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Effect of Treatment Time on Deep Eutectic Solvent Treatment of Scots Pine Wood

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Abstract

Aim of study: The influence of the treatment time (1 hour, 2 hours, and 3 hours) on the deep eutectic solvent (DES) treatment of Scots pine (*Pinus sylvestris* L.) wood is investigated in this study.

Area of the study: Determination of DES performance on the Scots pine wood chemical structure.

Material and methods: Choline chloride (ChCl) and lactic acid (LA) mixture with molar ratio of 1:10 (w:w) was used as a DES solvent. Treatments were carried out in an autoclave at 121 °C. The effects of DES treatment on the properties of wood and lignin samples of Scots pine were determined according to the relevant standards.

Main results: The delignification ratio, lignin purity, and lignin yield in the 3h-treated sample were determined to be 79.78%, 86.43%, and 82.48%, respectively. The crystallinity index (CrI) was increased from 55.87% to 71.58% with 3 h DES treatment. Brunauer-Emmett-Teller (BET) analysis results showed that the surface area of the sample increased with 3-h DES treatment (from 3.095 m^2/g to 3.621 m^2/g). The 1-hour DES-treated sample yielded the lightest colored lignin (L*: 71.62).

Research highlights: Treatment time of Scots pine wood during DES treatment has a significant effect on the wood and lignin properties.

Keywords: Deep Eutectic Solvent, Lignin, Scots pine, Crystallinity Index, XRD, BET, Biorefinery

Sarıçam Odununun Derin Ötektik Çözücü Muamelesi Üzerine Muamele Süresinin Etkisi

Öz

Çalışmanın amacı: Bu çalışmada, sarıçam (*Pinus sylvestris* L.) odununun derin ötektik çözücü (DÖÇ) muamele süresinin (1 saat, 2 saat ve 3 saat) etkileri araştırılmıştır.

Çalışma alanı: Çalışma Türkiye'deki Bartın ilinde gerçekleştirilmiştir.

Materyal ve yöntem: DÖÇ (kolin klorür (ChCl) ve laktik asit (LA)) muameleleri, 121 °C'de bir otoklavda gerçekleştirilmiştir. DÖÇ muamelesinin sarıçam odununun ve ligninin özellikleri üzerine etkileri ilgili standartlara göre belirlenmiştir.

Temel sonuçlar: 3 saat muamele edilmiş numunede delignifikasyon oranı, lignin saflığı ve lignin verimi sırasıyla %79,78, %86,43 ve %82,48 olarak belirlenmiştir. Kİ, 3 saat DÖÇ muamelesi ile %55,87'den %71,58'e yükselmiştir. 3 saat DÖÇ ile muamele edilmiş örneğin lignin saflığı, lignin verimi ve delignifikasyon oranı sırasıyla %86,43, %82,48 ve %79,78 olarak tespit edilmiştir. Brunauer-Emmett-Teller (BET) analiz sonuçları, numunenin yüzey alanının 3 saatlik DÖÇ muamelesi ile arttığını (3,095 m^2/g'den 3,621 m^2/g'ye) göstermiştir. 1 saat DÖÇ ile muamele edilmiş numune en açık renkli lignini vermiştir (L*: 71,62).

Araştırma vurguları: Sarıçam odununun DÖÇ muamelesi sırasında muamele süresi, odun ve lignin özellikleri üzerinde önemli etkilere sahiptir.

Anahtar Kelimeler: Derin Ötektik Çözücü, Lignin, Sarıçam, Kristallik Indisi, XRD, BET, Biyorafineri

Introduction

Deep eutectic solvents (DES)s, discovered at the beginning of the century as green chemicals, consist of two or more chemicals. They are low-cost, non-toxic, ecologically friendly, and biodegradable (Zhang et al., 2012; New et al., 2022). These benefits make them potential solvents for the pretreatment or extraction of biomass (Sumer and Van Lehn, 2022). During the last decade, DESs have been used widely in biomass treatment (Li et al., 2017; Pan et al., 2017; Lyu et al., 2018; Xu

et al., 2018; Kwon et al., 2020) and pulping (Choi et al., 2016a, b; Smink et al., 2019; Cui et al., 2022; Gülsoy et al., 2022a, b; Gülsoy, 2023).

There are several factors affecting the performance of DES treatments, such as treatment temperature, treatment time, solid/liquid ratio, DES type and their mole ratio, etc. Treatment time, ranging from minutes to hours, is a key factor in the DES efficiency in biomass pretreatments (Muley et al., 2019; Ma et al., 2021; Mankar et al., 2022; Pan et al., 2017; Lyu et al., 2018; Liu et al., 2019a). There is a linear correlation between treatment time and delignification (Škulcová et al., 2016; Xu et al., 2020). However, it was noted that after a certain period, there was an equilibrium between the biomass and the solvent (DES) and no further dissolution occurred. Carbohydrate degradation should be avoided during the extensive lignin yields. The cellulose fibers enlarge as the treatment time increases, and thus solvent penetration improves (Xu et al., 2020). Time prolongation is essential since it raises the cost of the procedure from an industrial standpoint (Ozturk et al., 2018).

