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DELIGNIFICATION OF PULP USING DEEP EUTECTIC SOLVENTS

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Abstract

Lot of works during the last decades have been focused on the new modes of pulp processing. One promising technology is the use of deep eutectic solvents. Deep eutectic solvents (DES) have opportunities to open new paths in the field of delignification methods.

This study was conducted to investigate the effects of deep eutectic solvent treatment on physical and chemical properties of delignified pulp. In the following experiment we used as an initial pulp the kraft pulp (Kappa No. 21.7; Degree of polymerization 1157). The pulp was treated with two different DES system based on choline chloride with lactic acid (1 : 9), and system alanine : lactic acid (1 : 9). The efficiency of delignification expressed as a decrease in kappa number on the unit change of the initial kappa number of pulp.

The order by the delignification efficiency growth is as follows: choline chloride : lactic acid (37.8%) > alanine : lactic acid (43.3%). During delignification by DESs, a degradation of pulp chain occurs, however a decrease in degree of polymerization was only 23 units versus kraft unbleached pulp, which represents maximum decrease by 2%. Delignified pulp with DESs has a brightness 34% and unbleached pulp achieved brightness 27%, therefore, it achieves the increase in brightness by 26%.The physical strength properties of DES delignified pulps were assessed in terms of tensile, tear and burst index and stiffness. Application of deep eutectic solvents were achieved to reduce tensile index by 13.2%, burst index by 14.3% and a tear index by 9.8%, and the pulp stiffness was increased by 4% again the unbleached pulp.

The results indicate that application of DESs might be an interesting alternative to oxygen delignification of pulp following kraft cooks.

***Key words**: Delignification, Deep eutectic solvents, Green chemistry, Pulp.*

1. Introduction

Recently, many studies concerning the environmental impact of deep eutectic solvents have shown that despite their unique properties and clear advantages in an ever wide range of applications and processes (Florindo *et al.,* [1]). Valorisation is a key component of an economic and environmental lignocellulosic biorefinery (Jablonsky *et al.,* [2]; Surina *et al.,* [3]). Lots of works during the last decades has been focused on the new pulp processing. Many kraft pulp mills are using oxygen delignification before bleaching to reduce the amount of chlorinated organic compounds in the bleach plant effluent (Springer and MsSweenyr, [4]). 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, [5]). The reasons for the limit of lignin removal during oxygen delignification are still under debate (Gellerstedt and Heuts, [6]; Shin *et al.,* [7]; Kontturi *et al.,* [8]), but the most explicit evidence suggests that covalent bonds between lignin and carbohydrates hinder the selective removal of lignin after a certain point (Chirat and Lachenal, [9]; Axelsson *et al.,* [10]). Independent of developing a more efficient result from oxygen delignification, exist of the field of research which focus on improving the strength properties of fibres (Kontturi *et al.,* [8]).

DESs have been also applied for the pretreatment and fractionation of lignocellulosic biomass. Interestingly, Francisco and co-workers [11] found that lignin had relatively high solubility in DES systems, especially in acidic DESs, being the solubility of cellulose and starch small or null in most of the cases. Kroon *et al.,* [12], tested the solubility of lignin, starch and cellulose for selected low transition temperature mixtures. Kroon *et al.,* [12] observed very low solubility of cellulose in selected mixtures. In addition, Jablonský *et al.,* [2], tested the delignification of wheat straw by choline chloride based DESs at 60 °C for 24 h, and showed that the DESs cannot selectively remove lignin from biomass. Recently, Kumar *et al.,* [13], studied the pretreatment of rice straw using natural DESs (lactic acid/betaine, lactic acid/choline chloride). The best delignification effect was achieved by lactic acid/choline chloride at molar ratio of 5 : 1 at 60 °C for 12 h. The results of the other studies indicated that DESs could be used as the promising media for delignification.

2. Materials and Methods

Choline chloride (ChCl) (≥ 98% mass fraction purity) was purchased from Sigma-Aldrich and was dried under vacuum prior to use. Lactic acid (90% solution) and alanine were purchased from Sigma-Aldrich and used as supplied.

2.1 Pulp characterization

The hardwood kraft pulp was obtained from Mondi SCP, Ružomberok, Slovakia. Characterization chemical properties of pulp before and after DES delignification are listed in Table 2 and Table 3. The Kappa number of the pulp was used to estimate the lignin content, and was determined according to Tappi standard method T-236. The viscosity of the pulp was used to estimate the intrinsic viscosity or degree of polymerization (DP) of the cellulose within the pulp fibre. The measurements were determined by dissolving the pulp in cupriethylene diamine solution, and then measuring the elution times in a capillary viscometer at constant temperature.

