

Article

Delignification of Wheat Straw Using DES-like Mixtures

Veronika Jančíková *, Michal Jablonský  and Katarína Voleková

Department of Wood, Pulp and Paper, Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia; michal.jablonsky@stuba.sk (M.J.); katavolekova@gmail.com (K.V.)

* Correspondence: veronika.jancikova@stuba.sk; Tel.: +421-917-369-516

Abstract: Wheat straw, an agricultural residue, is emerging as a viable alternative to wood biomass alongside other annual plants. The exploration of novel methods, particularly those involving ecofriendly solvents, is at the forefront of harnessing the potential of these annual crops. This study focuses on the delignification of wheat straw using DES-like mixtures composed of choline chloride and lactic acid in a molar ratio of 1:5. We closely monitored three critical factors influencing delignification: temperature, time, and the ratio of biomass to the DES-like mixtures. Temperature ranged from 80 to 160 °C, time varied from 60 to 240 min, and the ratio spanned from 1:10 to 1:60. The percentage of lignin remaining in the samples after delignification varied between 16.13% and 35.49%, while the cellulose content fell within the range of 43.77% to 69.53%. To pinpoint optimal conditions for delignification, we performed calculations. The ideal lignin content of 16.44% was achieved at a temperature of 111 °C, a duration of 60 min, and a biomass-to-solvent ratio of 1:27. For maximum delignification efficiency, reaching 37.32%, the optimal conditions were determined as a temperature of 120 °C, a duration of 150 min, and a ratio of 1:34.

Keywords: green solvents; DES-like mixtures; wheat straw; design of experiment; delignification



check for updates

Citation: Jančíková, V.; Jablonský, M.; Voleková, K. Delignification of Wheat Straw Using DES-like Mixtures.

Sustainability **2023**, *15*, 15343.

<https://doi.org/10.3390/su152115343>

su152115343

Academic Editor: Francesco Desogus

Received: 28 September 2023

Revised: 17 October 2023

Accepted: 17 October 2023

Published: 26 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Wheat straw, as a byproduct of wheat production, is an annually renewable, cost-effective, and rich source of natural fibers. It is considered one of the most abundant lignocellulosic agricultural residues worldwide, with a global annual production exceeding 800 million tons. Unfortunately, a significant portion of this residue is commonly disposed of through open-air burning, landfilling, or incineration. This practice has harmful effects on the environment, and adversely impacts human health. Hence, it is preferable to utilize wheat straw for the production of useful products [1].

Due to its high carbohydrate content, wheat straw is regarded as a potential source for ethanol in biorefinery processes. According to a basic scenario model, it is possible to produce 0.2 billion liters of denatured ethanol annually using approximately 900,000 tons of wheat straw as feedstock. Besides carbohydrates, wheat straw is also identified as a highly promising source of lignin. However, lignin extracted specifically from wheat straw is still underutilized in high-end applications. This can be improved by tailoring the characteristics of the lignin fraction, which are strongly linked to isolation techniques [2].

As previously mentioned, with an annual production of 800 million tons, these quantities are significant enough to consider wheat straw as a sustainable raw material source, readily available in abundance, and capable of serving as an alternative to wood in the paper and pulp industry. Until recently, straw pulp was primarily produced through the chemical pulping process. Chemical pulping of wheat straw involves extracting cellulose from the lignin-carbohydrate matrix by dissolving lignin and hemicellulose through the cleavage of covalent α -ether bonds that hold cellulose fibers together [1]. However, these conventional approaches are usually energy-intensive for pulp production and are rarely used due to environmental concerns and issues associated with the regeneration of alkaline

chemicals [2]. Moreover, current wheat straw processing methods are reported to cause air pollution, releasing significant amounts of greenhouse gases, particles, and smoke, which can pose a direct threat to human health [1,2]. Wheat straw can be used to manufacture various types of paper, including linerboard, corrugated medium, writing paper, and printing paper [1].

The use of lignocellulosic biomass, which includes agricultural residues, usually requires the use of isolation processes to separate the main and minor components. Different types of pretreatments are used to remove lignin from biomass, such as organosolv, ionic liquids, ozonolysis, and many other physicochemical pretreatments. In recent years, attention has been paid to the use of green solvents. These represent an alternative and sustainable approach to the fractionation and further refining of biomass components into various end products such as biofuels, furan derivatives and other high-value chemicals [3].

Several authors are devoted to this topic, focusing on the delignification of wheat straw using deep eutectic solvents-like mixtures (DES-like mixtures). Suopajarvi et al. in 2020 [3] used three different agricultural by-products (wheat straw, rapeseed stem and corn stalks) to compare the delignification and nanofibrillation effect of six different DES-like mixtures. The DES-like mixtures were in the form of solutions of various natural organic acids with choline chloride (ChCl), and one was in the composition of potassium carbonate (K_2CO_3) with glycerol. Delignification was performed under three conditions, namely at a temperature of 100 °C for 8 h, at a temperature of 100 °C for 16 h, and at a temperature of 80 °C for 4 h. The largest yield of lignin was obtained in both cases when using stems; specifically, when using the solvent ChCl and lactic acid (LacA), the yield was 5.7%, and when using the solvent composed of K_2CO_3 and glycerol, the largest yield was 11.8%. They also compared the strength properties of papers from the obtained pulps with those obtained using alkaline DES-like mixtures having better strength properties (132–170 MPa) compared to those obtained using acidic DES-like mixtures (24–132 MPa). A likely explanation for this difference may be that the alkaline DES-like mixtures also dissolved waxes and proteins, which can moderate the adhesion and network formation between the nanofibers. They also found using Fourier-transform infrared spectroscopy (FT-IR) that the obtained lignin fractions had different characteristics [3].

Delignification of wheat straw and pine was carried out in 2013 by Largo Garcia de Dios [4]. He used five different DES-like mixtures in the composition of ChCl with LacA, ChCl with oxalic acid, ChCl with malic acid, LacA with tetramethylammonium chloride and 2-chloroethyltrimethylammonium chloride in different ratios. He performed eight experiments, with the amount of lignin obtained after delignification ranging from 0.6 to 9.5%. He found that different types and structures of lignin are different when using different types of biomasses. Jablonský et al. in 2015 [5] also used different DES-like mixtures for the pretreatment of wheat straw. The DES-like mixtures consisted of ChCl and urea (1:2), ChCl and LacA (1:9 and 1:10), ChCl and malonic acid (1:1), ChCl and oxalic acid (1:1), ChCl and malic acid (1:1). The largest yield of lignin, representing 57.9%, was obtained using DES-like mixtures composed of ChCl and oxalic acid. Based on the selectivity of the removal of lignin and holocellulose from biomass, it follows that the best results were obtained using DES-like mixtures composed of ChCl and LacA in a molar ratio of 1:10 [5].

The aim of the study conducted by Yue et al. in 2020 [2] was to investigate the properties of two solid lignin fractions isolated from wheat straw using basic and acidic DES-like mixtures. The chemical properties and morphological characteristics of the two lignin fractions were evaluated by measuring their purity, elemental composition, molecular weight and particle size distribution, and microstructure. They found that lignin isolated using an alkaline DES-like mixture was less pure and had a smaller particle size, higher molecular weight, and thermal stability compared to lignin isolated using an acidic DES-like mixture. They also determined their lignin structure, which was different due to different selective breaks in the lignin bonds. These results suggest that pretreatments with DES-like mixtures could selectively extract lignin from wheat straw with different yield,

composition, morphology, and structure, which could then provide a theoretical basis for choosing a DES-like mixture for specifically designed lignin extraction [2].

The best delignification with a yield of 45% was achieved by microwave radiation at a temperature of 120 °C for 30 min with a three-component DES-like mixture at a ratio of biomass to solvent of 1:50. Good delignification results with a yield of 27% were also provided by a boiling solution of γ -valerolactone with water (8:2) during ultrasonic radiation (40 kHz, 200 W) lasting 60 min at a temperature of 50 °C. The resulting finding is that these proposed wheat straw pretreatment options present advantages in terms of sustainability compared to conventional pretreatment. These findings suggest that ultrasonic or microwave delignification are suitable environmentally friendly techniques. Additionally, these unconventional pretreatments can lead to the valorization of lignin and cellulose contained in wheat straw, and as such meet the requirements of the biorefinery concept [6].

