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DELIGNIFICATION OF PULP WITH TWO TERNARY DEEP EUTECTIC SOLVENTS: UREA-ACETAMIDE-GLYCEROL AND MALIC ACID-PROLINE-LACTIC ACID

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Abstract

Using deep eutectic solvents (DESs), which ones act as solvent systems, offer an interesting green alternative to conventional technology in materials science, especially in the biomass processing. There is lack of information dealing with the delignification and bleaching effect of DESs in broad-leaved fiber process. This work describes application of various DESs on unbleached pulp, to study the influence of dissolution of lignin and protection of cellulose in the delignification process.

In this work, two ternary deep eutectic solvents (urea-acetamide-glycerol) in molar ratio 1 : 2 : 3 and (malic acid-proline-lactic acid) in molar ratio 1 : 2 : 4 were synthesized and their density was studied in a temperature range of 25 to 75 ^{0}C. Unbleached pulp (Kappa 14) was treated with prepared ternary deep eutectic solvents. The treatment was carried out in a water bath at present temperature of 60 ^{0}C and atmospheric pressure for 2 hours. Solubility tests of cellulose were performed using pure cellulose (Whatman paper) in the DESs 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 ^{0}C for 2 h. The samples were filtered through glass fiber filters and dried at 105 ^{0}C to constant weight. The weight of dried residual solid components was calculated in order to evaluate the % solubility in the DES reagent.

Density of urea-acetamide-glycerol (molar ratio 1 : 2 : 3) decreased with a temperature from 1,220 to 1,199 g/cm^3 and density of malic acid-proline-lactic acid (molar ratio 1 : 2 : 4) decreased from 1,292 to 1,220 g/cm^3. Application of DESs to the lignocellulosic matrix - pulp does not resulted in a significant decrease of lignin content. Deep eutectic solvent (urea-acetamide-glycerol) in molar ratio 1 : 2 : 3 removed 5,4 % and DES (malic acid-proline-lactic acid) in molar ratio 1 : 2 : 4 removed 1.4 % lignin from unbleached pulp. The solubility of cellulose in ternary deep eutectic solvents was zero.

Results show that prepared ternary deep eutectic solvents are able to delignify the pulp. However, the efficiency of delignification is not comparable to that of oxygen delignification. At the same time, used deep eutectic solvents do not cause dissolution of cellulose in pulp fibers.

***Key words**: Ternary deep eutectic solvents, Pulp, Delignification.*

1. Introduction

Current technological processes used to produce fibrous materials from lignocellulosic raw materials require high chemical and energy consumption and cause significant environmental pollution. Oxygen delignification is often used for delignification of kraft pulp before bleaching to reduce the amount of chlorinated organic compounds in the bleach plant effluent (Springer and McSweeny, [1]). Modifying the conventional oxygen delignification, which would reduce the residual lignin content by more than 50 %, would reduce the consumption of bleaching chemicals and improve the environmental aspects of the process (Allison and McGrouther, [2]). The use of deep eutectic solvents (DESs) offers an interesting ”green” alternative to conventional technologies in the pulp industry (Choi *et al.*, [3]). These solvents can be used to dissolve lignocellulosic biomass or individual components of biomass such as lignin (Francisco *et al.,* [4]). The DESs have promising potential application in the treatment of biomass (Jablonsky *et al.,* [5], Kumar *et al.,* [6], Procentese *et al.,* [7], Skulcova *et al.,* [8]), pulp (Jablonsky *et al.,* [9], Skulcova *et al.,* [10]), paper, and recycling industries. DESs have attractive physicochemical properties such as: non-flammability, low vapor pressure, biocompatibility, biodegradability and wide liquid range. Before considering a new solvent for incorporation into an industrial application, a fundamental understanding must be established for the chemical and physical properties of the solvent (Huddleston *et al.,* [11]). Deep eutectic solvents open the way to pulp production at low temperatures and atmospheric pressures. Ternary deep eutectic solvents (TDESs) have been reported in order to increase the DESs range toward their applications (Chemat *et al.,* [12]). One hot topic where TDESs were applied at was CO_2 capturing. Sze *et al.,* [13], reported the use of three carbon dioxide capturing materials that formed TDESs mixtures with choline chloride and glycerol. On the other hand, Dai *et al.,* [14], synthesized TDESs using natural materials, which were plant's primary metabolites materials. Liu *et al.,* [15], synthesized and characterized the properties of several novel TDESs containing zinc halides that can be used both as catalyst and solvent in various catalytic reactions. These contribution studies made a clear evidence that the DESs have great flexibility in forms, synthesis and applications.

