Research Article

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Delignification of unbleached pulp by ternary deep eutectic solvents

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Abstract: The processing of lignocellulosic materials is very limited because of their low solubility in water and some organic solvents. Fifteen ternary deep eutectic solvents (DESs) were prepared and tested as solvents suitable for delignification of unbleached pulp. The selected ternary DESs are composed of quaternary ammonium salts and amino acids as hydrogen-bond acceptors, and organic acids and polyvalent alcohols as hydrogen bond donors, with molar ratios varying for the individual components. The delignification efficiency is significantly influenced by the degree of penetration of the solvent into the pulp fibre structure. Therefore, the density and viscosity analysis of individual solvents was performed. Unbleached beech pulp with initial kappa number 13.9 was treated with the prepared DESs. The kappa number indicates the residual lignin content or the bleachability of pulp. The efficiency of the solvents ranged from 1.4% to 28.1%. The most suitable for the pretreatment of fibres, based on lignin removal efficiency, were found to be three DESs, in the following order: malonic acid/choline chloride/1,3-propanediol (1:1:3) > choline chloride/acetamide/lactic acid (1:2:3) > choline chloride/urea/lactic acid (1:2:3).

Keywords: deep eutectic solvents, fibres, delignification, lignin, pulp

Abbreviations

Acet	acetamide
Alan	alanine
Bet	betaine
CitA	citric acid
ChCl	choline chloride
DESs	deep eutectic solvents
EG	ethylene glycol
Gly	glycerol
l	liquid
LacA	lactic acid
MaA	malic acid
MalA	malonic acid
OxA	oxalic acid
Pr-diol	1,3-propanediol
Prol	proline
s	solid
U	urea

1 Introduction

There are biochemical processes that are fundamental for the life on the Earth in general, and for the existence of human beings in particular. The major ones are natural photosynthetic processes, resulting in the formation of oxygen and the production of biomass. Together with air, water, and inorganic materials, biomass belongs to the main resources employed by humans to produce food, and everyday goods, including polymers. At present, politicians, decision-makers, the scientific community, and technologists are trying to exploit all the available resources by sustainable, eco-friendly methods. A set of principles to be met – known as green chemistry – was stipulated by Anastas and Warner [1] as follows: prevention, atom economy, less hazardous chemical syntheses, designing safer chemicals, safer solvents, and auxiliaries, design for energy efficiency, use of renewable feedstock, reducing derivatives, catalysis, design for degradation, real-time analysis for pollution prevention, and inherently

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safer chemistry for accident prevention. Among chemical operations, dissolution, extraction, and separation are to be mentioned, in particular, as the required solvents with particular properties that are consistent with the above-mentioned green chemistry principles. The pioneering research of Abbott et al. [2,3] brought about a new type of two- or more-component solvents, which were named deep eutectic solvents (DESs). Components used in DESs are usually organic compounds, often obtained from biotechnological processes. Thus, from the practical point of view, the distinction between chemical and biotechnological processes is, at least partially, blurred. The employment of DESs in chemical, as well as in biochemical and biotechnological processes, has been well documented in articles [4–10] and a further increase in their utilization is justifiably expected.

In the last five years, several research teams published data focused on the purposeful pretreatment and dissolution of the lignocellulose fragment from the following sources: cotton linter pulp [11,12], microcrystalline cellulose [13,14], hardwood or softwood pulp [15–24], loblolly pine particles [25], cellulose methyl carbamate [26], recycled boxboard, milk containerboard, and fluting board [16,22,27].

Although the results of several works suggest that the solubility of cellulose in most of these solvents is lower than 5%, or that cellulose is insoluble in such systems [3,5–7,21–23], DESs offer changes to the properties of cellulose, nanocrystals, and nanofibers.

In the field of biomass pretreatment and delignification with DESs, several DESs have been investigated, and the results of their usability have been examined [7]. Concerning biomass pretreatment and delignification, several DESs have been tested and their usability results have been examined [7].

One of the main tasks of this industry is the separation of lignin and cellulosic fractions from biomass. The separation of lignin and cellulosic fractions from biomass is one of the main foci of this industry. There are several methods and procedures to change the composition of the original lignocellulosic matrix aiming at eliminating one of its components (lignin or polysaccharides), thus obtaining new products (pulp, viscose pulp, microcrystalline cellulose, nanocellulose, etc.), and valorizing the biomass. These include processes such as solubilization, extraction, fractionation, deconstruction, delignification, and postdelignification.