The delignification of wheat straw was, for example, also addressed by Zhao et al. in 2018 [7] or Liu et al. in 2019 [8]. Zhao et al. delignified straw at a temperature of 90 °C for 12 h using DES-like mixture consisting of ChCl and monoethanolamine with 81% lignin removal and a DES-like mixture consisting of ChCl and diethanolamine with 73.5% lignin removal [7]. Liu et al. used triethylbenzylammonium chloride boiling solution with LacA, achieving 80% lignin removal [8].

The result of the work by Majová et al. [9]. demonstrated that yields after delignification of wheat straw ranged from 77.9 to 87.9% and noted a yield reduction of up to 10% at a 56 h dose. It is also interesting to observe the decrease in the lignin content with increasing delignification time, where in the 40 h dose the residual lignin represented 17.4%, and in the 56 h dose the lignin content was only 15.0%.

The goal of this work was the delignification of wheat straw using a green solvent, namely DES-like mixtures in the composition of choline chloride (ChCl) and lactic acid (LacA) in a molar ratio of 1:5. Part of the work is also the evaluation of delignification under different conditions according to the rotation experiment. We monitored three factors affecting delignification, namely temperature, time, and the ratio of used biomass to solvent. The boundary parameters of the observed factors were as follows: temperature in the range of 80–160 °C, time 60–240 min and the ratio of the amount of wheat straw to the solvent 1:10 to 1:60. Another goal was to determine the optimal delignification conditions in terms of lignin yield and delignification efficiency after application of DES-like mixtures (ChCl/LacA; 1:5). Our goal was to achieve the lowest possible lignin content in delignified wheat straw fibers, i.e., the greatest possible removal of lignin from the original biomass after the application of DES-like mixtures. Subsequently, the next task was to characterize the obtained fibers after the application of DES-like mixtures using several methods, such as optical microscopy, FT-IR, or Ultraviolet–visible spectroscopy (UV–Vis).

2. Materials and Methods

2.1. Biomass Sample Preparation

The wheat straw from Slovakia, specifically from the vicinity of Bratislava, was used as a raw biomass sample. Wheat straw was cleaned of external impurities, leaves and stems, and then cut into 2–3 cm pieces.

2.2. Chemicals

All reagents were of analytical grade. Choline chloride ($\geq 98\%$), lactic acid (90%), ice-cold acetic acid (99.8%), sulfuric acid (96%), sodium chlorite, ethyl alcohol (99%), concentrated nitric acid (65%), acetone (99.5%), sodium hydroxide, sodium sulfite, dioxane (99%) and distilled water were provided by Sigma-Aldrich, Bratislava, Slovakia. Choline chloride was dried in vacuum.

2.3. Preparation of DES-like Mixtures

The preparation of DES-like mixtures in the composition of choline chloride (ChCl) and lactic acid (LacA) in a molar ratio of 1:5 (with a water content of 7.82% by weight) consisted of weighing a precalculated amount of ChCl and LacA into a flask with a round bottom, and placing the flask in a water bath which took place with constant stirring for approximately 30 min at 80 °C until the ChCl dissolved, and a clear homogeneous liquid was obtained.

2.4. Delignification Procedure

Wheat straw samples (20 g of absolutely dry samples, size 2–3 cm) were mixed with 200 g of DES-like mixtures (ChCl/LacA; 1:5); thus, the ratio between the absolutely dry samples and DES-like mixtures was 1:10. The prepared and weighed DES-like mixtures with a weighed sample of wheat straw were placed in the boiler and the batch was started. After reaching the required temperature, the holding time was tracked according to the parameters of individual batches (according to the conditions of the rotary experiment, Table 1). At the end of the batch time, the boiler was cooled. We performed a total of 20 experiments, after which the leachate was separated from the delignified fibers by filtration on a Büchner funnel under reduced pressure using a water pump. During filtration, the fibers obtained were washed with exactly 2.5 L of hot water to neutral pH. The fibers thus obtained were then embedded for 24 h in a drying oven. At the end of the drying period, the fibers were weighed and then stored in an airtight bag in a desiccator until further use.

Table 1. Proposed delignification conditions for the rotary experiment.

Number of Experiment	Delignification Temperature (°C)	Delignification Time (min)	Biomass/Solvent Ratio (g/g)
1.	96	97	1:12
2.	144	97	1:12
3.	96	204	1:12
4.	144	204	1:12
5.	96	97	1:30
6.	144	97	1:30
7.	96	204	1:30
8.	144	204	1:30
9.	80	150	1:17
10.	160	150	1:17
11.	120	60	1:17
12.	120	240	1:17
13.	120	150	1:10
14.	120	150	1:60
15.	120	150	1:17
16.	120	150	1:17
17.	120	150	1:17
18.	120	150	1:17
19.	120	150	1:17
20.	120	150	1:17

2.5. Design of the Rotary Experiment

The term rotary experiment refers to a particular way of arranging the trials of a given experiment, and by using it we can evaluate the experiment mathematically and statistically as efficiently as possible. We used the Solver subroutine in Microsoft Excel version 10 to calculate the rotary experiment, and to obtain optimization values of the regression equations. In this work, a five-level experiment was applied, in which the influence of three factors on delignification was observed. These three factors include temperature, time, and the ratio of biomass to the solvent, specifically DES-like mixtures. Limit parameters at temperature were 80 °C and 160 °C, parameters at time ranged from 60 to 240 min, and the ratio of biomass to solvent was within the range from 1:10 to 1:60. The proposed delignification conditions for the rotary experiment (temperatures, times, and biomass to solvent ratios) are given in Table 1.

2.6. Analysis Methods

2.6.1. Compositional Analysis of Raw Biomass Sample

Before the individual delignification processes, wheat straw samples were characterized in terms of the chemical composition of the raw biomass sample. The resulting average values of the content of holocellulose (Wise et al., 1946) [10], dry matter (TAPPI T264 cm-97, 1996; Preparation of wood for chemical analysis) [11], Klason lignin (TAPPI T222 om-88, 1998; Acid-insoluble lignin in wood and pulp) [12], cellulose (modified Kurschner–Hoffer method; other information can be found in the Supplementary Material), extractive substances (TAPPI T204 cm-97, 2007; Solvent extractives of wood and pulp) [13], and ash (TAPPI T211 om-12, 2012; Ash in wood, pulp, paper and paperboard: combustion at 525 °C) [14] in raw biomass samples of wheat straw are shown in Table 2.

Table 2. Chemical composition and average values of individual components in the raw biomass samples (wheat straw).

Chemical Composition	Content (%)
Dry weight	94.33 ± 0.18
Cellulose	36.19 ± 1.40
Holocellulose	62.03 ± 0.32
Klason lignin	27.89 ± 0.79
Extractives	5.18 ± 0.46
Ash	4.56 ± 0.14

2.6.2. Delignification Efficiency

To determine the efficiency of delignification, we used the values of the lignin content determined according to the standard (TAPPI T222 om-88, 1998) [12], and the calculated content of lignin in the raw biomass samples listed in Table 2. We determined the efficiency of delignification according to Equation (1):

$$\text{Delignification efficiency} = \frac{\% \text{ of lignin (raw sample)} - \% \text{ of lignin (sample after delignification)}}{\% \text{ of lignin (raw sample)}} \times 100\% \quad (1)$$

2.6.3. Optical Microscopy

To observe the nature of the fibers after delignification we used a Leica DM6 M optical microscope (Leica Microsystems (SEA) Pte Ltd.; Singapore). We observed dry samples placed on a glass slide. We gently separated the samples with tweezers to better observe their character. For microscopy, we used three objectives with magnifications of 5×, 10× and 20×. Total magnification was approximately 230×, 480× and 930×.