In order to estimate the amount of scissions, the degree of polymerization (DP) of the carbohydrates was calculated from intrinsic viscosity using Mark-Houwink equation, where ([η]) is the intrinsic viscosity (ml/g) of pulp (Rydholm [14]).

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

Freeness of beaten pulps was measured according to TAPPI T227 om-99. The handsheet for testing of papermaking properties was formed according to TAPPI T205 sp-02. The handsheet of each beating condition was measured for optical and strength properties such as brightness (TAPPI T452 om-98), tensile strength (TAPPI T494 om-96), tearing strength (TAPPI T414 om-98), bursting strength (TAPPI T407 om-97).

2.2 Preparation and characterization of DESs

Deep eutectic solvents were prepared by heating method. The heating method is based on mixing the two components, which are then heated at 70 °C under constant stirring until a homogeneous liquid is formed. Physicochemical properties of deep eutectic solvents were measured in different temperature ranges. The viscosity of the deep eutectic solvents reagent was measured using Ubbelohde viscometer in range 28 - 90 °C. The density of DESs was determined by specific gravity bottles. Table 1 shows prepared DESs and some of them properties.

Table 1. Deep eutectic solvents

Sample	HBA : HBD	Molar ratio	Density [g/cm³] at 25 °C	Viscosity [mPa·s] at 28 °C
DES1	ChCl : lactic acid	1:9	1217	70.9
DES2	Alanine : lactic acid	1:9	1230	168.0

Legend: ChCl - choline chloride, HBA - hydrogen bond acceptor, HBD - hydrogen bond donor.

2.3 Evaluation of deep eutectic delignification of pulp

Selectivity of bleaching expressed as an increase in brightness on the unit change of the intrinsic viscosity:

$$Slc_B \frac{B_t - B_0}{[\eta]_0 - [\eta]_t} x100\ \% \quad (2)$$

Where: B_0 - initial brightness of pulp; B_t - brightness of pulp after delignification; $[\eta]_0$ - initial intrinsic viscosity of pulp; $[\eta]_t$ - intrinsic viscosity of pulp after delignification.

The selectivity of delignification (Slc_K) expressed as a decrease in kappa number on the unit change of the intrinsic viscosity was calculated from following equation:

$$Slc_K \frac{\kappa_0 - \kappa_t}{[\eta]_0 - [\eta]_t} x100\ \% \quad (3)$$

Where: K_0 - initial kappa number of pulp; K_t - kappa number of pulp after delignification; $[\eta]_0$ - initial intrinsic viscosity of pulp; $[\eta]_t$ - intrinsic viscosity of pulp after delignification.

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 following equation:

$$Efc_{\kappa} \frac{\kappa_0 - \kappa_t}{\kappa_0} x100\ \% \quad (4)$$

Where: K_0 - initial kappa number of pulp; K_t - kappa number of pulp after delignification.

3. Results and Discussion

3.1 Physicochemical properties of deep eutectic solvents

In this report we presented the research work on preparation and characterization of two deep eutectic solvents.

3.1.1 Viscosity

Viscosity data can be used for selection of optimal ratio of hydrogen bond donor and acceptor. In general, viscosity of DES is mainly affected by the chemical structure of DES such as type of HBD and HBA, temperature and water content. Viscosity is also important parameter for industrial applications, and is a critical property that must be accounted for equipment design and fluid flow calculation. These DESs systems are liquid at room temperature but their viscosity can be so high that there is a problem with flow and penetration. Preheating is a very simple technique that can be used to reduce the viscosity. Viscosities are decreasing with increasing temperature as show Figure 1 because of the weakening of van der Waals and hydrogen bond interactions. Depending on the molecular interactions are viscosities of DESs much higher than some conventional organic solvents. The obtained data shows that the DESs composed of choline chloride and lactic acid have lower viscosity values than the remaining DES (alanine : lactic acid), most likely due to the length of their chains in HBA, because it molar ratio is the same (1 : 9).