A recent study [28] on the delignification of pulps with different initial kappa numbers, 21.7, 11.8, and 14.3, in the presence of three ChCl-based DES systems ChCl/LacA (1:9), ChCl/OxA (1:1), ChCl/MaA (1:1), and Alan/LacA (1:9), suggested that pulp with a higher initial kappa number or lignin content possessed a greater fraction of easily removable lignin fragments. The impact of 15 different ternary systems was followed in the delignification of kraft hardwood pulp [6]. Considering the lignin removal efficiency, DESs can be ordered as follows: MalA/ChCl/Pr-diol (1:1:3) (39.80%) > Bet/Pr-diol/LacA (1:3:1) (36.53%) > MaA/Prol/LacA (1:2:4) (34.60%) > ChCl/Acet/LacA (1:2:3) (33.80%) > U/Acet/Gly (1:2:3) (31.73%). For other DESs, this efficiency is substantially lower, ranging from 9.27% to 5.80%.

Based on the published results on the efficiency of lignin removal from various kinds of biomasses, the most efficient DESs have been selected and included in Table 1. Table 1 contains only information about the processes where the efficiency of delignification over 50% has been achieved. The efficiency of delignification is expressed as the decrease in the content of lignin (or kappa number) on the unit change of the initial content of lignin (or kappa number).

The highest delignification has been achieved by the ternary ChCl/Gly/AlCl3.6H2O DES [29]: a removal efficiency of 98.5% was determined for ChCl/OxA (1:1); 98.5% for ChCl/LacA (1:2); 93.1% for ChCl/LacA (1:1.5) [30]; 91.82% for ChCl/LacA [17]; and 90.6% for ChCl/LacA (1:1) [31]. Thus, irrespective to the kind of biomass and operation conditions, ChCl/LacA is the most effective in removing lignin.

Most of DESs listed in Table 1 contain choline chloride as a hydrogen bond acceptor. The presence of choline chloride appears to improve the efficiency of delignification. In the work by Liu et al. [31], the authors suggested that the chloride ions in the DES cause the breakdown of lignin carbohydrate complexes, whereas Li et al. [32] presumed that chloride could help disrupt the intermolecular hydrogen bonding network of biomass and facilitate its dissolution.

There is a lack of work dealing with the economic evaluation of the DESs delignification process. In the work of Smink et al. [33], the conceptual process design was made for the delignification of lignocellulosic biomass using a deep eutectic solvent composed of lactic acid and choline chloride. Mass and energy balances were made using rigorous calculations. Optimizing the amounts of water and the DES used in the process reduced the estimated heat duty from 12.3 to 7.9 GJ·t^{-1} cellulose, which is 28% lower than the conventional kraft process.

In this publication, the effect of 15 different ternary DESs on the delignification of unbleached beech pulp was tested. Their delignification efficiency and the effect on the degradation of cellulose fibres were investigated.

Table 1: Application of DESs for different types of biomasses; the efficiency of delignification expressed as the decrease in the content of lignin (or kappa number) on the unit change of the initial content of lignin (or kappa number)

