Deep Eutectic Solvent Delignification: Impact of Initial Lignin

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This study aimed to resolve the issue of the lack of detailed understanding of the effect of initial lignin content in hardwood kraft pulps on pulp delignification by deep eutectic solvents. The authors used Kappa number of the concerned pulp, intrinsic viscosity, and selectivity and efficiency of delignification as the parameters of the effect. The pulp (50 g oven dry pulp) was treated with four different DESs systems based on choline chloride with lactic acid (1:9), oxalic acid (1:1), malic acid (1:1), and system alanine:lactic acid (1:9); the results were compared to those reached by oxygen delignification. The results showed that the pulp with a higher initial lignin content had a greater fraction of easily removed lignin fragments.

Keywords: Deep eutectic solvents; Delignification; Oxygen delignification; Pulp

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INTRODUCTION

Valorisation is a key component of an economic and environmental lignocellulosic biorefinery (Jablonský *et al.* 2015; Šurina *et al.* 2015). Many studies during recent decades have focused on new modes of pulp processing. Many kraft pulp mills use oxygen delignification before bleaching to reduce the amount of chlorinated organic compounds in the bleach plant effluent (Springer and McSweeny 1993). The response variables following oxygen delignification have been found to depend upon the cooking conditions applied in the digester.

Extending conventional oxygen treatments to remove more than 50% of the residual pulp lignin would further decrease bleach chemical demands and increase environmental benefits (Allison and McGrouther 1995). To achieve higher delignification degrees of pulp without its deterioration, it has been suggested to conduct either preliminary lignin activation by means of chemicals with higher oxidation potential than oxygen or perform delignification in two stages (Danielewicz and Surma-Ślusarska 2006). The Kappa number *versus* time data could be fit to a classical power law model, indicative of lignin fragmentation occurring by an infinite number of parallel first order reactions (Schöön 1982). There was a systematic increase in the oxygen delignification rate, as measured by a reduction in the Kappa number and an increase in the rate constant, with decreasing brownstock pulp yield in the digester. The pulp selectivity, measured as the change in pulp viscosity with changes in Kappa number, increased with increasing pulp yield until reaching a maximum. Some treatment methods require extreme conditions such as high temperatures and pressures, or bases and special facilities. In addition, most methods that have been employed are not "green". For this reason, more efficient methods of pretreatment/fractionation in terms of reducing energy intensity and technology simplifying must be sought. One of the promising technologies is the use of deep eutectic solvents (DESs). These DESs are referred to as "green" solvents. These solvents can be used to dissolve lignocellulosic biomass or individual components of biomass such as lignin (Francisco *et al.* 2012). The DESs have promising potential application in the pulp, paper, and recycling industries. Along with advantages of their low price and simple preparation, DESs are considered green solvents due to their biodegradability and biocompatibility. Several papers describe delignification of different biomasses by DESs, *e.g.* fractionation of biomass from wheat straw (de Dios 2013; Jablonský *et al.* 2015; Škulcová *et al.* 2016a), rice straw (Kumar *et al.* 2016), pine wood (de Dios 2013), and thermomechanical pulp (TMP) (Choi *et al.* 2016). A limiting factor for the use of DESs is their viscosity. To accomplish delignification, the penetration of the solvent into the inner structure of the materials is of importance. To improve the penetration of liquid into the solid material, the use of ultrasound or increasing hydro-module *via* added water (Škulcová *et al.* 2016b) can be applied.

The objective of the presented study is to experimentally investigate the effect of initial content of lignin in pulp on the response of the pulps to low consistency deep eutectic solvent delignification, characterize and quantify the effects of delignification by DESs, and to compare the results obtained with those applying oxygen delignification.

EXPERIMENTAL

Materials

Evaluation of solubility of cellulose in DES reagent

All of the chemicals were purchased from Sigma Aldrich (Bratislava, Slovakia). The solutions were stirred in a water bath to form a homogeneous liquid. Specific solubility tests were performed using pure cellulose (Whatman paper, Sigma Aldrich, Slovakia) in the DES reagents. In 50 mL glass bottles, 0.5 g of the respective component was added separately into 20 mL of DES reagent and then incubated at 60 °C for 2 h. The samples were filtered through preweighed glass fiber filters and dried at 50 °C for overnight. The weight of dried residual solid components was calculated in order to evaluate the % solubility in the DES reagent.