2.6.4. Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was performed on a Thermo Scientific Nicolet iS20 FT-IR Spectrometer (Thermo Fischer Scientific Inc., Waltham, MA, USA). For the determination, we used preprepared tablets of samples before and after delignification. Their preparation grinding the samples to a size of 0.14–0.33 mm on a grinder, which we then dried to absolutely dry fibers. The next step in their preparation was pressing, while we weighed approximately 0.300 ± 0.050 mg of the sample into the press. Pressing it consisted of two steps: in the first step we used a pressure of 5 tons during the first minute, and in the second step we used a pressure of 8 tons during the next minute. Subsequently, we selected the samples from the and we obtained tablets of about 2 mm thick. We used the tablets prepared in this way to determine functional groups in samples using FT-IR analysis. Before the actual measurement, we also prepared the measurement conditions. These consisted of setting the number of scans, which was 32, and a wavenumber with an interval of $4000\text{--}600\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . We measured each sample twice from each side of the tablet in different places. From these measurements, we obtained the average values of the measured absorbance at a given wavelength.

2.6.5. Ultraviolet–Visible Spectroscopy (UV–Vis)

For spectroscopic analysis, we used a UV-1600 series spectrophotometer (Biobase group; China) with monitored absorbance in the range of 200–800 nm at a spectral resolution of 1 nm. The analysis procedure consisted of weighing 1.2 g of pulp after delignification into a plastic tube together with 4.5 mL of dioxane. The tube was sealed, placed on a shaker and the pulp and dioxane were allowed to mix for 30 min. After this time, we separated the solution from the fibers by filtration under reduced pressure, collecting the obtained solution in a clean tube. The volume in the tube was 2 mL. To this 2 mL of solution, we added another 2 mL of dioxane to obtain a volume of 4 mL. From the solution thus prepared, we took 0.5 mL, which was then further diluted by adding 2.5 mL of dioxane. UV–Vis spectroscopy was performed on the prepared diluted samples together with a blank experiment using pure dioxane. Origin Pro 8.5 was used to evaluate the UV–Vis analysis.

3. Results

3.1. Evaluation of the Rotary Experiment

To evaluate the effect of wheat straw delignification using DES-like mixtures based on ChCl and LacA in a molar ratio of 1:5, a predesigned rotary experiment consisting of 20 experiments was used. In the conducted rotary experiment, we investigated the effect of three factors on wheat straw delignification (Table 1). The limiting parameters of the factors were chosen on the basis of previous knowledge and practice. After conducting the rotary experiment, we focused on the characterization of the samples after the application of DES-like mixtures. The measured parameters included the delignification efficiency, and as in the case of the original biomass (Table 2), we characterized the obtained pulp in terms of cellulose, lignin, holocellulose and ash content in the samples after delignification using DES-like mixtures based on ChCl/LacA in a molar ratio of 1:5. The obtained data are summarized in Table 3.

The cellulose content ranged from 43.77% to 69.53%. The lowest cellulose content was obtained in sample 10 with a temperature limiting factor of up to $160\text{ }^{\circ}\text{C}$. On the contrary, the highest cellulose content was obtained in sample 14. In experiment 14, we used a limiting ratio factor of 1:60. An interesting observation is that although we obtained the lowest yield in this experiment (14), we also obtained the highest cellulose content. We also observe obtaining the same cellulose content representing 58.18% in experiments 11 and 12, which were characterized using a limiting factor of time, which was only 60 min in experiment 11, and up to 240 min in experiment 12. Experiment 9, in which the highest pulp yield was obtained, has a relatively low percentage in terms of cellulose content, only 45.01%, representing the second lowest cellulose content in the experiments, after experiment 10. The same trend as for cellulose content is also observed for holocellulose

content. The highest holocellulose content was obtained in sample 14 with a value of 80.30%, and the lowest holocellulose content was obtained in sample 10 with a value of 59.17%.

Table 3. Values of delignification efficiency and cellulose, holocellulose, ash and lignin content after delignification according to rotary experiment.

Number of Experiment	Delignification Efficiency (%)	Cellulose (%)	Holocellulose (%)	Ash (%)	Lignin (%)
1.	28.11	65.65	72.34	2.81	20.05
2.	−3.16	53.98	66.97	4.28	28.77
3.	18.72	57.27	72.12	4.39	22.67
4.	−18.39	52.75	62.55	4.75	33.02
5.	35.53	50.52	71.44	6.06	17.98
6.	17.71	74.44	72.67	4.53	22.95
7.	18.86	51.75	71.97	3.91	22.63
8.	12.01	65.93	71.28	3.31	24.54
9.	22.70	45.01	69.61	3.99	21.56
10.	−27.25	43.77	59.17	5.35	35.49
11.	29.40	58.18	79.61	3.05	19.69
12.	31.09	58.18	70.85	4.04	19.22
13.	1.11	53.21	66.66	5.08	27.58
14.	42.17	69.53	80.30	4.26	16.13
15.	30.66	60.88	74.96	4.99	19.34
16.	35.17	59.81	77.66	4.83	18.8
17.	32.99	58.89	75.18	4.41	18.69
18.	31.12	59.39	73.30	4.07	19.21
19.	31.98	61.29	74.95	4.35	18.97
20.	28.68	58.61	76.70	4.33	19.89

We saw greater differences when comparing the residual lignin content in the samples after delignification, as its value ranged from 16.13 to 35.49%. The highest lignin content was obtained in sample 10, up to 35.49%. This value of lignin content after experiment 10 and also after experiments 2 and 4 is higher than the lignin content of the original biomass. At the same time, all these three samples did not have the perfect character of fibers obtained after delignification, but rather have the form of powder. In terms of temperature monitoring, we see that the high temperature used in this way (160 °C for experiment 10, and 144 °C for experiments 2 and 4) already results in an increase in lignin content. On the other hand, however, it is interesting to observe samples 6 and 8 with temperature also 144 °C, but with an increased biomass to solvent ratio to 1:30. After these experiments, we obtained a lower lignin content of only 22.95% in sample 6 and 25.54% in sample 8. By lowering the temperature to 80 °C and 120 °C, we can observe a lower lignin content in samples 9, 11, 12 and 15 to 20, in which we used the same ratio of 1:17. In all these delignified samples, the lignin content ranged from 18.08 to 21.56%. The lowest lignin content was obtained after experiment 14 with conditions of 120 °C, time of 150 min, and biomass to solvent ratio of 1:60. This sample also had the highest cellulose content (69.53%) and holocellulose content (80.30%).

The ash content after delignification ranged from 2.81 to 6.06%, while the ash content of the original biomass was 4.56%. Interestingly, the lowest ash content was in the sample after experiment 1 with conditions of 96 °C, 97 min, and a ratio of 1:12. On the contrary, the highest ash content was in the sample (experiment 5) in which we used the same heat-temperature and time and only the ratio used (1:30) was different.

After determining the lignin content according to the procedure described in Section 2.6.1 (TAPPI T222 om-88, 1998) [12], we calculated the delignification efficiency according to formula (1). The results obtained are also shown in Table 3. The delignification efficiency itself ranged from −27.25 to 42.17%. The highest efficiency was obtained in sample 14 characterized by the

highest ratio of biomass to solvent used. High efficiency was also achieved in sample 5 with a value of 35.53%, or sample 15 with a value of 30.66%. In contrast to these values, negative values of delignification efficiency were obtained for experiments 2, 4 and 10. These samples are characterized by a higher lignin content than the original biomass itself. The negative value of the delignification efficiency and thus the higher value of the lignin content in the pulp may be because the lignin gradually adsorbed back onto the fibers during delignification. At the same time, degradation of the carbohydrate fraction may also have occurred, as can be seen in the holocellulose content of these samples.

We also observe that the lower the lignin content in the sample after delignification, the higher the effect delignification. It is interesting to observe, for example, the difference in efficiency values for samples 13 and 14, which differ only in the ratio used. With sample 14 with a ratio of 1:60, we obtained efficiency 42.17% and for sample 13 with a ratio of 1:10 only 1.11%. On the other hand, with sample 11 we achieved efficiency 29.40% and for sample 12 the efficiency was 31.09%. These two samples were characterized by the same temperature and ratio, but with a different time. By comparing samples 1 and 3 with samples 5 and 7, we see that when using a different temperature or ratio compared to samples 11 and 12, we obtain different effectiveness. We obtained relatively high efficiencies at lower temperatures up to 120 °C.

