp. (min)	Cooking time at max. temp. (min)	Cooking temp. (° C)
DES-1	4/10	-	-	2,5/1	471,67	60	80	175
DES-2	5/10	-	-	2,5/1	527,52	60	80	175
DES-3	6/10	-	-	2,5/1	583,37	60	80	175
DES-4	4/10	-	-	2,5/1	471,67	60	100	175
DES-5	5/10	-	-	2,5/1	527,52	60	100	175
DES-6	6/10	-	-	2,5/1	583,37	60	100	175
Soda-1	-	14	-	5/1	700	60	80	150
Soda-2	-	18	-	5/1	700	60	80	150
Kraft-1	-	10	14	5/1	700	60	80	150
Kraft-2	-	14	18	5/1	700	60	80	150

A laboratory-type 15-L electrically heated rotary digester was used in all pulping experiments. In order to remove the black liquor after soda or kraft cooking, the pulps were washed with tap water and disintegrated. The DES pulps were also washed with 95 % ethanol until the washing liquid appeared clear (Oh *et al*. 2020; Li *et al*. 2021). A Somerville-type pulp screen retained the rejects with a 0,15-mm slotted plate according to TAPPI T 275 (TAPPI 2002). All pulps were beaten according to TAPPI T 200 (TAPPI 2015) to 33° SR and 43° SR in a Valley Beater for comparison under the same conditions. The kappa number, viscosity, screened yield, and freeness levels of all pulps were determined according to TAPPI T 236 (TAPPI 1999), SCAN-CM 15-62 (SCAN 1962), TAPPI T 210 (TAPPI 2003), and ISO 5267-1 (ISO 1999), respectively. Ten handsheets (75 g/m^2) were formed with a Rapid-Kothen Sheet Former according to ISO 5269-2 (ISO 2004). The handsheets were conditioned according to TAPPI T 402 (TAPPI 2003). The tensile index, tensile energy absorption (TEA), and stretch were determined by ISO 1924-3 (ISO 2005). The burst index, tear index, brightness, opacity, bulk, and air permeability of the handsheets were measured TAPPI T 403 (TAPPI 2002), TAPPI T 414 (TAPPI 1998), TAPPI T 525 (TAPPI 2002), TAPPI T 519 (TAPPI 2002), TAPPI T 220 (TAPPI 2001), and ISO 5636-3 (ISO 2013), respectively.

The data belonging to the DES, kraft, and soda pulp properties of the sweet sorghum stalks 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 paper properties were evaluated statistically using SPSS software.

RESULTS AND DISCUSSION

Tables 2 and 3 show the chemical composition and fiber properties of the sorghum stalks, respectively. The chemical and fiber properties of the sorghum stalks were similar to those obtained in several other studies. The differences could be attributed to altitude, soil characteristics, and local climatic factors.

Table 2: Comparison of sweet sorghum stalk chemical composition in the present study and other studies.

Experiments	This study	Khristova and Gabir (1990)	Jiménez *et al.* (1993)	Belayachi and Delmas (1995)	Gençer and Şahin (2015)	Saeed *et al.* (2017)	Gençer and Hatıl (2019)
Holocellulose (%)	77,28 ± 1,98	68,60	65,83	61,62	71,00	54,80	77,80
α-cellulose (%)	44,83 ± 0,45	34,20	41,50	44,95	40,30	35,40	40,70
Klason lignin (%)	14,16 ± 0,15	12,20	15,64	14,92	13,00	10,30	14,40
Ethanol solubility (%)	24,45 ± 1,15	10,60*	7,99*	24,00*	15,30	-	19,00
1% NaOH solubility (%)	50,36 ± 0,39	44,80	41,64	63,10	47,10	16,20	46,10
Hot water solubility (%)	29,21 ± 0,54	21,40	21,70	43,80	19,70	13,20	22,90
Cold water solubility (%)	28,95 ± 0,68	-	-	-	15,10	11,60	20,00

*Alcohol-benzene solubility

Table 3: Comparison of sweet sorghum stalk fiber properties in the present study and other studies.