Pulp characterization

The Kappa number of the pulp, determined according to the TAPPI T236 (1996) standard, was used to estimate the lignin content. The intrinsic viscosity of the pulp was used to estimate degree of polymerization (DP) of the cellulose within the pulp fiber. The measurements were performed by dissolving the pulp in cupriethylene diamine solution, and then measuring the elution times in a capillary viscometer (Vistec, Praha, Czech Republic) at constant temperature. To estimate the amount of scissions, the degree of polymerization of the carbohydrates was calculated from intrinsic viscosity using the Mark-Houwink equation (Eq. 1), where ($[\eta]$) is the intrinsic viscosity (mL/g) of pulp (Rydholm 1965):

$$DP^{0.905} = 0.75\,[\eta] \qquad (1)$$

The cellulose chain scission number (CS) was calculated by applying the following equation, Eq. 2 (Lindholm 1990),

$$CS = \frac{DP_0 - DP_t}{DP_t} \qquad (2)$$

where CS is the cellulose chain scission number and DP_0 and DP_t are the degree of polymerization before and after scissions, respectively.

The selectivity of delignification (Slc_κ, %) expressed as a decrease in Kappa number, κ, on the unit change of the intrinsic viscosity was calculated from Eq. 3,

$$Slc_\kappa\,(\%) = \frac{\kappa_0 - \kappa_t}{[\eta]_0 - [\eta]_t}\,x\,100 \qquad (3)$$

where κ_0 is the initial Kappa number of pulp, κ_t is the cellulose chain scission number Kappa number of pulp after delignification, $[\eta]_0$ is the initial intrinsic viscosity of pulp (mL/g), $[\eta]_t$ is the intrinsic viscosity of pulp after delignification (mL/g).

The efficiency of delignification (Efc_κ) expressed as a decrease in Kappa number on the unit change of the initial Kappa number of pulp was calculated from Eq. 4:

$$Efc_\kappa = \frac{\kappa_0 - \kappa_t}{\kappa_0}\,x\,100\,\% \qquad (4)$$

The pulps in this investigation originated from kraft cooks of hardwood and oxygen delignified pulps using mainly beech wood. Table 1 shows the pulp designations and properties.

Table 1. Analysis of Pulp Properties

Pulp Designation	Kappa No.	Viscosity (mL/g)	Initial Degree of Polymerization
Kraft pulp 1 (industrial)*[1]	21.7	789	1157
Oxygen delignified pulp 1 (industrial)*[1]	11.8	569	805
Kraft pulp 2 (industrial)*[2]	14.3	851	1258
* [1]Mondi SCP, Ružomberok Slovakia; [2]BUKÓZA HOLDING, a. s., Hencovce, Slovakia			

Deep eutectic solvent delignification

All of the chemicals were purchased from Sigma Aldrich (Bratislava, Slovakia). The solutions were stirred in a water bath to form a homogeneous liquid. Pulp (50 g absolute dry weight, STN EN ISO 638 (2009)) and 115 mL water were added into individual DESs at a ratio of 1:20 (wt/wt). The consistency of pulp was 4.8%. The DESs, choline chloride, and lactic acid (1:9), oxalic acid (1:1), malic acid (1:1), and system alanine:lactic acid (1:9) were used, and delignification was carried out for 1 h in a drying oven with a preset temperature of 60 °C. The delignified pulp was washed with deionized water.

RESULTS AND DISCUSSION

The cellulose was stirred into 10 DES at 60 °C to perform an initial screening of DESs ability to dissolve cellulose. Table 2 shows the maximum solubilities of cellulose in DES. The ChCl and lactic acid at any molar ratio, and ChCl:malic acid; ChCL:oxalic acid dehydrate had a null cellulose dissolving ability. The ChCl:malonic acid, ChCl:glycerol, betaine:lactic acid, and ChCl:glycolic acid showed relatively high cellulose solubilities (4.2 % wt; 4.9 % wt; 1.5 % wt; 0.5 % wt, respectively). The present research was focused on the application of DESs for delignification of pulp. In other experiments, DESs with the least solubility of cellulose to prevent degradation during delignification of pulp were used.