In the next part of the work, we focused on the evaluation of the obtained values of variables such as delignification efficiency, cellulose, holocellulose, lignin, and ash content (Table 3) using the method consisting in the analysis of variance ANOVA. Subsequently, we obtained a set of regression equations, and the least squares method was used to obtain the calculated coefficients of the quadratic model. For the coefficients for delignification efficiency, cellulose and holocellulose content, we observed the maximum obtained, and for lignin and ash content, we observed the minimum obtained. Using the Solver subroutine in Microsoft Excel and applying regression equations, we determined the optimal conditions for delignification. We searched for the optimal conditions for all five parameters of interest and the results are summarized in Table 4. Other information can be found in the Supplementary Material of this article (Tables S1 and S2).

Table 4. Calculated optimal conditions for delignification for the observed parameters using DES-like mixtures in the composition ChCl/LacA in molar ratio 1:5.

Monitored Substance Content in Biomass	Lignin (%)	Cellulose (%)	Holocellulose (%)	Ash (%)	Delignification Efficiency (%)
Ideal yield (%)	16.44	67.74	80.31	1.55	37.32
Temperature (°C)	111	143	120	80	120
Time (min)	60	240	150	60	150
Biomass/solvent ratio (g/g)	1:27	1:58	1:17	1:10	1:34

The planned experiment was designed to obtain optimal conditions in terms of the resulting percentage of lignin in the pulp. The optimum conditions for obtaining the most the lowest lignin content of 16.44% at our chosen cut-off parameters are: temperature (111 °C), time (60 min), and ratio of biomass to solvent (1:27). For maximum delignification efficiency, reaching 37.32%, the optimal conditions were determined as a temperature of 120 °C, a duration of 150 min, and a ratio of 1:34.

3.2. Characterization of Obtained Pulp after Rotary Experiment

In this part of the work, we investigated and characterized the fibers of the original biomass and the pulp obtained after delignification using different analyses. First, we observed the fibers using optical microscopy to better understand and observe the change in their character. We observed each sample at three magnifications, and our goal was to see the character and shape of each fiber as we observed it. In Figure 1, the character of the fibers of the original biomass can be seen. These fibers are relatively smooth, without any distinct protrusions. It can also be seen that they are relatively longer than the fibers obtained after delignification (Figure 2).



Figure 1. Original biomass shown on an optical microscope at 230 \times magnification (a) and 930 \times (b).

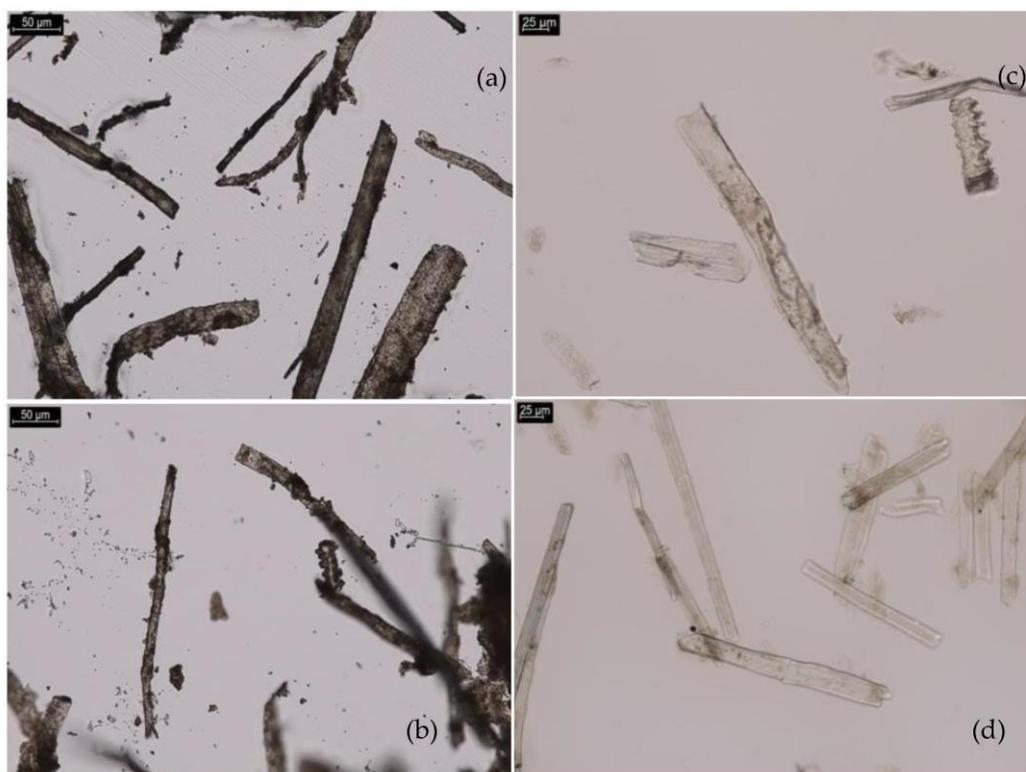


Figure 2. Comparison of fibers after delignification using DES-like mixtures in ChCl/LacA composition in a molar ratio of 1:5 on an optical microscope on samples 2 (a) and 10 (b), and samples 2 (c) and 10 (d) after the addition of dioxane at 930 \times magnification.

At the same time, we saw brown fragments attached to them, which we assumed could be the re-adsorbed lignin. To confirm our hypothesis, we performed a dioxane

test on these samples. We placed a few fibers of the sample on a slide. This sample was under a microscope at $930\times$ magnification. We then added a few drops of dioxane and watched what happened. After a while, the dioxane began to dissolve the trapped brown fragments on the sample. As a result, the fibers were no longer free of brown fragments, which dissolved in the presence of dioxane. This test confirmed the presence of lignin in the sample, as dioxane dissolves lignin. Our hypothesis was confirmed by this experiment, and we tried to confirm it using other methods in this work. Other results can be found in the Supplementary Material of this article (Tables S3–S8).

Another analysis to characterize the obtained pulps was UV–Vis spectroscopy where we spectrophotometrically determined brown fragments on the fiber surface. The obtained dependence of absorbance on wavelength is shown in Figure 3, and we used the OriginPro 8.5 program for the evaluation. The lowest absorbance was obtained for sample 14, characterized by the lowest percentage of lignin with an absorbance value of 2.03 at a wavelength of 240 nm. In contrast, sample 10 with the highest percent lignin has an absorbance value as high as 2.72 at 245 nm. The highest absorbance values for all three samples are between 240 and 300 nm. This confirms the presence of lignin in the solution and hence on the original samples, since the absorption bands centered at 280 nm are attributed to lignin [15]. As a reference sample, we chose lignin obtained by the natron and sulfate methods. Comparing the reference samples with our samples, we see that sample 10 is almost identical to the reference samples. This proves our hypothesis that the brown fragments from the fiber surface are indeed lignin.

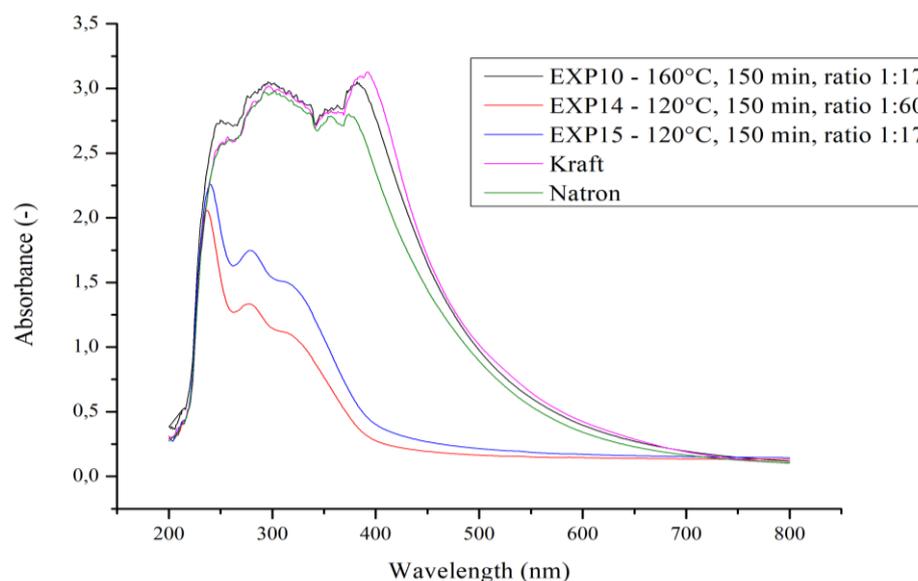


Figure 3. Wavelength dependence of absorbance of a dilute solution of dioxane with lignin for samples 10, 14 and 15 obtained after delignification using DES-like mixtures based on ChCl/LacA in molar ratio 1:5.