Experiments	This study	Khristova and Gabir (1990)	Albert *et al.* (2011)	Khazaeian *et al.* (2015)	Gençer and Şahin (2015)	Saeed *et al.* (2017)	Gençer and Hatıl (2019)
Fiber length (mm)	1,02 ± 0,03	0,90	1,77	1,80	2,31	0,52	2,10
Fiber width (µm)	18,84 ± 1,56	10,10	19,53	13,80	16,0	26,80	14,32
Lumen width (µm)	6,74 ± 0,30	8,30	6,60	7,90	5,58	-	4,05
Cell wall thickness (µm)	5,36 ± 0,31	0,90	6,46	2,90	5,21	-	5,00
Slenderness ratio	54,14	85	90,37	-	144,65	-	150,00
Flexibility ratio	35,77	82	33,79	-	34,90	-	28,28
Runkel ratio	1,59	-	1,90	-	1,87	-	2,47

Some properties of the DES, kraft, and soda pulps are given in Table 4. Prior to ethyl alcohol washing, the screened yield of the DES pulps was higher than for the kraft-1 and soda-1 pulps. The DES pulp having the highest screened yield was DES-5, with 37,31 %. This value was similar to that of the kraft-2 (37,67 %) and soda-2 (37,00 %) pulps. After washing with ethyl alcohol, all DES pulps screened yield was reduced. This can be attributed to the removal (by washing) of the water-insoluble wood components dissolved during cooking. The screened yield of the DES pulp samples after washing with ethyl alcohol was similar to that of the kraft-2 and soda-2 pulps. In the DES pulp samples washed with ethyl alcohol, the highest screened yield (33,56 %) was determined in DES-5.

The total yields of the DES, kraft, and soda pulps exhibited similar values. In the washed samples, the total yield of all DES pulps was lower than those of the kraft and soda pulps, whereas the pulp having the highest total yield (38,06 %) was DES-5, which was similar to that of kraft-2 (39,21 %). In the DES pulps with 80 min cooking time at maximum temperature, the screened yield increased in parallel with the ChCl amount in the DES cooking liquor. In addition, the screened yield of the DES pulps increased with increasing cooking time except for the sample with the 6/10 ChCl/EG mol ratio (Table 4). Lim *et al*. (2019) reported that the cellulose content in rice straw increased from 35,6 % to 73,8 % after DES (K_2CO_3/Gly) pulping.

The reject ratios of all DES pulps were lower than those of kraft-1 and soda-1 pulps. The lowest reject ratio (2,73 %) was determined in DES-6. The reject ratio of the DES pulps changed irregularly with the increasing ChCl amounts in the DES cooking liquor.

As expected, the reject ratio of the DES pulps was reduced with increasing cooking time except for the sample with 5/10 ChCl/EG mol ratio (Table 4).

The kappa numbers of all DES pulps were higher than those of the kraft and soda pulps. In the DES pulps with 100 min cooking time at maximum temperature, the kappa number increased in parallel with the ChCl amount in the DES cooking liquor. Francisco *et al*. (2013) evaluated the solubility of kraft lignin in ChCl:LA (1:1.3, 1:2, 1:5, and 1:10, respectively). The authors revealed that lignin solubility increased with decreasing ChCl amounts. Smink *et al*. (2019) carried out the pulping experiments of *Eucalyptus globulus* chips using lactic acid (LA) with and without the addition ChCl. They found that ChCl-LA pulping experiments had a higher delignification rate than LA pulping experiments. The nature of lignin is highly dependent on the biomass source and isolation method. Also, lignin is an inhomogeneous polymer, meaning some lignin fractions have a higher solubility than others Smink *et al*. (2019). In addition, the delignification rate depends on the type of hydrogen bond acceptor and hydrogen bond donor in the DES composition. On the other hand, the kappa number of the DES pulps increased with increasing cooking time except for the sample with 4/10 ChCl/EG mol ratio (Table 4). The lowest kappa number (61,20) was determined in DES-4 pulp. This value was close to the kappa number of soda-1 pulp (56,43). However, the reject ratio of DES-4 pulp (3,72 %) was lower than for soda-1 (9,79 %). The high kappa numbers of the DES pulps can be explained by the insufficient delignification during DES pulping or possibly by precipitation of lignin dissolving back onto the fiber surface. However, it is certain that the lignin is removed by DES cooking. Choi *et al*. (2016a) reported that that the kappa number of DES (lactic acid and betaine)-treated TMP was reduced with higher molar ratio increments of lactic acid in the DES. The authors also reported that lignin was partly extracted from the TMP fibers. Majová *et al*. (2017) found that the kappa number of kraft pulp decreased from 21,7 to 12,3 with alanine/lactic acid treatment. They also found that pulp with a higher initial kappa number (or lignin content) had a greater fraction of easily removed lignin fragments. 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) stated that the lignin content in rice straw decreased from 24,4 % to 2,8 % after DES (K_2CO_3/Gly) pulping. Fiskari *et al*. (2020) reported that DESs consisting of choline chloride/lactic acid, choline chloride/oxalic acid, and choline chloride/urea decreased the lignin content of Asplund fibers by approximately 50 %. Majová *et al*. (2017) noted that the viscosity of kraft pulp slightly decreased, from 789 mL/g to 784 mL/g, with alanine/lactic acid treatment. The viscosity values of the present study's DES, kraft, and soda pulps were similar (Table 4). Based on the results, it is evident that the DES pulps were comparable to the kraft and soda pulps in terms of pulp yield, reject ratio, kappa number, and pulp viscosity. Results also indicated that the ChCl amount in the DES cooking liquor and cooking time at maximum temperature significantly affected the pulp yield, reject ratio, and kappa number.