Table 2. Solubility of Cellulose in DESs

DES	Molar ratio	Solubility of cellulose (% wt)
ChCl: malonic acid	1:1	4.2
betaine: lactic acid	1:2	1.5
ChCl: glycolic acid	1:3	0.5
ChCl: malic acid	1:1	0
alanine: lactic acid	1:9	0.2
ChCl:glycerol	1:2	4.9
ChCl:oxalic acid dihydrate	1:1	0
ChCl: lactic acid	1:5	0
ChCl: lactic acid	1:9	0
ChCl:lactic acid	1:10	0

The characterization and effect on pulp properties after DES delignification are listed in Table 3. In this work, pulps with different initial Kappa numbers: 21.7, 11.8, and 14.3 were used. Options to replace oxygen delignification for selected DESs were investigated. The pulp with κ_0 = 21.7 subjected to oxygen delignification (Mondi SCP Kraft pulping, realized in a pulp mill) reached κ_t = 11.8. This means that the efficiency of delignification was 45.6%. From the viewpoint of pulp degradation, the original degree of polymerization (1157) decreased to 805 units, which represented a 30.4% decrease. The cellulose chain scission number, expressing the degradation, was 0.436.

The effects of four different DES were investigated, and the efficiency of delignification ranged from 37.8% to 43.3%. The order by the delignification efficiency growth was as follows: ChCl:lactic acid (37.8%) > ChCl:oxalic acid (38.7%) > ChCl:malic acid (39.2%) > Alanine:lactic acid (43.3%). The results indicated that the application of DESs might be an interesting alternative to oxygen delignification of pulp following kraft cooks. This conclusion was also supported by the quantity selectivity of delignification, Slc_κ for which the order of selectivity was as follows: alanine:lactic acid (206.48%) < ChCl:lactic acid < ChCl:malic acid < ChCl:oxalic acid. The lowest selectivity was reached by oxygen delignification (4.48%).

When working with DESs, degradation of the pulp chain occurs. However, a decrease in the degree of polymerization was only 227 units *versus* kraft pulp 1, which represented a maximum decrease of 19.6%. To compare a level of degradation, the chain scission number may be used, ranging from 0.243 (ChCl:oxalic acid) to 0.006 (alanine:lactic acid). The results obtained document that DESs caused a lower degree of pulp chain degradation than that for oxygen delignification. Of the DESs applied, the highest level of degradation was identified for ChCl:oxalic acid.

Table 3. Characterization and Effect on Pulp Properties after DES Delignification

	Kappa No.	Viscosity (mL/g)	DP	CS	Slc_{κ} (%)	Efc_{κ} (%)
Kraft pulp 1 *[1]	21.7	789	1157	-	-	-
ChCl:oxalic acid	13.3	648	930	0.243	5.96	38.7
ChCl:malic acid	13.2	772	1130	0.023	52.02	39.2
alanine:lactic acid	12.3	784	1149	0.006	206.48	43.3
ChCl:lactic acid	13.5	775	1134	0.020	58.27	37.8
Oxygen delignified pulp 1 (industrial) *[1]	11.8	569	805	0.436	4.48	45.6
Oxygen delignified pulp 1 (industrial) *[1]	11.8	569	805	-	-	-
ChCl:oxalic acid	11.7	185	233	2.450	0.03	0.8
ChCl:malic acid	10.4	406	554	0.452	0.86	11.9
alanine:lactic acid	10.4	532	747	0.077	3.79	11.9
ChCl:lactic acid	10.1	429	590	0.365	1.22	14.4
Kraft pulp 2 (industrial)*[2]	14.3	851	1258	-	-	-
ChCl:oxalic acid	11.1	490	683	0.842	0.88	22.4
ChCl:malic acid	12.3	780	1113	0.131	2.82	14.0
alanine:lactic acid	11.2	800	1160	0.084	6.01	21.7
ChCl:lactic acid	11.8	745	1085	0.160	2.34	17.5

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In the following experiment, the authors used the oxygen delignified pulp I (Kappa n. 11.8; DP 569) as an initial pulp. The delignification by DESs, following oxygen delignification, led to a maximal decrease in lignin content by 1.7 Kappa units, which represents the efficiency of delignification varying from 14.4% to 0.8% for individual DESs. The highest efficiency was reached applying ChCl:lactic acid (14.4%), and the lowest using ChCl:oxalic acid (0.8%). When applying ChCl:malic acid and alanine:lactic acid, the efficiency was Efc_{κ} = 11.9%. As for degradation, the lowest level was reached using alanine:lactic acid (decrease of 37 units of *DP*; *CS* = 0.077), followed by ChCl:lactic acid (decrease of 140 units of *DP*, *CS* = 0.365), and ChCl:malic acid (decrease of 163 units of *DP*; *CS* = 0.452). The use of ChCl:oxalic acid caused the highest level of degradation (decrease of 384 units of *DP*, *CS* = 2.450).