After characterizing the samples using UV–Vis analysis, we used FT-IR analysis. It is known from the literature that FT-IR is an important technique in the analysis of biomass and its structure, and subsequently in the characterization of changes in the structure of lignocellulosic materials as a result of various chemical and physical treatments. Pawlak-Kruczek et al. [16] summarized the FT-IR bands and maximum values that were identified in various studies dealing with biomass and characterization of its structure. We used the obtained spectra to characterize the fibers in terms of changes in the functional groups of lignin, cellulose, and hemicelluloses after delignification. In Figure 4, we displayed the obtained spectrum for our raw biomass—wheat straw. The area between 3100 and 3500 cm^{-1} is due to the stretching of hydroxyl groups in holocellulose and lignin. Value 897 cm^{-1} corresponds to β -glycosidic bonds in cellulose, which can be proven presence

of increased cellulose content in samples after delignification [15–19]. As it increases absorbance value at a wavelength of 897 cm^{-1} , thereby increasing the cellulose content in the sample. Values 1380 and 1320 cm^{-1} correspond to the C=C bonds of the aromatic nucleus in lignin. Peaks at 1714 and 1654 cm^{-1} correspond to conjugated and unconjugated carbonyl bonds. The stretching of the aromatic core in lignin is observed at peaks with the value 1595 and 1510 cm^{-1} . These signals describe the aromatic vibrations characteristic of lignin syringyl and guaiacyl type [18,19].

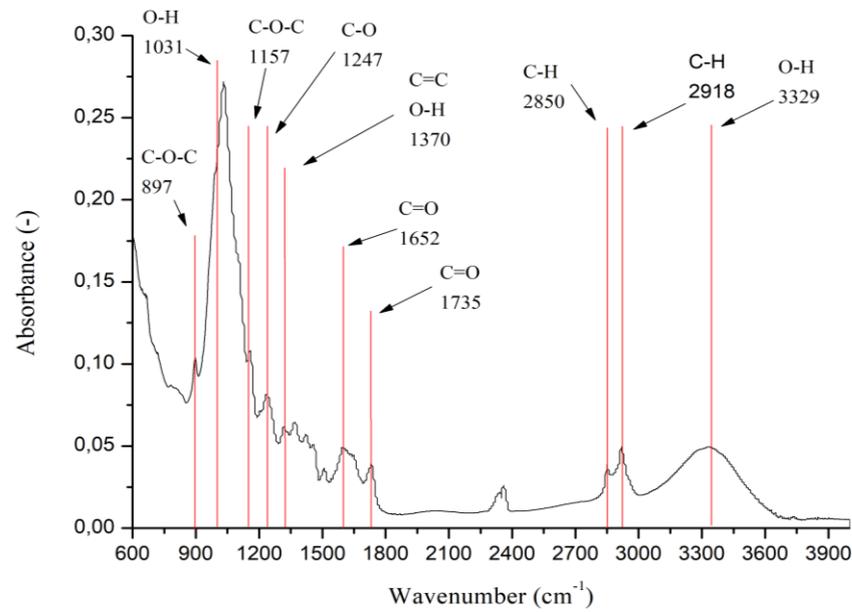


Figure 4. FT-IR spectrum of raw biomass (wheat straw).

The comparison of samples 9 and 10 with the raw biomass is worth paying attention to. Sample 10 has almost the same absorbance values and sample 9 shows even lower absorbance values either at the values for lignin or cellulose. These two samples are characterized by temperature boundary parameters, where in the case of sample 9, we used a temperature of $80\text{ }^{\circ}\text{C}$, and for sample 10 a temperature of up to $160\text{ }^{\circ}\text{C}$. Comparing samples 10 and 14, for which we obtained the lowest and highest cellulose content, we see a clear difference in the peaks corresponding to cellulose. Sample 10 achieves an absorbance of only 0.27 and sample 14 achieves absorbance values up to 0.46 at a wavelength of 1055 cm^{-1} (Figure 5).

Subsequently, to further confirm our hypothesis, we left the dioxane solution with dissolved brown fragments to dry in the oven. After drying, we mixed the brown solid fraction with potassium bromide and measured the prepared samples by FT-IR analysis. Figure 6 shows the obtained spectrum of lignin isolated by us from the fibers. In the given spectrum, peaks with relatively strong absorbance can be seen at wavenumbers of approximately 1100 , 1700 , 2900 and 3390 cm^{-1} . In 2023, Ivanova et al. [17] addressed the characterization of alkali lignin, also using FT-IR analysis. The functional group belonging to the 3390 cm^{-1} wavenumbers a hydroxyl group of phenolics that belongs to lignin. At the same time, we observe almost the same character of the spectrum at a wavenumber of 2935 cm^{-1} which is characteristic of the vibration of the C-H groups [17]. A slight increase in absorbance at 1595 cm^{-1} also confirms the presence of lignin, since this wavenumber is characteristic of the C-H, C=O and O-H vibrations of the aromatic nuclei. High absorbance at 1166 cm^{-1} is further evidence of the presence of lignin as it is attributed to the presence of guaiacyl, which is one of the monolignols from which the substructures of phenol are formed [17]. At the same time, the wavenumber of 1301 cm^{-1} is attributed to the functional groups of guaiacyl, but also to the O-H groups of phenolic and non-ether bonds [17]. In contrast, the 1234 cm^{-1} wavenumber is characteristic for the functional groups of

syringyl, which also belongs to the monolignol-forming substructures phenolic subunits like guaiacyl [17] Interval $1130\text{--}1160\text{ cm}^{-1}$ is typical for O-H bonds of secondary alcohols and condensed aromatic nuclei [17].

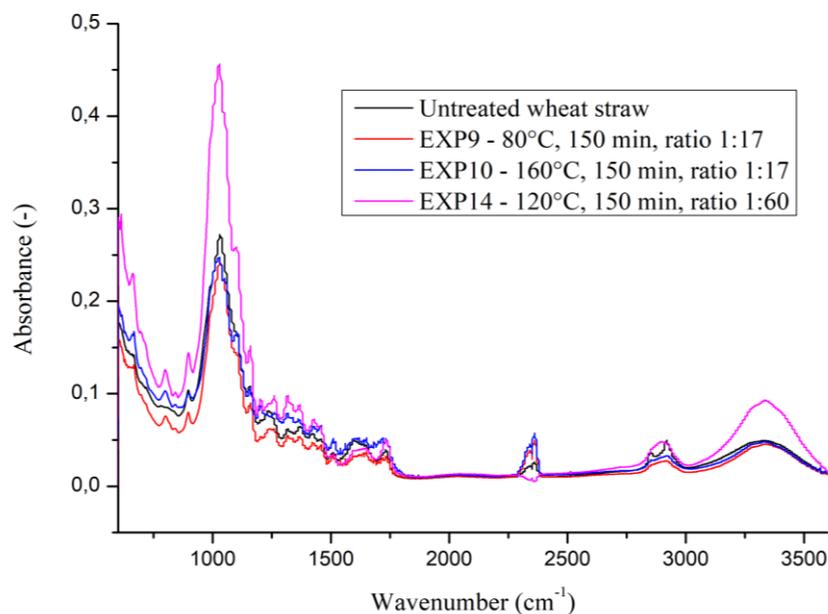


Figure 5. FT-IR spectra of the untreated wheat straw and samples 9, 10 and 14 after delignification using DES-like mixtures based on ChCl/LacA in molar ratio 1:5.