Table 4: Some properties of DES, kraft, and soda pulps.

Cooking	Screened yield (%)	Reject (%)	Total yield (%)	Screened yield after ethyl alcohol washing (%)	Total yield after ethyl alcohol washing (%)	Kappa number	Viscosity (cm^3/g)
DES-1	35,18	5,98	41,16	29,30	35,28	70,14	1188
DES-2	35,71	4,40	40,11	30,33	34,73	61,75	1173
DES-3	37,10	4,77	41,87	33,05	37,82	72,54	1158
DES-4	37,27	3,72	40,99	32,66	36,38	61,20	1231
DES-5	37,31	4,50	41,81	33,56	38,06	73,43	1173
DES-6	36,03	2,73	38,76	32,38	35,11	74,64	1180
Soda-1	31,42	9,79	41,21	-	-	56,43	1173
Soda-2	37,00	3,46	40,46	-	-	33,68	1181
Kraft-1	32,85	8,59	41,44	-	-	49,55	1150
Kraft-2	37,67	1,54	39,21	-	-	15,94	1170

The freeness levels of unbeaten pulps of DES1, DES2, DES3, DES4, DES5, and DES6 were 19° SR, 22° SR, 24° SR, 22° SR, 23° SR, and 26° SR, respectively. On the other hand, the freeness levels of unbeaten pulps of soda-1, soda-2, kraft-1, and kraft-2 were 20° SR, 18° SR, 23° SR, and 21° SR, respectively. As shown in Fig. 1, the DES pulps reached the target freeness levels significantly faster than the kraft and soda pulps. The response of pulps to beating is significant for the energy consumption of mills and usually depends on the chemical composition of pulps (Gulsoy and Eroglu 2011a). Pulps containing high levels of lignin are more difficult to beat. Although the DES pulps had more lignin than the kraft and soda pulps (Table 4), they were more easily beaten (Fig. 1). For example, DES-4 pulp with a kappa number of 61,20 reached 33° SR and 43° SR at 210 s and 250 s, respectively. However, soda-1 pulp with a kappa number of 56,43 reached 33° SR and 43° SR at 315 s and 390 s, respectively. This can be attributed to the softening of the fibers during DES pulping. The pulp reaching the fastest 33° SR and 43° SR was DES-6 at 120 s and 225 s, respectively.