Solvent	Molar ratio	Sample	Conditions	Effects	Ref.
ChCl/Gly/AlCl$_3$·6H$_2$O	1:2:(0.1; 0.13; 0.2; 0.28; 0.33)	Poplar wood	1 g sample, 20 g DES, 110°C, 120°C, 130°C for 4 h	Efficiency of delignification 61.29%, 75.15%, 89.22%, 66.44%, 87.83%, 98.45%, 79.07%, 93.40%, 105.00%, 83.66%, 95.46%, 105.21%, 83.57%, 95.11%, 105.26%	[29]
ChCl/OxA	1:1	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	98.5%	[30]
ChCl/LacA	1:2	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 70°C, 80°C, 90°C, 100°C, and 110°C for 24 h	18.1%, 31.1%, 42.7%, 65.8%, 95.5%	[30]
ChCl/LacA	1:15	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	93.1%	[30]
ChCl/LacA	1:2 1:4 1:6 1:8 1:10 1:12	*Salix matsudana cv. Zhuliu* (Willow)	2.5 g samples, solid/solvent ratio 1:30, 90–120°C, and time 6–42 h	Molar ratio 1:10 at 120°C, 12 h, efficiency of delignification 91.82%	[17]
ChCl/OxA·2H$_2$O	1:1	Poplar wood flour	0.5 g sample, 10 g DES heat in oil bath: 80°C, 110°C, 9 h	90.6% for 110°C	[31]
ChCl/EG	1:2	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	87.6%	[30]
ChCl/LacA	1:10	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	86.1%	[30]
ChCl/OxA·2H$_2$O	1:1	Poplar wood flour	0.5 g sample, 10 g DES heat in microwave; 800 W, 80°C, heating-up 2 min, retention time 1, 3, and 8 min	81.8% for 3 min, 78.2% for 8 min	[31]
ChCl/LacA	1:2	*Switchgrass* L. *Corn stover* L. *Miscanthus* L.	2.5 g sample, 25 g DES, microwave irradiation 45 s, 800 W	72.23% 79.60% 77.47%	[34]
ChCl/LacA		Poplar wood	0.6 g samples, 6 g DES 90°C, 6 h; 120°C, 3 h; 145°C, 69 h; 180°C, 0.5 h	90°C, 25.2% 120°C, 72.1% 145°C, 78.5%	[35]
ChCl/LacA	1:5	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	77.9%	[30]
ChCl/LacA	1:2; 1:5; 1:9	Wheat straw	5% biomass loading, DES total volume 200 mL, 60°C, 12 h, 100 rpm	64%, 75.6%, 74.2%	[36]
ChCl/Gly	1:2	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	71.3%	[30]
Bet/LacA	1:2; 1:5	Wheat straw	5% biomass loading, DES total volume 200 mL, 60°C, 12 h, 100 rpm	65.6%, 70.4%	[36]

(*continued*)

Table 1: (*continued*)

Solvent	Molar ratio	Sample	Conditions	Effects	Ref.
ChCl/LacA	1:2	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	64.7%	[30]
ChCl/LacA	1:1 1:2 1:5 1:9	Rice straw (9% lignin content)	20% solids loading of rice straw with DES at 1 atm and 121°C for 1 h	Lignin content for treated samples: 9% 8% 7% 4% (63% Efc_{K})	[37]
LacA/guanidine·HCl	1:1	Rice straw	0.3 g biomass, 6 g DES, mixing and refluxing, 120°C, 6 h	61.0%	[38]
ChCl/LacA		Douglas fir	0.6 g samples, 6 g DES, 90°C, 6 h; 120°C, 3 h; 145°C, 9 h; 180°C, 0.5 h	145°C, 58.2%	[35]
$ChCl/OxA{\cdot}2H_2O$	1:1	Wheat straw	2.5 g wheat straw, 50 g DES, 24 h, 60°C	57.9%	[39]
ChCl/MalA	1:1	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	56.5%	[30]
ChCl/glycolic acid	1:2	Corncob	0.3 g corncob, 6 g DESs magnetically stirred at 90°C for 24 h	56.4%	[30]
ChCl/LacA	1:2	*Salix matsudana cv. Zhuliu* (Willow)	2.5 g samples, solid to liquid 1:30, 90°C, 100°C, 110°C, 120°C, 6 h	120°C, 52.4%	[17]
ChCl/ chloropropionic acid	1:1	Rice straw	0.3 g biomass, 6 g DES, mixing and refluxing, 80°C, 6 h	52.0%	[38]
ChCl/LacA	1:1	Rice straw	0.3 g biomass, 6 g DES, mixing and refluxing, 80°C, 6 h	51.4%	[38]
ChCl/MaA	1:1	Rice straw	0.3 g biomass, 6 g DES, mixing and refluxing, 80°C, 6 h	51.3%	[38]

2 Materials and methods

2.1 Preparation and physicochemical properties of DESs

Acetamide (99%, s), alanine (≥99%, s), glycine (≥99%, s), choline chloride (≥98%, s), lactic acid (90%, l), malic acid (≥98%, s), malonic acid (99%, s), urea (99.5%, s), proline (99%, s), and 1,3-propanediol (99%, l) were purchased from Sigma Aldrich (Bratislava, Slovakia). Glycerol (99%, s) and citric acid (99.5%, s) were obtained from Centralchem, s.r.o. (Bratislava, Slovakia). Betaine (98%, s) and ethylene glycol (≥99%, l) were purchased from VWR International, s.r.o. (Bratislava, Slovakia).