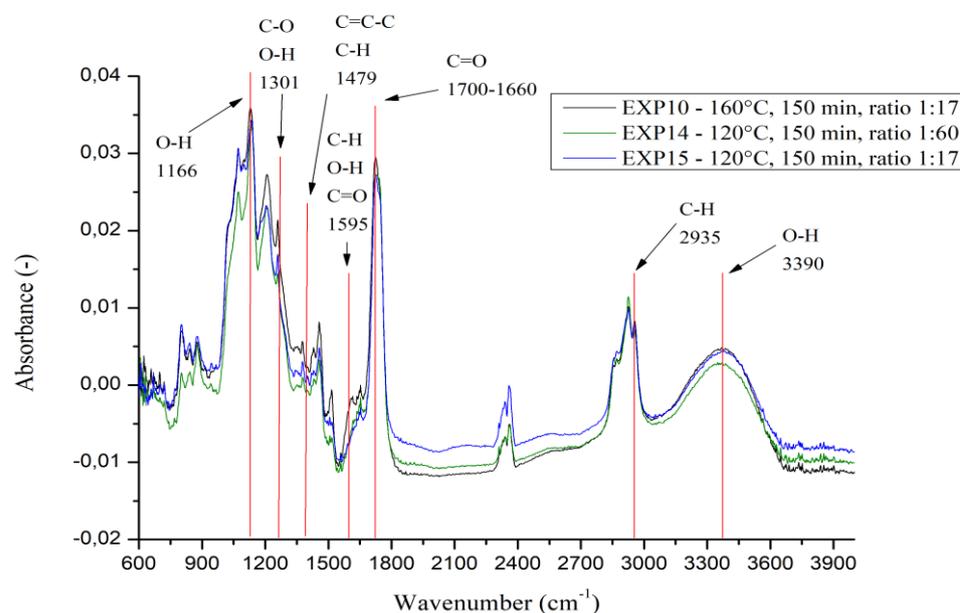


Figure 6. FT-IR spectrum of lignin isolated from fibers after delignification using DES-like mixtures based on ChCl/LacA in molar ratio 1:5.

Using FT-IR analysis, we also compared the isolated lignin from the leachates after delignification. We chose samples 2, 4, 10 and 14 for comparison. The amount of C=C bonds belonging to lignin at a wavenumber of 1380 cm^{-1} in sample 10 differs rapidly compared to the other three samples [18,19]. This smaller amount of lignin isolated from the leachate could be explained by the adsorption of lignin on the fibers during delignification, thus suggesting a lower lignin content in the leachate.

Subsequently, we compared the isolated lignin from the leachate with the lignin obtained from the fibers (Figure 6). Observing the absorbance at a wavenumber of 897 cm^{-1}

and 1055 cm^{-1} characteristic for cellulose, we see smaller values compared to the original biomass [19]. We observe the same at a wavelength of 1247 cm^{-1} . Comparing the absorbance of lignin, we see only slight differences, but the largest difference can be observed at a wavenumber of 1700 cm^{-1} characteristic of the vibration of C=O bonds in COOH functional groups. The absorbance values for lignin isolated from the fibers are considerably lower compared to lignin isolated directly from the leachate; however, by comparing the peaks for the functional group characteristic of lignin, we see that lignin is obtained in both cases, just in different amounts. This also confirms our hypothesis of lignin being adsorbed back onto the surface of the fibers. Additionally, thanks to this method together with the previous methods we were able to confirm our hypothesis of re-adsorbed lignin on the fiber surface. Other results can be found in the Supplementary Material of this article (Table S9).

3.3. Comparison of Obtained Results with Others Delignification Processes

Our next step in this work was to compare the results we obtained with those of other studies that also delignified wheat straw. As a first step, we focused on comparing delignification of wheat straw using conventional solvents. In Figure 7 we can see how the Kappa number changes when delignified with different processes—soda process, soda-anthraquinone process, Kraft process, organosolv process or delignification with ethanolamine.

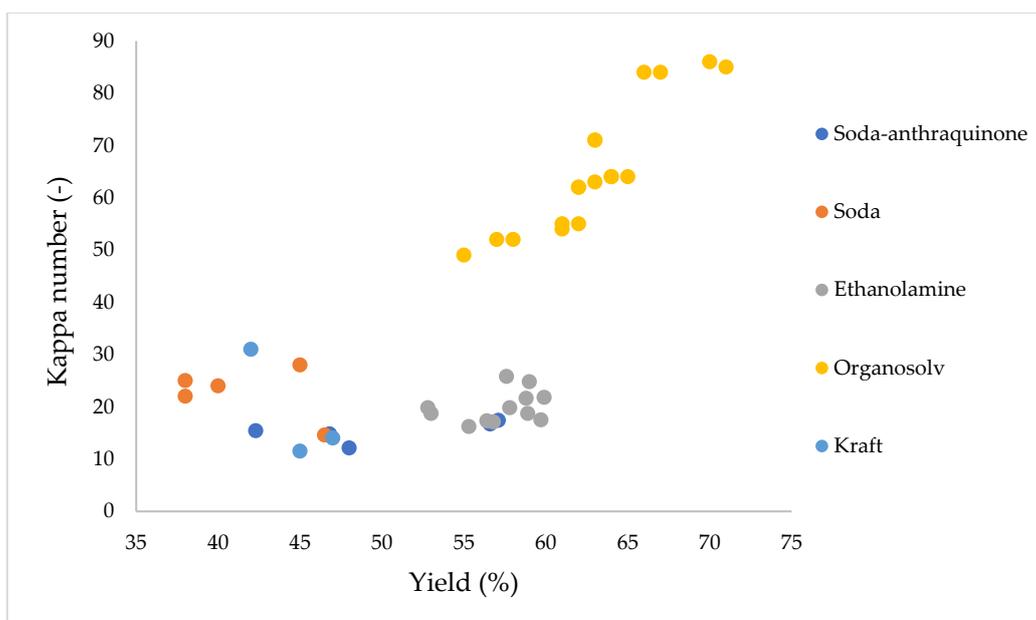


Figure 7. Comparison of Kappa number from yields in wheat straw delignification using different conventional solvents [20–23].

The aim of delignification is to obtain the smallest possible Kappa number, since this number represents the amount of lignin removed. The soda, Kraft, and soda-anthraquinone processes give us approximately the same Kappa numbers at yields ranging from 38 to 57.1%. For example, compared to soda process, we see that delignification with ethanolamine yields approximately the same pulp Kappa number, but their yields are significantly different. For the soda process, the yields are approximately between 38 and 46.5%, and with ethanolamine the yields are as high as 52.8–59.7%. Saberikah et al. in 2011 [22] delignified wheat straw with aqueous glycerol solution at different times. The pulp obtained in this way reached a Kappa number of 49–86, which is higher than that of other methods. At the same time, using the organosolv process, the highest yields were obtained, ranging between 55 and 70%. As can be seen from Figure 6, the results obtained in the delignification of wheat straw depend not only on the nature of the fibers used, but also on the type of process used, time, temperature, or the presence of a catalyst.

The next step was to conduct a literature search in terms of the resulting lignin content in wheat straw after delignification from yield using different solvents. Contents of lignin as well as yields differ when different delignification solvents are used, as can be seen on Figure 8. Yields range from 40.1 to 94.93% and lignin content ranges from 1.66 to 17.4%. The lowest lignin contents are achieved with organosolv delignification, ASD (solvent-accelerated delignification) and ASD-anthraquinone by delignification or when using soda and soda-anthraquinone process. In 2007, Ziaie-Shirkolaei et al. [24] obtained pulp after delignification by the Kraft process with a yield of 40.5–43% at a lignin content of only 5.01–6.6%. In contrast, pulp was obtained during delignification using the organosolv method with a yield of up to 50.33–66.56%, but with a higher lignin content, which was in the range of 5.01–10.88% [24]. Similarly, the addition of anthraquinone to the solvent affects lignin content, with lower lignin content achieved in its presence.