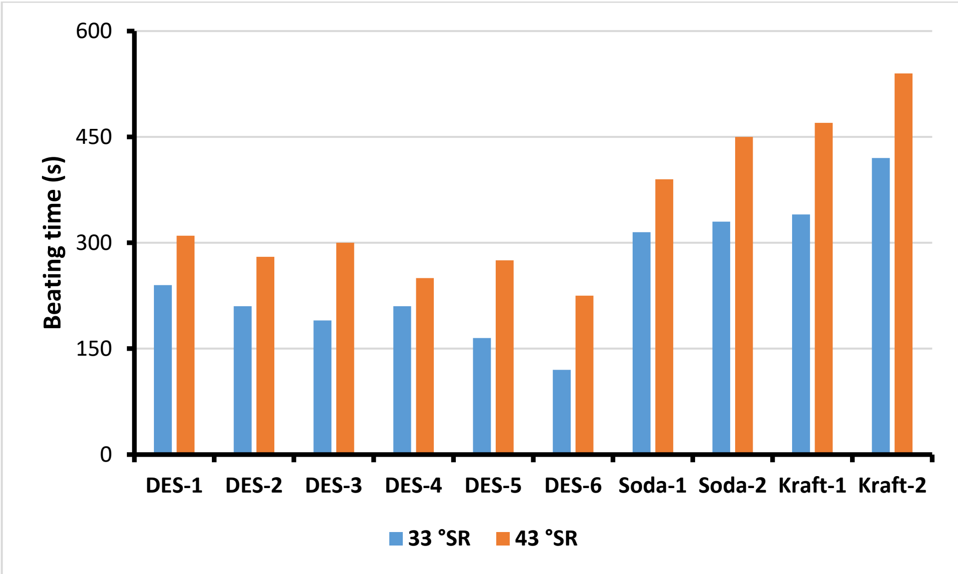

Figure 1: Beating time required for a given freeness level of DES, kraft, and soda pulps.

Some properties of all pulp handsheets at three different beating levels are shown in Table 5. Although the tear index of the unbeaten and beaten DES pulps was higher, the brightness and strength properties were lower than those of the kraft and soda pulps (*p* <0,05). However, the DES pulp handsheets had higher air permeability, bulk, and opacity than the soda and kraft pulps (*p* <0,05). The effect of the beating on the paper properties of the DES pulps was similar to the effects on the soda and kraft pulps. The tensile index, burst index, TEA, and stretch of all pulps increased in parallel with beating levels. The tear index, air permeability, and bulk of all pulps decreased with increments in the beating level. However, the brightness of the DES pulps changed irregularly with beating, whereas the brightness of the soda and kraft pulps decreased with beating. On the other hand, the effect of beating on the opacity of the DES pulps was insignificant.

In the unbeaten, 33° SR, and 43° SR samples of the DES pulps, the highest tensile index values were determined as 42,52 N·m/g, 56,74 N·m/g, and 65,16 N·m/g in DES-6, DES-1, and DES-2 pulps, respectively. However, in the unbeaten, 33° SR, and 43° SR samples of the soda and kraft pulps, the lowest tensile index values were 64,01 N·m/g, 81,69 N·m/g, and 83,79 N·m/g in soda-1, kraft-1, and kraft-1 pulps, respectively. The tensile index of the DES pulps was significantly lower statistically than for the soda and kraft pulps (p <0,05). The highest stretch values of unbeaten and beaten (33° SR and 43° SR) DES pulps were 3,70 %, 11,26 %, and 12,87 % higher than those of the soda and kraft pulps, respectively (Table 5). In the unbeaten, 33° SR, and 43° SR samples of DES pulps, the highest TEA values were 52,36 J/m^2, 65,67 J/m^2, and 79,28 J/m^2 in DES-6, DES-5, and DES-2 pulps, respectively. On the other hand, in the unbeaten, 33° SR, and 43° SR samples of soda and kraft pulps, the lowest TEA values were 58,97 J/m^2, 76,79 J/m^2, and 78,61 J/m^2 in soda-1, kraft-1, and kraft-1 pulps, respectively. The results showed that the TEA value of the DES-2 pulp beaten up to 43° SR was comparable to the kraft-1 pulp at the same beating degree. The highest tear index values of unbeaten and beaten (33° SR and 43° SR) DES pulps were 26,67 %, 29,91 %, and 22,22 % higher than those of the soda and kraft pulps, respectively (Table 5). In the unbeaten, 33° SR, and 43° SR samples of DES pulps, the highest burst index values were 1,81 k·Pa·m^2/g, 2,63 k·Pa·m^2/g, and 2,87 k·Pa·m^2/g in DES-6, DES-2, and DES-2 pulps, respectively. In the unbeaten, 33° SR, and 43° SR samples of soda and kraft pulps, the lowest burst index values were 2,73 k·Pa·m^2/g, 3,67 k·Pa·m^2/g, and 3,83 k·Pa·m^2/g in kraft-1, soda-1, and soda-1 pulps, respectively. The DES pulps exhibited lower burst index values than the kraft and soda pulps. The results showed that the DES pulps had lower strength properties compared to the soda and kraft pulps. However, the stretch and tear index of the DES pulps were comparable to the kraft and soda pulps. The tear index depends on the individual fiber strength, whereas the tensile and burst indices of handsheets depend on the bonding ability of the fibers (Gülsoy *et al.* 2016). Thus, we can say that the DES pulp fibers had higher individual fiber strength and lower fiber bonding compared to traditional pulps. These findings can also be ascribed to the higher kappa number of the DES pulps compared to the traditional pulps. Residual lignin increases fiber stiffness and hence, reduces fiber-bonding ability. The strength of the DES pulps increased in parallel with the ChCl amount in the DES cooking liquor. In addition, it increased with increasing cooking time (Table 5). It was found that the chemical composition of DESs affects the pulp strength as well as the delignification rate during DES pulping. Choi *et al*. (2016a) noted that pulps' burst and tensile indices were increased when a higher molar ratio of lactic acid was used in the DES preparation. The authors also reported that the tear index of the handsheets was reduced with the increasing molar ratio of lactic acid in the DES. Jablonsky *et al*. (2018) reported that the strength properties of untreated hardwood kraft pulp such as the tensile, burst, and tear indices decreased with ChCl/lactic acid and alanine/lactic acid treatment. Suopajärvi *et al*. (2020) noted that the nanopapers from alkaline DES-treated corn stalks, wheat straw, and rapeseed stems had better tensile strength and strain than nanopapers from acidic DESs. The untreated pulp of Asplund fibers had an equal or higher tensile index than DES-treated pulp at all freeness levels (Fiskari *et al.* 2020).