Ternary DESs were prepared by the heating method. All chemicals were weighed in the corresponding molar ratios by using an analytical balance AX205(Mettler Toledo GmbH, Greifensee, Switzerland). Mixtures of the corresponding reagents with the required molar ratio were heated in a glass spherical flask and stirred by vacuum rotary evaporator Stuart RE300 in water bath Stuart RE300OB (Keison Products, Chelmsford, England), at the appropriate temperature (70–90°C) and atmospheric pressure. A homogeneous liquid was obtained and then allowed to cool to room temperature. The list of the prepared ternary DESs is given in Table 2. The viscoelastic properties of the obtained solvents were characterized on a Brookfield DV 2+ viscometer (AMETEC, Inc. Lorch, Germany). Viscosity was measured at different revolutions (5, 10, 20, 50, and 100 rpm), using a spindle 18 with an adapter. Density was determined with a pycnometer. Pycnometer calibration was performed with distilled water. The water contents were determined with a TITRINO 702 SM (Metrohm Ltd., Herisau, Switzerland), and a Karl–Fischer coulometric titrator. All measurements were performed three times with individual samples.

Table 2: Composition of ternary DESs

Sample	Ternary DES	Molar ratio	Temperature of preparation (°C)
DES1	Bet:EG:Gly	1:2:2	70
DES2	Bet:EG:LacA	1:1:1	80
DES3	Alan:LacA:CitA	1:3:1	90
DES4	ChCl:EG:LacA	1:2:1	80
DES5	Bet:Gly:CitA	1:2:1	90
DES6	Prol:LacA:CitA	1:3:1	90
DES7	Prol:Gly:CitA	1:4:1	90
DES8	MaA:Prol:LacA	1:2:4	80
DES9	ChCl:U:LacA	1:2:3	70
DES10	MaA:Alan:LacA	1:1:3	90
DES11	Bet:Pr-diol:LacA	1:3:1	70
DES12	Bet:U:Gly	1:2:3	80
DES13	ChCl:Acet:LacA	1:2:3	80
DES14	MalA:ChCl:Pr-diol	1:1:3	70
DES15	U:Acet:Gly	1:2:3	80

2.2 Evaluation of cellulose solubility in DES reagents

Specific solubility tests were performed using pure cellulose (Whatman paper, Sigma Aldrich, Slovakia) in DES reagents. In 50 mL glass bottles, 0.5 g of cellulose was added separately into 20 g of the DES reagent and then incubated at 60°C for 2 h. The samples were filtered through a fritted glass funnel and dried at 105°C overnight. The weight of the dried residual solid components was measured in order to evaluate solubility (in wt%) in the DES reagent.

2.3 Pulp characterization

The kappa number was estimated using the Tappi standard method T-236, excessively described in ref. [40]. The Mark–Houwink equation was used to calculate the degree of polymerization (DP) where $[\eta]$ is the intrinsic viscosity ($\mathrm{mL \cdot g^{-1}}$) of the pulp [41] and details are given elsewhere [6]:

$$\mathrm{DP}^{0.905} = 0.75[\eta] \tag{1}$$

The cellulose chain scission number (CS), which represents the average number of CSs per cellulose chain unit during the time course of degradation, was calculated applying the following equation:

$$\mathrm{CS} = \frac{\mathrm{DP}_0 - \mathrm{DP}_t}{\mathrm{DP}_t} \tag{2}$$

where DP_0 and DP_t are the degree of polymerization before and after scission, respectively [42].

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

$$Slc_\kappa = \frac{\kappa_0 - \kappa_t}{[\eta]_0 - [\eta]_t} \tag{3}$$

where κ_0 is the initial kappa number of pulp; κ_t the kappa number of pulp after delignification; $[\eta]_0$ the initial intrinsic viscosity of pulp; and $[\eta]_t$ the intrinsic viscosity of pulp after delignification.

The efficiency of delignification (Efc_{κ}), expressed as a decrease in the kappa number on the unit change of the initial kappa number of pulp, was calculated based on the following equation:

$$Efc_{\kappa} = \frac{\kappa_0 - \kappa_t}{\kappa_0} \tag{4}$$

A pulp sample (10 g absolute dry weight) and 33 g of water were added into individual DESs in an amount of 200 g. The delignification took 2 h in a drying oven at 60°C. The sample was washed using hot water to a neutral pH, filtered, and air-dried. The values of kappa number and viscosity were determined four times, while the experiments of pulp delignification with the 15 ternary DESs were replicated twice.