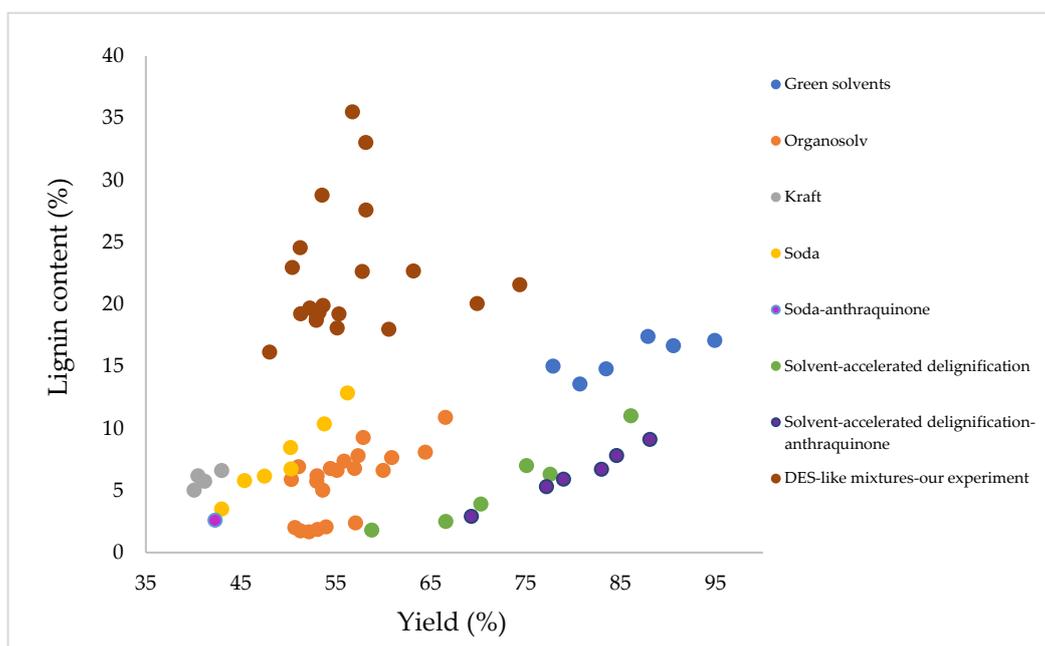


Figure 8. Comparison of lignin content from yield after delignification of wheat straw using various solvents (different delignification processes) [5,9,23–25].

Furthermore, we compared our results with those obtained in other studies. Our achieved pulp yields after delignification ranged from 48.05% to 74.39%. This means that we obtained higher yields compared to processes such as Kraft, soda, or soda-anthraquinone. However, the lignin content in our samples after delignification significantly differs, with values ranging from 16.13% to 35.49%. When comparing our results with conventional solvents, we observe a noticeable difference. Our yields are approximately the same as those obtained in the soda and organosolv processes, but the resulting lignin contents are significantly higher. Comparing with the Kraft process, our lignin content in the samples is about four to five times higher, while our yield is roughly 1.5 times higher. When comparing our results with those obtained with green solvents, we find that our yields are lower. Green solvent yields range from 80.74% to 94.93%, which is significantly higher than our yields. However, we observe higher lignin content in our samples, ranging from 16.13% to 35.49%, which is much higher compared to other green solvents.

In summary, the results obtained during the delignification of wheat straw depend on various factors such as the type of solvent, process conditions, and the presence of additives. Solvents resembling DES-like mixtures represent an alternative to delignifying lignocellulosic biomass using conventional chemical treatments. The development and study of new ecological green solvents are advancing due to the increasing demand for green technologies and research in green chemistry. Green solvents, including DES-like

mixtures, are expected to have low toxicity for both humans and the environment, be biodegradable, and offer the possibility of regeneration. However, the application and recycling of DES-like mixtures are limited by their thermal instability and susceptibility to contaminants that could interfere with interactions between hydrogen bond acceptors and hydrogen bond donors. Research is needed to develop stable and recyclable DES-like mixtures systems, especially for conversions requiring elevated temperatures. The broad range of combinations of hydrogen bond acceptors and hydrogen bond donors in DES-like mixtures, and biomass complicates the selection of suitable DES-like mixtures for biomass pretreatment. The effect of acidity/alkalinity is significant in the application of solvents and systems for various applications and affects the chemical reactions that take place. This fact has a fundamental impact on the different selectivity, efficiency, and behaviour of solvent systems after their application in various areas—fractionation of biomass, catalytic reactions, dissolution of substances, and adsorption of substances. Understanding the basic mechanism between DES-like mixtures and biomass is key to effectively utilizing DES-like mixtures for biomass pretreatment [26].

4. Conclusions

Our goal in this work was the delignification of wheat straw using DES-like mixtures based on choline chloride and lactic acid in a molar ratio of 1:5 using a rotary experiment. Our task was to monitor the influence of three factors on delignification, namely temperature, time, and ratio of biomass to the solvent at the boundary parameters chosen by us. For the temperature, we chose borderline parameters of 80 °C and 160 °C, at a time of 60 and 240 min and a ratio of 1:10 and 1:60. Delignification was underway according to the set parameters obtained using the rotary experiment. We watched the resulting efficiency of delignification and at the same time the change in the content of cellulose, holocellulose, lignin, and ash compared to untreated raw biomass. We also compared the obtained values with each other to monitor the effect of different temperature, time, and ratio of biomass to solvent in delignification. The efficiency of delignification ranged from –27.25 to 42.17%. The cellulose content in our samples after delignification increased to 43.77–69.53% compared to the raw biomass, in which the cellulose content was 36.19%. An interesting finding was that the lignin content in the original biomass was 27.89%, but after delignification its content ranged from 16.13 to 35.49%. Specifically, in three samples (2, 4 and 10) its content was higher than in the raw biomass. This increase could be caused by the back-adsorption of lignin onto the fibers during delignification, which we tried to prove with different methods in this work. We prepared the rotary experiment to determine the optimal conditions for the delignification of wheat straw in terms of lignin content. The optimal lignin content after delignification should be 16.44% at a temperature of 111 °C, a time of 60 min and a ratio of biomass to solvent of 1:27. One of the goals was to conduct a literature search from the point of view of delignification of wheat straws either with conventional or green solvents. We subsequently compared the percentage obtained by the lignin representation in samples delignified according to the rotary experiment with the data obtained during the search, which we summarized in Figure 7. Yields in these studies ranged from 40.1 to 94.93%, and the lignin content ranged from 1.66 to 17.4%. As can be observed, the yields obtained by us are with the yields obtained in the studies are approximately the same, as they ranged from 48.05 to 74.39%. However, the percentage of lignin in our case was about half as high, with values from 16.13 to 35.49%. Although we achieved higher lignin contents in our delignification and lower yields compared to other studies, the use of green solvents is still preferable an alternative for delignification of wheat straw or other annual plants. Their properties represent an advantage in terms of use, as they are non-flammable, biodegradable, environmentally friendly or economically advantageous.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su152115343/s1>, Table S1: Obtained group analysis of variance in terms of lignin content; Table S2: Obtained coefficients of regression equations when monitoring the efficiency of delignification and content of lignin, cellulose, holocellulose and ash; Table S3: Optical microscopy images on samples after delignification using DES-like mixtures in a composition

of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 1 to 3); Table S4: Optical microscopy images on samples after delignification using DES-like mixtures in a composition of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 4 to 6); Table S5: Optical microscopy images on samples after delignification using DES-like mixtures in a composition of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 7 to 9); Table S6: Optical microscopy images on samples after delignification using DES-like mixtures in a composition of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 10 to 12); Table S7: Optical microscopy images on samples after delignification using DES-like mixtures in a composition of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 13 to 15); Table S8: Optical microscopy images on samples after delignification using DES-like mixtures in a composition of choline chloride and lactic acid in a molar ratio of 1:5 at magnifications of 230×, 480×, and 930× (experiment 16 to 20); Table S9: FT-IR spectra of pulps obtained after delignification according to the rotary experiment using DES-like mixtures based on choline chloride and lactic acid in a molar ratio of 1:5; Figure S1: Dependence of delignification efficiency on delignification time and temperature.