Table 5. Handsheet properties of DES, soda, and kraft pulps at different beating levels.

Pulp freeness (° SR)	Cooking	Tensile index (N·m/g)	Stretch (%)	TEA (J/m^2)	Tear index (m·N·m^2/g)	Burst index (k·Pa·m^2/g)	Air permeability (mL/min.)	Bulk (cm^3/g)	Brightness (%)	Opacity (%)
Unbeaten	DES-1	33,47a*	1,60a	30,02a	4,27cd	1,32a	5000f	1,93d	10,66f	99,89c
	DES-2	38,34c	1,86bc	39,62c	4,50d	1,57bc	4162e	1,75c	9,68c	99,85c
	DES-3	36,14b	1,89bc	37,71c	4,21cd	1,62c	2619c	1,75c	9,84d	99,90c
	DES-4	33,99a	1,82b	34,67b	4,29cd	1,49b	4147e	1,78c	10,46a	99,91c
	DES-5	38,06bc	2,06d	44,15d	4,13c	1,65c	3551d	1,75c	9,19b	99,95c
	DES-6	42,52d	2,16e	52,36e	4,16c	1,81d	1880a	1,68b	9,01a	99,97c
	Soda-1	64,01e	1,82b	58,97f	3,26b	2,82e	1887a	1,67b	24,10h	99,57b
	Soda-2	71,91g	1,92c	70,05g	3,30b	3,17f	1845a	1,57a	32,74j	98,86a
	Kraft-1	64,62e	1,84bc	60,76f	2,94a	2,73e	2260b	1,57a	20,83g	99,85c
	Kraft-2	68,46f	2,08de	72,34h	3,16ab	3,13f	2257b	1,69b	27,73i	99,50b
33	DES-1	56,74cd	1,95ab	59,15a	3,07cd	2,56bc	853g	1,62f	10,81f	99,92d
	DES-2	58,17d	2,04b	63,78b	3,03c	2,63b	553d	1,47c	10,15d	99,83d
	DES-3	51,61b	2,31c	64,89b	3,41e	2,34a	837g	1,58ef	9,92c	99,93d
	DES-4	54,54bc	2,21c	65,34b	3,23de	2,46b	651e	1,52cd	10,51e	99,88d
	DES-5	53,24ab	2,28c	65,67b	3,24de	2,33a	972h	1,57de	9,52b	99,94d
	DES-6	51,09a	2,07b	57,91a	3,30e	2,33a	777f	1,55de	9,20a	99,96d
	Soda-1	82,20e	1,94ab	78,86c	2,27ab	3,67d	239b	1,39b	22,89h	99,31c
	Soda-2	85,04f	1,94ab	82,39d	2,39b	3,88e	273c	1,36ab	31,18j	98,48a
	Kraft-1	81,69f	1,90a	76,79c	2,16a	3,68d	277c	1,33a	19,71g	99,75d
	Kraft-2	85,43e	2,05b	87,65e	2,11a	3,76d	192a	1,39b	25,90i	98,87b
43	DES-1	61,68ab	1,96ab	63,70a	2,67cd	2,65a	287g	1,51c	10,34d	99,93ef
	DES-2	65,16c	2,20cd	79,28d	2,70cd	2,87c	201d	1,45bc	9,49cbc	99,87ef
	DES-3	60,91ab	2,33e	76,81cd	2,79d	2,70ab	228f	1,45bc	9,56c	99,83e
	DES-4	60,76a	2,30e	76,16c	2,97f	2,86c	217e	1,44bc	10,39d	99,90ef
	DES-5	63,45bc	2,26de	76,59cd	2,54c	2,79bc	218ef	1,42bc	9,30ab	99,97f
	DES-6	60,29a	2,13c	69,37b	2,66cd	2,61a	210de	1,44bc	9,10a	99,96f
	Soda-1	86,28de	2,02b	87,11f	2,31b	3,83d	109c	1,34ab	22,21f	99,09c
	Soda-2	89,76f	1,89a	83,71e	2,00a	4,19f	73b	1,29a	29,31h	97,74a
	Kraft-1	83,79d	1,90a	78,61cd	1,94a	4,05e	75b	1,27a	18,81e	99,50d
	Kraft-2	86,81e	2,03b	88,26f	1,93a	3,97e	52a	1,34ab	24,83g	98,53b