Table 3: Physicochemical properties of ternary DESs

DES	Density at 60°C ($kg{\cdot}m^{-3}$)	Viscosity at 60°C (mPa·s)	Water content (wt%)	Solubility of cellulose (wt%)
DES1	1,163 ± 3	37.6 ± 0.6	0.34 ± 0.01	0.04 ± 0.00
DES2	1,193 ± 11	33.8 ± 0.4	5.74 ± 0.07	0.58 ± 0.01
DES3	1,331 ± 8	453.5 ± 0.6	7.45 ± 0.10	0.00 ± 0.00
DES4	1,163 ± 16	9.6 ± 1.0	6.79 ± 0.09	0.53 ± 0.01
DES5	1,246 ± 15	*	4.10 ± 0.05	0.02 ± 0.00
DES6	1,223 ± 19	375.5 ± 1.9	7.19 ± 0.09	0.00 ± 0.00
DES7	1,284 ± 8	318.5 ± 2.3	4.04 ± 0.05	0.00 ± 0.00
DES8	1,275 ± 17	288.1 ± 1.9	6.94 ± 0.09	0.03 ± 0.00
DES9	1,206 ± 14	28.6 ± 0.3	6.89 ± 0.10	0.08 ± 0.00
DES10	1,286 ± 17	291.2 ± 2.1	8.31 ± 0.11	0.00 ± 0.00
DES11	1,098 ± 9	25.2 ± 0.8	4.50 ± 0.06	0.87 ± 0.02
DES12	1,264 ± 3	84.1 ± 1.1	0.64 ± 0.02	1.24 ± 0.03
DES13	1,180 ± 8	20.2 ± 0.6	6.36 ± 0.08	0.66 ± 0.02
DES14	1,155 ± 14	23.0 ± 1.0	5.14 ± 0.07	2.09 ± 0.08
DES15	1,208 ± 11	27.4 ± 1.0	0.33 ± 0.01	0.32 ± 0.01

* Viscosity could not be measured below 70°C.

3 Results and discussion

In any chemical pulping process, it is essential to achieve adequate penetration of liquids into the raw material. The efficiency of delignification is greatly influenced by the degree of solvent penetration into the fibre structure. Therefore, the density and viscosity analysis of individual solvents was performed. It is generally known that the lower the density and viscosity of the solvent, the better the penetration into the delignified raw material. High viscosity is always a major difficulty in the use of DESs for any application but it can be significantly reduced by increasing the temperature, the HBA, or the water content. From the properties of the examined solvents listed in Table 3, it can be noted that mixture DES 3, with the composition Alan:LacA:CitA in a 1:3:1 molar ratio, showed the highest viscosity (453.5 mPa·s at 60°C). For this reason, it would be difficult for this solvent to penetrate the structure of the pulp, thereby causing the smallest change in the kappa number, $\Delta\kappa$ (before and after the delignification of the pulp). The physicochemical properties of all the investigated ternary DESs have been described in detail by Jablonsky et al. [6].

Other high-viscosity solvents include DES 5, DES 6, and DES 7. These mixtures contain amino acids in combination with CitA, which is a tricarboxylic acid bearing a hydroxy substituent in its structure. DESs containing acids with a less complicated structure, such as MalA or LacA (without the presence of any other carboxylic acid in the mixture), show much lower viscosities. DES 4 (ChCl:EG:LacA (1:2:1)) has the lowest viscosity at the temperature of 60°C, reaching a value of 9.6 mPa·s.