Research work on preparation and characterization of two ternary deep eutectic solvents is presented in this report. The effects of these eutectic solvents on biomass components such as lignin and cellulose were investigated. Density and viscosity are one of the most important physical properties of solvents. The accessibility of the lignocellulose material for delignification by DES depends on several factors. The essential factors limiting the access of the fibers are macro and microstructure of the fibers (Wojcak and Pekarovicova, [16]). In the case of solid matrix samples, DESs applications have been limited, especially due to their viscosity.

2. Materials and Methods

2.1 Preparation and characterization of TDESs

Proline, acetamide, DL-malic acid (≥ 99% mass fraction purity) and urea (99.5% mass fraction purity) were purchased from Sigma-Aldrich. Lactic acid (90% solution) was purchased from VWR Chemicals and glycerol (≥ 99% mass fraction purity) was purchased from Centralchem s. r. o. Ternary deep eutectic solvents were prepared by the heating method. Mixtures of the corresponding reagents with required molar ratio were heated and stirred in a water bath at the appropriate temperature (70 - 90 ^{0}C). A homogeneous liquid was obtained and then allowed to be cooled to room temperature. Physicochemical properties of deep eutectic solvents were measured in different temperature ranges. The dynamic viscosity measurement was measured in a rotating viscometer (Brookfield DV 2+) in the temperature range 30 - 90 ^{0}C. Densities were determined with a pycnometer in the range 25 - 75 ^{0}C.

2.2 Evaluation of solubility of cellulose in TDES reagent

Solubility tests of cellulose were performed using pure cellulose (Whatman paper) in the DESs 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 ^{0}C for 2 h. The samples were filtered through glass fiber filters and dried at 105 ^{0}C to constant weight. The weight of dried residual solid components was calculated to evaluate the % solubility in the DES reagent. Table 1 shows prepared DESs and some of their properties.

2.3 Pulp characterization

The hardwood kraft pulp was obtained from MONDI SCP, Ružomberok, Slovakia. Characterization of chemical properties of pulp before and after DES delignification are listed in Table 3 and Table 4. The Kappa number of the pulp was used to estimate the lignin content and was determined according to Technical Association of the Pulp and Paper Industry (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, [17]).

The selectivity of delignification (Slc_{κ}, %) expressed as

Table 1. Properties of prepared DESs

Sample	DES	Molar ratio	Density (kg.m^{-3}) at 25 ^{0}C	Viscosity (mPa.s) at 90 ^{0}C	Solubility of cellulose (% wt)
DES1	Urea : Acetamide : Glycerol	1 : 2 : 3	1220	9.1	0.32
DES2	Malic acid : Proline : Latic acid	1 : 2 : 4	1292	58.4	0.03

a decrease in Kappa number, κ, on the unit change of the intrinsic viscosity was calculated from Eq. 2:

$$\mathrm{Slc}_{\kappa} = \frac{\kappa_0 - \kappa_t}{[\eta]_0 - [\eta]_t} \mathrm{x}100\ \% \qquad (2)$$

Where: κ_0 is the initial Kappa number of pulp, κ_t is the 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. 3:

$$\mathrm{Efc}_{\kappa} = \frac{\kappa_0 - \kappa_t}{\kappa_0} \mathrm{x}100\ \% \qquad (3)$$

2.4 Evaluation of deep eutectic delignification of pulp

Deep eutectic solvents were applied on unbleached beech pulp to follow the efficiency of the mixture in the process of removing lignin residues after kraft delignification. The treatment was carried out in a water bath with continuous stirring, at preset temperature of 60 ^{0}C and atmospheric pressure for 2 hours. Residual lignin content (Kappa number) and viscosity of pulp after DESs delignification were determined using standard TAPPI methods. The efficiency of the solvents was analyzed through the selectivity, calculated from viscosity and Kappa number.