*The same letter in the columns denotes no statistically significant differences between the groups.

In the unbeaten pulps, comparable air permeability values were determined in DES-6 pulp. This can be explained by the high ° SR value of the unbeaten DES-6 pulp sample

(26° SR). The air permeability of paper decreases with increasing beating levels due to the reduction of the porous areas in the paper (Gulsoy and Eroglu 2011b). Beaten samples of the DES pulps exhibited higher air permeability values than the soda and kraft pulps (p <0,05). At all freeness levels of the DES pulps, the bulk of the handsheets was lower than with the soda and kraft pulps. This demonstrated that the DES pulp fibers had lower bonding ability than traditional ones. In the DES pulp samples, the effect on air permeability and bulk of the ChCl amount in the cooking liquor and the cooking time were statistically significant (p <0,05). Choi *et al*. (2016a) reported that the bulk of TMP handsheets decreased with DES treatment. Another study (Choi *et al*. 2016b) noted that the bulk of BCTMP and BKP handsheets increased with DES treatment.

As shown in Table 5, the DES pulps had lower brightness and higher opacity than the traditional pulps. The low brightness values of the DES pulps can be ascribed to their high kappa numbers (Table 4). Another possible explanation could be the precipitation of lignin dissolving back onto fibers due to the high cooking temperature during DES pulping. The brightness of the DES pulps decreased with increasing amounts of ChCl in the DES cooking liquor and cooking time (Table 5). In the DES pulp samples, the effects of the ChCl amount in the cooking liquor and the cooking time on opacity were statistically insignificant (p >0,05). Choi *et al*. (2016a) reported that lactic acid and betaine DES treatment did not affect the optical properties of TMP handsheets. The brightness of kraft pulp was observed to increase with DES treatment (Škulcová *et al.* 2017). Jablonsky *et al*. (2018) noted 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.

CONCLUSIONS

During the last decades, many studies have been focused on using deep eutectic solvents in the delignification of several lignocellulosic materials. These studies are promising for future practical applications in pulping. Moreover, the alternative solvent in DES pulping is biodegradable, environmentally friendly, and greener than the traditional pulping chemicals. Based on the results, it is clear that the DES pulps were comparable to the kraft and soda pulps in terms of pulp yield, reject, kappa number, pulp viscosity, stretch, and TEA properties. Increasing the ChCl amount and cooking time boosted the strength properties of the DES pulps. Consequently, the use of DESs in new laboratory and industrial applications will increase in the near future, and DESs may prove to be a viable alternative to traditional pulping.

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