The pulp properties after delignification are listed in Table 4, revealing the effect of each DES investigated here. In this work, unbleached beech pulp, with an initial kappa number of 13.9 and an average degree of polymerization of 1,034, was used. The most effective solvent for dissolving the lignin from the pulp was DES 14 (MalA:ChCl:Pr-diol (1:1:3)), which led to a decrease in the kappa number from the original value of 13.9–10.0, representing efficiency of 28.06%. The DP in this case

Table 4: Pulp properties after delignification with different DESs (initial kappa number = 13.9 and DP = 1,034)

DES	Kappa No.	Efc_{κ} (%)	Slc_{κ} (%)	DP	CS
1	12.60	9.35	13.36	1,019	0.02
2	11.85	14.75	19.71	1,018	0.02
3	12.10	12.95	26.80	1,024	0.01
4	11.75	15.47	10.20	1,001	0.03
5	12.15	12.59	18.26	1,019	0.02
6	11.70	15.83	14.14	1,009	0.02
7	11.00	20.86	15.75	1,005	0.03
8	10.90	21.58	5.66	950	0.09
9	10.65	23.38	53.53	1,025	0.01
10	10.85	21.94	8.50	977	0.06
11	10.70	23.02	14.00	998	0.04
12	10.95	21.22	26.75	1,017	0.02
13	10.20	26.62	12.34	986	0.05
14	10.00	28.06	15.62	994	0.04
15	13.70	1.44	10.13	1,031	0.01

decreased by 3.5% from 1,034 to 994. The most significant degradation of the cellulose chain was observed in the delignification with DES 8 (MaA:Prol:LacA (1:2:4)). The DP decreased from 1,034 to 950, representing a 7.4% decrease.

Considering the lignin removal efficiency, the DESs are ordered as follows: DES 14 (MalA:ChCl:Pr-diol (1:1:3)) (28.06%) > DES 13 (ChCl:Acet:LacA (1:2:3)) (26.62%) > DES 9 (ChCl:U:LacA (1:2:3)) (23.38%) > DES 11 (Bet:Pr-diol:LacA (1:3:1)) (23.02%) > DES 10 (MaA:Alan:LacA, (1:1:3)) (21.94%) > DES 8 (MaA:Prol:LacA (1:2:4)) (21.58%) > DES 12 (Bet:U:Gly (1:2:3)) (21.22%) > DES 7 (Prol:Gly:CitA (1:4:1)) (20.86%). The lignin removal efficiency of the other DESs is relatively lower, on a scale from 15.83% to 1.44%.

The presence of 1,3-propanediol in the DESs may have an enhancing effect on the delignification efficiency, as described in the findings of Kandanelli et al. [43]. They developed a novel ternary system consisting of a deep eutectic solvent–alcohol (DES-OL) mixture for the effective delignification of lignocellulosic biomass. DES was based on choline chloride and oxalic acid in a molar ratio of 1:1. *n*-Butanol, *n*-propanol, and ethyl acetate were used to form the DES-OL system [43]. Lignin removal was observed to be in the range of 23–31% for all the tested biomass samples with DES, which in contrast with DES-OL where ~50% delignification was observed for all the tested biomass samples (rice husk, rice straw, and wheat straw). Delignification using the DES-OL system was at least 50% higher than that of pure DES treatment.

The highest selectivity in the removal of lignin, Slc_κ, was demonstrated by DES 9 (ChCl:U:LacA (1:2:3)). The values of $Slc_\kappa = 53.53\%$ and CS = 0.01 indicated a significant removal of lignin by this solvent, as well as the selectivity of the process. In this case, the DP decreased only by 0.85% (Table 4) for DES 9.

In the work by Majová et al. [28], beech pulp with an initial kappa number of 14.3 was delignified with four different binary DESs. An efficiency of 21.7% was achieved after delignification with the DES Alan:LacA (1:9), which is comparable to that achieved with DES 10 (MaA:Alan:LacA (1:1:3) used in the present study. DES 3, also containing Alan and LacA, reached an efficiency of only 12.95%. This may be explained by the presence of CitA, which increases the viscosity of the solvent and thus prevents the penetration of the solvent into the fiber. When using the DES ChCl:LacA (1:9), an efficiency of 17.5% was achieved. Three of the ternary DESs prepared in this work contain these substances in different combinations: DES9 (ChCl:U:LacA (1:2:3)) and DES13 (ChCl:Acet:LacA (1:2:3)) reached similar efficiency of 23.38% and 26.62%, respectively, while DES 4 (ChCl:EG:LacA (1:2:1)) achieved a significantly lower efficiency of 15.47%. Based on these results, it can be assumed that the presence of an amide in the eutectic mixture may have a positive effect on the efficiency of delignification.