3. Results and Discussion

Viscosity is one of the most important properties of any solvent. Viscosity of most DESs at ambient conditions is very large, being related to van der Waals forces, hydrogen bonding, and electrostatic interactions, as well as to the nature of individual components and their molar ratio, water content, and temperature (García *et al.,* [18]). Most DESs have a viscosity higher than 100 mPa.s at room temperature. However, DESs with low viscosity are desirable for their applications as green solvents.

Viscosities of examined TDESs are decreasing with temperature as show Figure 1. Each TDESs attained its lowest viscosity at the highest tested temperature of 95 ^{0}C. Increased kinetic energy through heating may weaken the attractive forces between molecules and thus may cause a decrease in viscosity. The obtained data shows that the TDESs composed of urea-acetamide-glycerol have lower viscosity values than the TDES malic acid-proline-lactic acid.

The density of DESs varies greatly from temperature and individual components. It has been shown that the density decreases linearly with increasing temperature. This phenomenon is due to vibration of the anions and cations during heating in the eutectic mixture. Vibrations may cause a molecular alteration in DESs due to weak interactions between the ions. As a result, the density of the fluid is reduced.

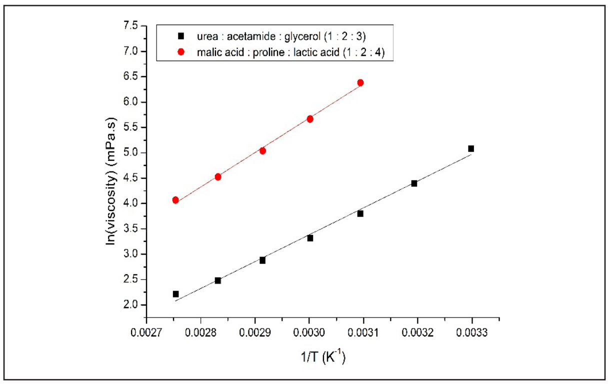

Figure 1. Effect of temperature on the viscosity of TDESs in range 303.15 - 363.15 K

The experimental density results for the samples of TDESs as a function of temperature are plotted in Figure 2. The density of TDES urea-acetamide-glycerol decreased with a temperature from 1220 to 1199 kg/m^3 and density of malic acid-proline-lactic acid decreased from 1292 to 1220 kg/m^3. The obtained data shows that the TDES composed of urea, acetamide and glycerol have lower density values than the TDES containing malic acid, proline and lactic acid. The density decreases linearly with temperature for DESs in the whole studied temperature range, and a linear equation was used to express the correlation with the temperature:

$$\rho = a + b\mathrm{x}T \qquad (4)$$

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

The a and b values derived from equation 4 for the studied TDESs are presented in Table 2.

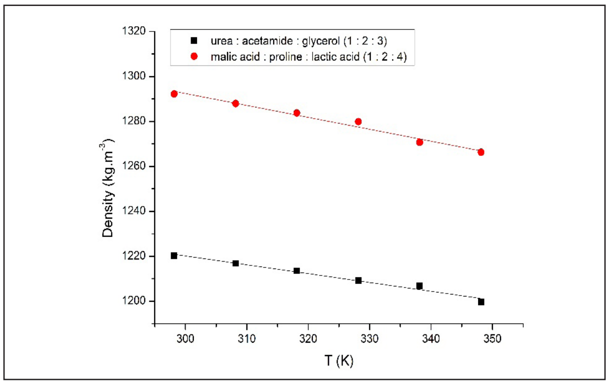

Figure 2. Densities of TDESs as a function of temperature in range 298.15 - 348.15 K

Table 2. Values of parameters *a* and b for equations which describe viscosity and density of studied TDESs

Sample	ln(viscosity) = a + bx1/T		ρ = a + bxT	
	T € <303.15; 363.15> °C		T € <298.15; 348.15> C	
	a	b	a	b
DES 1	-12.50	5296.28	1338.13	-0.39
DES 2	-14.67	6785.63	1451.45	-0.53