3.1.2 Density

The experimental density results for the samples of DESs as a function of temperature are plotted in Figure 2. The obtained data shows that the DESs composed of choline chloride and lactic acid have lower density values than the remaining DES (alanine : lactic acid). As observed, the density decreases linearly with temperature for DESs in the whole temperature range studied, and a linear equation was used to express the correlation with the temperature:

$$\rho = a + bT \quad (5)$$

Where: ρ corresponds to density in kg m^{-3}; T is the temperature in ^{0}C and; a and b are the fitting parameters.

The a and b values derived from e.q. 5 for the studied DESs are presented in Table 2.

3.1.3 pH properties

pH is physical property that has essential impact on reaction. pH is depended on hydrogen bond donor and it is decreasing with increased temperature. DESs based on lactic acid and choline chloride or alanine are non-toxic and eco-friendly mixtures and it is very important to know their pH value. The pH values indicate that this type of solvents can be used in industrial application where acidic medium is needed (Figure 3).

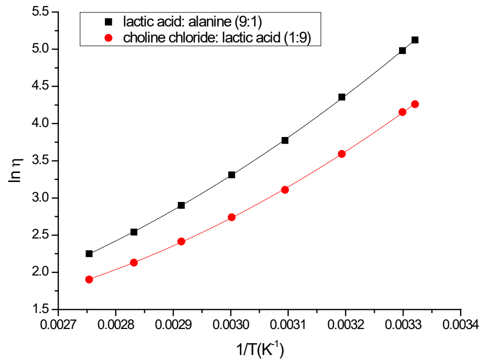

Figure 1. Effect of temperature on the viscosity of DESs in range 28 - 90 ^{0}C

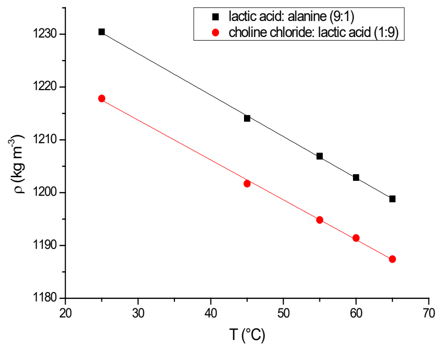

Figure 2. Densities of lactic acid based DESs as a function of temperature from 25 - 65 ^{0}C

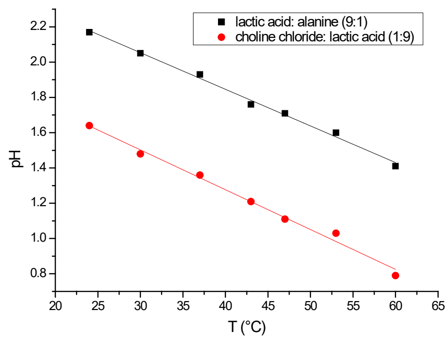

Figure 3. pH for lactic acid based DESs (c = 0.5 mol/L) as a function of temperature from 23 - 60 ^{0}C

Table 2. Values of parameters *a* and b for three equations which describe viscosity, density and pH of studied DES

DES	ln(η) = a*exp(b/T)		ρ = a + bT		*pH = a + bT	
	T € < 28; 90 > ºC		T € < 25; 65 > ºC		T € < 23; 60 > ºC	
	a	b	a	b	a	b
lactic acid : alanine (9 : 1)	45.45*10-3	1425.11	1249.90	- 78.56*10^{-3}	2.67	- 20.77*10^{-3}
choline chloride : lactic acid (1 : 9)	38.93*10^{-3}	1415.48	1236.41	- 75.53*10^{-3}	2.18	- 22.58*10^{-3}

* pH determination was measured for DES concentration c = 0.5 mol/L

3.1.4 DES delignification

The original pulp had a Kappa number equal to 21.7. After DES delignification, the Kappa number decreased to 13.5 for the ChCl: lactic acid system and to 12.3 for alanine: lactic acid. The order by the delignification efficiency (Efc_K) growth is as follows: choline chloride: lactic acid (37.8%) > alanine: lactic acid (43.3%). During delignification using DESs, a degradation of pulp chain occurs, however a decrease in degree of polymerization was only 23 units versus kraft unbleached pulp, which represents maximum decrease by 2%. Delignified pulp with DESs has brightness 34% and unbleached pulp achieved brightness 27%, therefore, it achieves the increase in brightness by 26%. The selectivity parameter of bleaching for the alanine : lactic acid system was 127.7%, and for ChCl : lactic acid was 50.2%. The selectivity of delignification (SlcK) expressed as a decrease in the kappa number on the unit change of intrinsic viscosity was highest for alanine : lactic acid (206.5%) than for choline chloride : lactic acid was 58.3%. Based on the parameters of selectivity, the better system was alanine : lactic acid. This is consistent with the fact that if the lignin is removed, also the brightness should be increased. DES based on choline chloride: lactic acid degrades the cellulosic chain very slightly compared to alanine : lactic acid DES. The selectivity of delignification has not the effect on direct enhancement of the strength properties of paper (Table 3).