In the work by Jablonsky et al. [6] , the same solvents were used to delignify pulp with a kappa number of 15.0. The first five solvents that achieved the highest efficiency were as follows: MalA:ChCl:Pr-diol (1:1:3) (39.8%) > Bet:Pr-diol:LacA (1:3:1) (36.53%) > MaA:Prol:LacA (1:2:4) (34.60%) > ChCl:Acet:LacA (1:2:3) (33.80%) > U:Acet:Gly (1:2:3) (31.73%). These results correspond to the findings of Majová et al. [28], which revealed that the delignification efficiency depends on the initial lignin content of the pulp. The higher the lignin content, the greater the delignification efficiency. When comparing the top five solvents reported to achieve the best results by Majová et al. [28] and Jablonsky et al. [6], we can notice an agreement in three cases, namely DES 14 (MalA:ChCl:Pr-diol (1:1:3)), DES 13 (ChCl:Acet:LacA (1:2:3)), and DES 11 (Bet:Pr-diol:LacA (1:3:1)).

In the work of Pérez et al. [44], the DES composed of LacA and ChCl in a weight ratio of 10:1 was used for delignification of Asplund fibers. With a cooking time of 1 h at 100°C and a DES-to-wood ratio of 27:1, it was possible to achieve a delignification degree lower than 16%. At 130°C, the delignification degree was approximately 63%.

The delignification of the low-energy mechanical pulp with four different DESs based on ChCl with U, LacA, MaA, and OxA was investigated in the work by Fiskari et al. [45]. It was demonstrated that DESs could reduce the lignin content by almost 50% and a minor decrease in the tensile index was observed.

Several methods for delignifying pulps with organic solvents have been documented. The effects of ionic liquid (ILs) pretreatment (1-butyl-3-methylimidazolium hydrogen sulfate; triethylammonium hydrogen sulfate) on the composition of the bleached pulp during a sequence of ODP bleaching (oxygen-chlorine dioxide and peroxide stage) showed that the IL pretreatment protected the pulp fibers by increasing the cellulose content and viscosity and enhanced lignin removal during ODP bleaching [46]. The lignin content of the bleached pulp pretreated by 1-butyl-3-methylimidazolium hydrogen sulphate and triethylammonium hydrogen sulphate was decreased by 1.8% and 17.7% compared to the pretreatment-free bleached pulp. The results showed that ILs pretreatment can enhance the bleachability of pulps.

Delignification of kraft pulp with peroxymonophosphoric and peroximonosulphuric acid was described in ref. [47]. Delignification took place at a low temperature of 24°C and the lignin removal efficiency was from 64.7%

to 90% for peroxymonophosphoric acid but the reaction time was up to 24 h.

Organosolv processes use a broad range of organic solvents including methanol, ethanol, propanol, butanol, isobutyl alcohol, benzyl alcohol, glycerol, glycol, ethylene glycol, triethylene glycol, phenol, acetone, formic acid, acetic acid, propionic acid, diethyl ether, amines, ethers, esters, formaldehyde, and chloroethanol, among others, either in a pure form or in aqueous solutions to which a catalyst (an acid, base, or salt) may be added [48]. Different organosolv pulping methods for delignification of raw materials (*Acanthopanax senticosus* remainder) were investigated in the work by Lu et al. [49]. The results showed that the lignin extraction efficiency of 1,4-butanediol–acetic acid–water method was the highest (39%) among the methods of this paper. This organosolv process was carried out at 200°C for 120 min.

The decrease in DP is associated with the scission of cellulose chains. Ding and Wang [50] introduced the continuous scalar variable δ and named it “percentage retention of DP”:

$$\delta = \mathrm{DP}_t/\mathrm{DP}_0 \tag{5}$$

where DP_0 denotes the initial degree of polymerization and DP_t the real degree of polymerization, which decreased as a result of the deterioration caused by the degradation of cellulose. At the beginning of the processing-related degradation ($t = 0$), $\delta = 1$ during degradation, and its value decreases to $\delta = 0$, which means the total damage of the sample. Then, the degradation variable of cellulose can be defined in terms of the percentage of DP loss as:

$$\omega_{\mathrm{DP}} = 1 - \delta = 1 - \mathrm{DP}_t/\mathrm{DP}_0 \tag{6}$$

where ω_{DP} is the accumulated DP loss of cellulose.