Characterization and effect on pulp properties after TDESs delignification are listed in Table 3. Unbleached pulp with initial Kappa number 14 was used. The Kappa number indicates the residual lignin content or bleachability of pulp. The Kappa number determination was used to estimate the lignin content of pulp by measuring the pulp oxidation capacity. TDES (malic acid-proline-lactic acid) caused a decrease of kappa number representing the efficiency of 1.4%. The efficiency of TDES (urea-acetamide-glycerol) in molar ratio 1 : 2 : 3 has reached value 5.4%. However, the efficiency of delignification is not comparable to that of oxygen delignification.

In work Majova *et al.,* [19], a series of binary deep eutectic solvents were used for delignification of pulps with different initial kappa numbers. The efficiency of delignification in the range of 14 to 22% for the pulp with initial Kappa of 14.3 was achieved.

From the viewpoint of pulp degradation, the original degree of polymerization (1226) decreased to 1150 units after TDES (urea-acetamide-glycerol), which represented a 6.2% decrease. TDES malic acid-proline-lactic acid caused a higher (10%) decrease of DP.

Table 3. Characterization and effect on pulp properties after TDESs delignification

Sample	Kappa No.	Viscosity (mL/g)	DP	Slc_{κ} (%)	Efc_{κ} (%)
Kraft pulp	14	832	1226	-	-
DES1	13.3	785	1150	1.5	5.4
DES2	13.8	756	1103	0.3	1.4

Decrease in DP is associated with scission of cellulose chains. This phenomenon is clearly documented in several papers (Calvini [20], Ding and Wang, [21], Ding and Wang, [22], Ekenstamn, [23], Emsley *et al.,* [24]). Ding and Wang, [22], introduced continuous scalar variable δ, and named it "percentage retention of DP":

$$\delta = DP_t/DP_0 \tag{5}$$

Where: DP_0 denotes the initial degree of polymerization and DP_t the real degree of polymerization, decreased as a result of deterioration due to degradation of cellulose.

At the beginning of processing-related degradation (t = 0), δ =1, during degradation its value decreases, and δ = 0 which means total damage of the sample. Degradation variable of cellulose can then be defined in terms of the percentage DP loss as:

$$\omega_{DP} = 1 - \delta = 1 - DP_t/DP_0 \tag{6}$$

Where: ω_{DP} is the accumulated DP loss of cellulose.

The extent of degradation can be, thus, expressed also using the above relation. At the beginning $\omega_{DP} = 0$, i.e. an average DP is preserved. $\omega_{DP} = 1$ represents a (theoretical) total damage of the sample depending on specific experimental conditions. It is generally accepted that when DP has decreased to an average DP of about 200, the paper will lose all its mechanical strength; if $DP_0 = 1000$, then δ = 0.2, and the accumulated degradation critical value $\omega_{DPcr} = 0.8$. When comparing the degradation of cellulose, it is obvious that the effect of DESs differs. The degradation of cellulose expressed as DP loss is 0.06 after treatment with urea-acetamide-glycerol and 0.10 with use of malic acid-proline-lactic acid.

Table 4. Calculated properties of pulp before and after TDESs delignification

Sample	δ^{*}	ω_{DP}^{**}
Kraft pulp	1.00	0.00
DES1	0.94	0.06
DES2	0.90	0.10

Legend: *δ – Percentage retention of degree of polymerization; ** ω_{DP} – is the accumulated degree of polymerization loss of cellulose.

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4. Conclusions

- The excellent properties of deep eutectic solvents highlight their advantages as promising not expensive green solvents for the delignification of pulp and replacement of oxygen delignification. The viscosity, and density were investigated for two ternary deep eutectic solvent mixtures (urea-acetamide-glycerol and malic acid-proline-lactic acid).

- The results have indicated different properties for both mixtures. Results show that prepared ternary deep eutectic solvents are able to delignify the pulp. However, the efficiency of delignification is not comparable to that of oxygen delignification. At the same time, they do not cause significant dissolution of cellulose in pulp fibers.

5. References

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