Kraft pulp 2 (industrial) has a Kappa number of 14.3 and *DP* of 1258. Due to the DESs treatment, the efficiency of delignification was for individual DESs as follows: ChCl:malic acid (14.0%) > ChCl:lactic acid (17.5%) > alanine:lactic acid (21.7%) > ChCl:oxalic acid (22.4%). As for the degradation of the pulp chain, when expressed as CS, it ranged from 0.088 to 0.842, the smallest value was reached using alanine:lactic acid. From the viewpoint of selectivity of delignification, the most suitable seemed to be alanine:lactic acid (Slc_{κ} 6.01%), followed by ChCl:malic acid (2.82%), ChCl:lactic acid (2.34%), and ChCl:oxalic acid (0.88%).

It has been shown that pulp with a higher initial Kappa number or lignin content would possess a greater fraction of easily removed lignin fragments. The amount of lignin to be removed is much higher than in the case of conventional pulps with a Kappa number of 10. In contrast, the residual lignin in the pulp of a high Kappa number may be less altered chemically, and thus easier to remove.

At the same time, it was documented that taking the selectivity and efficiency into account, the best performance was exhibited by the DES composed of alanine and lactic acid. This DES even at varying content of lignin in the treated pulp provided the best results within delignification, not altering noticeably the pulp chain. A recent study (Soares *et al.* 2017) revealed that the lignin solubility in aqueous solution of DES results from a hydrotropic mechanism, which was confirmed by dynamic light scattering analysis. Both hydrogen bond donors and acceptors play a significant role in the solubilisation of lignin with a possible synergistic effect between the DES and starting material (Soares *et al.* 2017). Another important factor is the acid strength. These factors influence depolymerisation of individual components and thus affect the efficiency of DES (Jablonský *et al.* 2015). Soares *et al.* (2017) found that the solubility of a model compound (syringic acid) was affected by the hydrogen bond acceptors, increasing in the sequence of ChCl < proline < betaine < urea, independently of the carboxylic acids. Based on the structure of compounds investigated by Soares *et al.* (2017) it can be rationalized that due to hydrotropic mechanism of lignin dissolution, the system alanin: lactic acid has a more profound effect on lignin removal than the other examined DESs.

In a study by Choi *et al.* (2016) the effect of a deep eutectic solvent on the processing properties (tear, tensile, and burst indices) of the TMP fibers and handsheets was investigated. The DES was prepared by mixing lactic acid and betaine at the different molar ratio (2:1 and 5:1), and the time of delignification was 24 h. The lignin was partially removed from the TMP fiber and the efficiency of lignin removal was less than 10%.

When comparing the authors' results with those obtained by other authors, it was obvious that the choice of eutectic mixture greatly influenced both the efficiency and selectivity of the delignification process. Similarly, as in the case of oxygen delignification, it was established that a higher lignin content in the initial pulp has an impact on the selectivity. It can be predicted that in the future some DESs could substitute oxygen for delignification, keeping the efficiency of lignin removal at approximately 45%. An advantage of such substitution lies also in a smaller extent of cellulose chain degradation and thus better selectivity of delignification process.