Author Contributions: Conceptualization, V.J. and M.J.; methodology, K.V. and V.J.; software, K.V.; validation, V.J., K.V. and M.J.; formal analysis, V.J.; investigation, K.V. and V.J.; resources, V.J. and K.V.; data curation, K.V.; writing—original draft preparation, V.J.; writing—review and editing, V.J. and M.J.; visualization, V.J.; supervision, M.J.; project administration, M.J.; funding acquisition, M.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Slovak Research and Development Agency under the contracts Nos. APVV-22-0277, APVV-22-0388, and VEGA Grant 1/0651/23.

Institutional Review Board Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sharma, D.; Nagpal, R.; Agrawal, S.; Bhardwaj, N.; Mahajan, R. Eco-friendly bleaching of agrowaste wheat straw using crude alkalo-thermotolerant cellulase-free xylano-pectinolytic enzymes. *Appl. Biochem. Biotechnol.* **2022**, *194*, 620–634. [[CrossRef](#)] [[PubMed](#)]
2. Yue, X.; Suopajarvi, T.; Mankinen, O.; Mikola, M.; Mikkelsen, A.; Ahola, J.; Hiltunen, S.; Komulainen, S.; Kantola, A.M.; Telkki, V.; et al. Comparison of lignin fractions isolated from wheat straw using alkaline and acidic deep eutectic solvents. *J. Agric. Food Chem.* **2020**, *68*, 15074–15084. [[CrossRef](#)] [[PubMed](#)]
3. Suopajarvi, T.; Ricci, P.; Karvonen, V.; Ottolina, G.; Liimatainen, H. Acidic and alkaline deep eutectic solvents in delignification and nanofibrillation of corn stalk, wheat straw, and rapeseed stem residues. *Ind. Crops Prod.* **2020**, *145*, 111956. [[CrossRef](#)]
4. De Dios, L.G. Phase Equilibria for Extraction Processes with Designer Solvent. Ph.D. Thesis, University of Santiago de Compostela, Santiago de Compostela, Spain, 2013.
5. Jablonský, M.; Škulcová, A.; Kamenská, L.; Vrška, M.; Šima, J. Deep eutectic solvents: Fractionation of wheat straw. *BioResources* **2015**, *10*, 8039–8047. [[CrossRef](#)]
6. Gaudino, E.C.; Tabasso, S.; Grillo, G.; Cravotto, G.; Dreyer, T.; Schories, G.; Altenberg, S.; Jashina, L.; Telysheva, G. Wheat straw lignin extraction with bio-based solvents using enabling technologies. *Comptes Rendus Chim.* **2018**, *21*, 563–571. [[CrossRef](#)]
7. Chen, Z.; Ragauskas, A.; Wan, C. Lignin extraction and upgrading using deep eutectic solvents. *Ind. Crops Prod.* **2020**, *147*, 112241. [[CrossRef](#)]
8. Bajpai, P. *Deep Eutectic Solvents for Pretreatment of Lignocellulosic Biomass*, 1st ed.; Springer: Singapore, 2021; pp. 2191–5318.
9. Tan, J.; Yu, D.; Yuan, J.; Wu, H.; Luo, H.; Zhang, H.; Li, X.; Li, H.; Yang, S. Efficient delignification of wheat straw for microbial lipid production enabled by a novel ternary deep eutectic solvent containing ethylene glycol. *Fuel* **2023**, *347*, 128485. [[CrossRef](#)]
10. Wise, L.E.; Murphy, M.; D’Addieco, A.A. Chlorite holocellulose, its fractionation and nearing on summative wood analysis and studies on the hemicellulose. *Tech. Assoc. Pap.* **1946**, *29*, 210–218.
11. TAPPI T264 cm-97 1996; Preparation of Wood for Chemical Analysis. TAPPI Press: Atlanta, GA, USA, 1996.
12. TAPPI T222 om-98 1996; Acid-Insoluble Lignin in Wood and Pulp. TAPPI Press: Atlanta, GA, USA, 1996.
13. TAPPI T204 cm-97 2007; Solvent Extractives of Wood and Pulp. TAPPI Press: Atlanta, GA, USA, 2007.
14. TAPPI T211 om-12 2012; Ash in Wood, Pulp, Paper, and Paperboard: Combustion at 525 °C. TAPPI Press: Atlanta, GA, USA, 2012.
15. Zhang, Y.; Ren, H.; Li, B.; Udin, S.M.; Maarof, H.; Zhou, W.; Cheng, F.; Yang, J.; Liu, Y.; Alias, H.; et al. Mechanistic insights into the lignin dissolution behavior in amino acid based deep eutectic solvents. *Int. J. Biol. Macromol.* **2023**, *242*, 124829. [[CrossRef](#)]
16. Pawlak-Kruczek, H.; Arora, A.; Gupta, A.; Saeed, M.A.; Niedzwiecki, L.; Andrews, G.; Phylaktou, H.; Gibbs, B.; Newlaczyl, A.; Livesey, P.M. Biocoal—Quality control and assurance. *Biomass Bioenergy* **2020**, *135*, 105509. [[CrossRef](#)]

17. Ivanova, D.; Toneva, M.; Simeonov, E.; Nikolova, B.; Semkova, S.; Antov, G.; Yaneva, Z. Newly Synthesized Lignin Microparticles as Bioinspired Oral Drug-Delivery Vehicles: Flavonoid-Carrier Potential and In Vitro Radical-Scavenging Activity. *Pharmaceutics* **2023**, *15*, 1067. [[CrossRef](#)] [[PubMed](#)]
18. Soares, B.; da Costa Lopes, A.M.; Silvestre, A.J.; Pinto, P.C.R.; Freire, C.S.; Coutinho, J.A. Wood delignification with aqueous solutions of deep eutectic solvents. *Ind. Crops Prod.* **2021**, *160*, 113128. [[CrossRef](#)]
19. Chi, S.; Yu, G.; Zhang, X.; Zhang, Y.; Liu, C.; Li, Z.; Li, B.; Cui, Q. Response Surface Optimization of Ammonium Sulfite Pretreatment for Fermentable Sugar Production from Wheat Straw. *BioResources* **2019**, *14*, 4603–4622. [[CrossRef](#)]
20. Pakkanen, H.A.N.N.U. Characterization of Organic Material Dissolved during Alkaline Pulping of Wood and Non-Wood Feedstocks. Ph.D. Thesis, University of Jyväskylä, Jyväskylä, Finland, 2012.
21. Hedjazi, S.; Kordsachia, O.; Patt, R.; Kreipl, A. MEA/water/AQ-pulping of wheat straw. *Holzforschung* **2009**, *63*, 505–512. [[CrossRef](#)]
22. Saberikhah, E.; Mohammadi Rovshandeh, J.; Rezayati-Charani, P. Organosolv pulping of wheat straw by glycerol. *Cellul. Chem. Technol.* **2011**, *45*, 67–75.
23. Barbash, V.; Trembus, I.; Shevchenko, V. Ammonia-sulfite-ethanol pulp from wheat straw. *Cellul. Chem. Technol.* **2014**, *48*, 345–353.
24. Ziaei, S.Y.; Mohammadi, R.D.J.; Khajeian, M.; Rezayati, C.P. Study on cellulose degradation during organosolv delignification of wheat straw and evaluation of pulp properties. *Iran. Polym. J.* **2007**, *16*, 83–96.
25. Barbash, V.; Trembus, I.; Sokolovska, N. Performic pulp from wheat straw. *Cellul. Chem. Technol.* **2018**, *52*, 673–680.
26. Jančíková, V.; Jablonský, M.; Voleková, K.; Šurina, I. Summarizing the Effect of Acidity and Water Content of Deep Eutectic Solvent-like Mixtures—A Review. *Energies* **2023**, *15*, 9333. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.