The extent of degradation can be, thus, also expressed using the above relation. At the beginning $\omega_{\mathrm{DP}} = 0$, i.e., an average DP is preserved. $\omega_{\mathrm{DP}} = 1$ represents a (theoretical) total damage of the sample, depending on specific experimental conditions. It is generally accepted that when the DP decreases to an average of about 200, the paper will lose all its mechanical strength; if $\mathrm{DP}_0 = 1{,}000$, then $\delta = 0.2$, and the accumulated degradation critical value $\omega_{\mathrm{DPcr}} = 0.8$. When comparing the degradation of cellulose, it is obvious that the effect of DESs differs.

In terms of cellulose degradation, none of the DESs used led to a significant scission of the cellulose chain during the delignification of the pulp (Table 5). DES15 (U:Acet:Gly (1:2:3)), DES3 (Alan:LacA:CitA (1:3:1)), DES5 (Bet:Gly:CitA (1:2:1)), and DES9 (ChCl:U:LacA (1:2:3)) caused the lowest decrease of ω_{DP} of 0.00, 0.01, 0.01, and 0.01, respectively. Based on the DP loss of cellulose, the highest decrease was observed by DES8 (MaA:Prol:LacA (1:2:4)) and DES10 (MaA:Alan:LacA (1:1:3)). Both solvents contain two carboxylic acids – MaA and LacA. In the work of Jablonsky et al. [51], the effect of DESs on cellulose degradation after the delignification of pulp with a kappa number of 14.3 is described. The DES ChCl:MaA (1:1) led to the degradation of cellulose, expressed as a DP loss of 0.12, DES ChCl:LacA (1:9) caused a DP loss of 0.14, and that of DES LacA:Alan (1:9) of 0.08.

Delignification with DESs has the undeniable advantage that it does not cause a significant decrease in the degree of polymerization of cellulose compared to the conventional oxygen delignification process. In Majová et al. [28], the properties of pulp after delignification with DESs and after oxygen delignification are compared. The degree of polymerization decreased by up to 30.4% after oxygen delignification. On the other hand, after delignification with DES14, a decrease in DP of only 3.9% occurred. The efficiency of delignification is strongly influenced by the initial amount of lignin, as described in Majová et al. [28].

The use of DESs in delignification appears to be an efficient procedure that could significantly contribute to the lignin removal in the process of post-delignification of the pulp or to replace some bleaching processes. These processes would require less energy consumption, simpler equipment (lower temperature, atmospheric pressure), with a low impact on environmental pollution. Reducing the lignin content makes it possible to reduce the amount of chemicals used in other bleaching stages (e.g., particularly $\mathrm{ClO_2}$). A SWOT (strengths, weaknesses, opportunities, and threats) analysis was used to assess the current situation from various perspectives. Such a method of analysis outlines possible alternatives for

Table 5: Percentage retention of DP and accumulated DP loss of cellulose in pulp fibres after delignification with DESs

DES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
δ	0.98	0.98	0.99	0.97	0.99	0.98	0.97	0.92	0.99	0.94	0.96	0.98	0.95	0.96	1.00
ω_{DP}	0.02	0.02	0.01	0.03	0.01	0.02	0.03	0.08	0.01	0.06	0.04	0.02	0.05	0.04	0.00

Table 6: SWOT analysis for DESs delignification

Strengths	Weakness
Replacement of conventional procedures and chemicals	Not completely solved issue of recycling (number of recycling cycles, degradation products)
Green solvents – environmentally friendly	The need to change the surfaces of technological equipment – replacement
More energy efficient – lower batch temperature	The need for new mixing equipment
More economical process and the ability to ensure higher production – shorter batch time	Change of regeneration stage technology
Opportunities	**Threats**
Support for the industry produce DESs	Increasing prices of DES components
Increasing pulp production volumes	Additional costs when modifying the operation

future development, possibilities for their use, or their solution (Table 6).

4 Conclusion

The effect of 15 different ternary DESs on the efficiency of lignin removal from the pulp was compared. The rate of lignin removal from pulp is strongly influenced by the viscosity of DESs, which is one of their essential properties. It is generally known that the higher a solvent's viscosity, the more complicated its penetration into a fiber structure. Among the investigated DESs, the most suitable solvent for pulp delignification appeared to be DES 14, composed of malonic acid, choline chloride, and 1,3-propanediol, in a molar ratio of 1:1:3, which reached a lignin removal efficiency of 28.06%. Based on the analysis of the loss of the polymerization degree, it was confirmed that the DESs used produced no significant damage to cellulose fibers.

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