The question of lignin solubility was investigated in several works. Yiin *et al.* (2016) found that increasing water content in the system malic acid:sucrose:water (MSW 1:1:1; MSW 1:1:2; MSW 1:1:3) and temperature (from 60 °C to 100 °C), the lignin solubility increases. An analogous effect was also observed for other DESs systems (MSW 1:1:10; MSW 1:2:10; MSW 1:3:10); as well for the system malic acid:monosodium glutamate:water (MMSGW 3:1:1; MMSGW 3:1:2; MMSGW 3:1:10). The effect of water on lignin solubility was supported also by Kumar *et al.* (2016) together with a remarkable effect of solids loading on biomass pretreatment– the higher solids loading, the lower lignin solubility. De Dios (2013) identified that the solubility of an individual DES depends on the biomass type. This effect was explained by the different structure and type of lignin found in each kind of biomass. For pine wood, the following trend has been found for the solubilisation of lignin: 2-chloroethyltrimethylammonium chloride:lactic acid (1:5) > tetramethylammonium chloride:lactic acid (1:3) > ChCl:lactic acid (1:9) ≈ ChCl:oxalic acid (1:1) > 2-chloroethyltrimethylammonium chloride:lactic acid (1:2) > tetramethylammonium chloride:lactic acid (1:2) > ChCl:lactic acid (1:2) > ChCl:malic acid (1:1). In the case of wheat straw, the trend is as follows: tetramethylammonium chloride:lactic acid (1:3) >

tetramethylammonium chloride:lactic acid (1:2) > ChCl:oxalic acid (1:1) 2-chloroethyltrimethylammonium chloride:lactic acid (1:2) > ChCl:lactic acid (1:9) > ChCl:lactic acid (1:2) > ChCl:malic acid (1:1) > 2-chloroethyltrimethylammonium chloride:lactic acid (1:5). The delignification of rice straw *via* the ChCl:lactic acid (1:5) pretreatment resulted in a decrease of lignin content from 9.1% to 3.8%, with no substantial effect on polysaccharide fraction. In Jablonský *et al.* (2015), wheat straw was pre-treated with six different DES systems composed of choline chloride with urea (1:2), malonic acid (1:1), lactic (1:9; 1:10), malic (1:1), and oxalic acid (1:1). It was shown that the DESs themselves cannot selectively remove lignin from biomass. Research on lignocellulosic biomass pretreatment or delignification of pulp by DESs is still in its early stage. Much effort is needed to evaluate the feasibility of DESs on pretreatment or delignification.

Recycling of DES

The benefits of using DESs as a reaction medium are highlighted by the fact that they are biodegradable, non-toxic, recyclable, and can easily be prepared using cheap raw materials. Lignin dissolved in DES is isolated as a solid substance due to the action of an anti-solvent (water, ethanol). Subsequent evaporation of anti-solvent or simple freeze-drying of the washed solutions leads to recovery of DES for further use. This DES recycling technique has been performed by several authors (Francisco *et al.* 2012; de Dios 2013; Jeong *et al.* 2015). DES can be recovered from the water by adding an aprotic solvent non-displaying hydrogen bonding (e.g. acetone) which causes DES precipitation. Subsequent to DES separation off as a solid it can be turned to liquid by heating and reused. The only energy requirement was then the separation of acetone from water by distillation, allowing also for the water and the acetone to be reused (Kroon *et al.* 2013).

Comparison oxygen delignification and DES delignification

The goal of oxygen delignification is to reduce the lignin content in unbleached pulp before using more expensive bleaching chemicals. Oxygen delignification can be done in medium or high consistency. A high consistency oxygen stage is more expensive and more difficult to process. Medium consistency oxygen delignification can be performed as a single- or two-stage system. Today it is a standard stage in the production of bleached chemical pulp. The conditions of oxygen delignification in a two- or three-stage process are shown in Table 4.

Table 4. Conditions for Oxygen Delignification

Reference	Stage	Temperature (°C)	Pressure (MPa)	Time (min)
Colodette *et al*. 2007	First stage	100	0.6	15
	Second stage	105	0.5	45
Venson *et al*. 2015	First stage	90 – 100 – 115	0.39	60
	Second stage	100	0.39	45
Jafari *et al.* 2014	First stage	85	0.7	30
	Second stage	95	0.7	60
Draude *et al.* 2001	First stage	90	0.3	40
	Second stage	96	1.0	40
Akim *et al.* 2001	First stage	90	0.68	20
	Second stage	90	0.68	20
	Third stage	90	0.68	20

CONCLUSION

1. Deep eutectic solvent (DES) delignification has potential to replace oxygen delignification after kraft pulping.
2. It has been shown that a pulp with a higher initial Kappa number or lignin content possessed a greater fraction of easily removed lignin fragments.
3. Among the investigated DES (ChCl:oxalic acid; ChCl:malic acid; alanine:lactic acid; ChCl:lactic acid), the most suitable seemed to be a treatment using the alanine:lactic acid system, which provided relatively high delignification efficiency and selectivity.

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