Indeed, there are several factors which dictate the strength properties of a fiber network. The degree of polymerization of the cellulose in the fibres, represented by viscosity, is only one of them (Kontturi *et al.,* [8]). Although the fibre strength is an important property of quality, the strength of the fibre network is also strongly influenced by the bonding between the fibres (Rydholm, [14]). Therefore, it is very important to monitor the impact of delignification on the mechanical properties of the fibres. The physical strength properties of delignified pulps using DESs were assessed in terms of tensile, tear and burst index and stiffness (Table 4). Application of deep eutectic solvents were achieved to reduce tensile index by 13.2%, burst index by 14.3% and tear index by 9.8%. The pulp stiffness was increased by 4% against the unbleached pulp.

Table 3. Characterization chemical properties of pulp before and after DES delignification

Parameters	Kappa n.	Viscosity (mL/g)	Degree of polymerization	Brightness (%)	Slc_B	Slc_K	Efc_K
Kraft pulp	21.7	789	1157	27.02	-	-	-
DES1: ChCl : lactic acid	13.5	775	1134	34.05	50.21	58.27	37.8
DES2: alanine : lactic acid	12.3	784	1149	33.38	127.70	206.48	43.3

Table 4. Mechanical properties of kraft pulps after DES treatment

Sample	Beating [°SR]	Tensile index [Nm/g]	Burst index [kPa·m²/g]	Tear index [mN·m²/g]	Stiffness [mN]
Pulp	30	72.02	4.2	7.1	126
DES1	30	62.49	3.6	6.4	131
DES2	30	63.00	3.6	6.6	130

UV-Vis analysis of DES extracted liquor showed a strong peak at 267 nm, suggesting that the extracted solution contains components with aromatic rings (Figures 4 and 5). These prominent peaks correspond to the principle aromatic components of lignin (Kumar *et al.,* [13]).

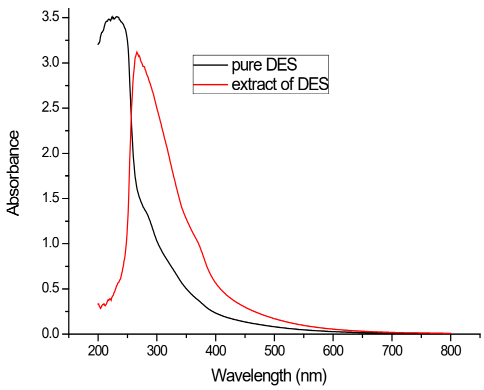

Figure 4. Spectral analysis of extract for DES1 (choline chloride : lactic acid (1 : 9))

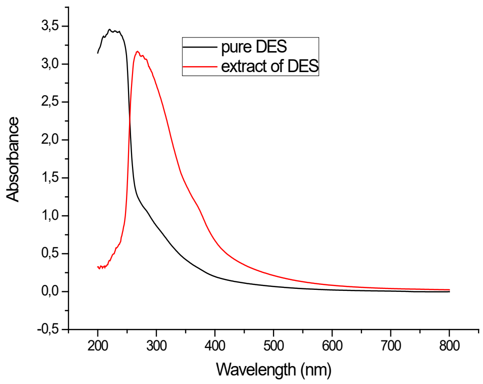

Figure 5. Spectral analysis of extract for DES2 (alanine : lactic acid (1 : 9))

4. Conclusions

- Physical properties (densities, viscosities and pH) were studied for DESs prepared using choline chloride : lactic acid and alanine : lactic acid at the same molar ratio (1 : 9). The obtained data shows that the DESs composed of choline chloride and lactic acid had lower density, viscosity and pH values than the second DES (alanine : lactic acid).

- Actually, it has been documented that due to selectivity and efficiency of delignification, the best DES system is alanine : lactic acid. Obtained results showed that the type of DES influenced on mechanical properties of delignified pulp.

- Results indicate that application of DESs might be an interesting alternative to oxygen delignification of pulp following kraft cooks.

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