Several authors have investigated the effect of treatment time on the effectiveness of biomass DES treatment. According to Pan et al. (2017), extending the treatment time from 4 hours to 8 hours enhanced the delignification ratio from 35.71% to 44.74% in the treatment of rice straw with ChCl and urea in a 1:2 molar ratio. According to Li et al. (2017), when willow wood was treated with ChCl and lactic acid (1:10 mol ratio), the delignification ratio rose up to 12 hours, and insignificant delignification ratios were achieved when the treatment time was beyond 12 hours. For example, although 12 hours of treatment results in 91.8% delignification ratio, increasing time to 42 hours results in 94.2% delignification ratio. After DES pretreatment of ChCl/glycerol (1:2), liquid/solid ratio 10, 160 °C, glucose yields increased by 84% with increased time 2 h, 4 h, and 8 h for corn stover (Xu et al., 2018). Lyu et al. (2018) studied the effects of treatment time (6, 9, 12, 18, and 24 h.) on purity and structural characterization of DES-lignin samples extracted from willow (*Salix matsudana* cv. Zhuliu). Liu et al. (2019a) treated wheat straw with DES (triethylbenzyl ammonium chloride/lactic acid - 1:9 molar ratio) at a pretreatment temperature of 100 °C to investigate the effects of different pretreatment times (2 h, 4 h, 6 h, 8 h, 10 h, and 12 h). They found that weight loss, lignin removal, and xylan removal correlated positively with treatment time. Fiskari et al. (2020) discovered that prolonged time from 3 hours to 6 hours in the DES treatment of mechanical pulps increased the amounts of lignin removed, but increasing the time to 15 hours decreased the amount of removed lignin. The re-precipitation of the dissolved lignin on the fibers caused a reduction in the delignification ratio after 15 hours of treatment. In the case of *Pinus densiflora* wood treated with DES (ChCl/LA and ChCl/glycerine), the residual solid waste yield had a negative correlation with treatment time (Kwon et al., 2020).

Effect of treatment time on the efficiency of DES treatment with Scots pine wood has not previously been evaluated. Scots pine wood was treated with ChCl and LA (1:10) at 121 °C for varied reaction times (1h, 2h, and 3h). Wood chemical composition, solid residue yield, delignification ratio, lignin yield, lignin purity, and lignin color will be analyzed. X-ray diffraction (XRD) was done to see the CrI of samples. Additionally, the surface areas of control and DES-treated wood samples were determined using BET analysis.

Materials and Methods

Materials

Scots pine (*Pinus sylvestris* L.) wood, obtained from Bartın Province, Türkiye, was used in this study. Samples were grounded with a Willey Mill and sieved to 60 mesh by Retsch AS 200 sieve shaker. Choline chloride (ChCl) CAS: 67-48-1 and lactic acid (LA) CAS: 79-33-4 were purchased from Sigma Aldrich.

Preparation of DES

The DES mixture was prepared with a molar ratio of 1:10 (w:w) of ChCl and LA. The mixture was heated at 70 °C with continuous stirring for 30 minutes until a clear solution formed. To minimize moisture

absorption, it was then cooled to room temperature in a glass desiccator.

Lignin Extraction

The lignin extraction was done in a 500 ml autoclave bottle using Hirayama HV-110 autoclave. Scots pine wood (dry mass 20.0 g) was mixed with DES (200.0 g) and heated at 121 °C for various reaction times (1h, 2h, and 3h) (Figure 1). The autoclave bottle was filled with 200 mL of ethanol at the end of this procedure. The solid residue was then filtered through a medium porosity (2 number) Gooch crucible and washed twice with ethanol before drying at 103 °C in an oven. To recycle ethanol, the filtrate was evaporated in a rotatory evaporator at 45 °C. After that, 500 ml of deionized water was added to the remaining solution to separate out lignin (Figure 2). The lignin samples were filtered using a Whatman No. 42 filter paper and washed with ethanol/distilled water 1:9 (v/v) (Figure 3). Finally, the lignin samples were dried in a freeze-dryer.

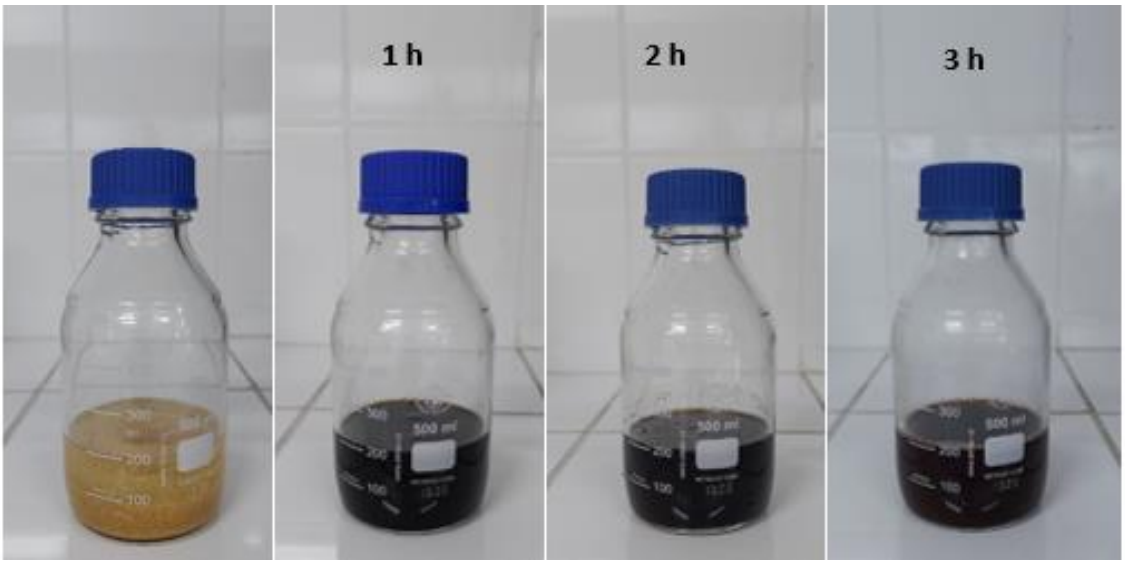

Figure 1. DES treatments of Scots pine wood

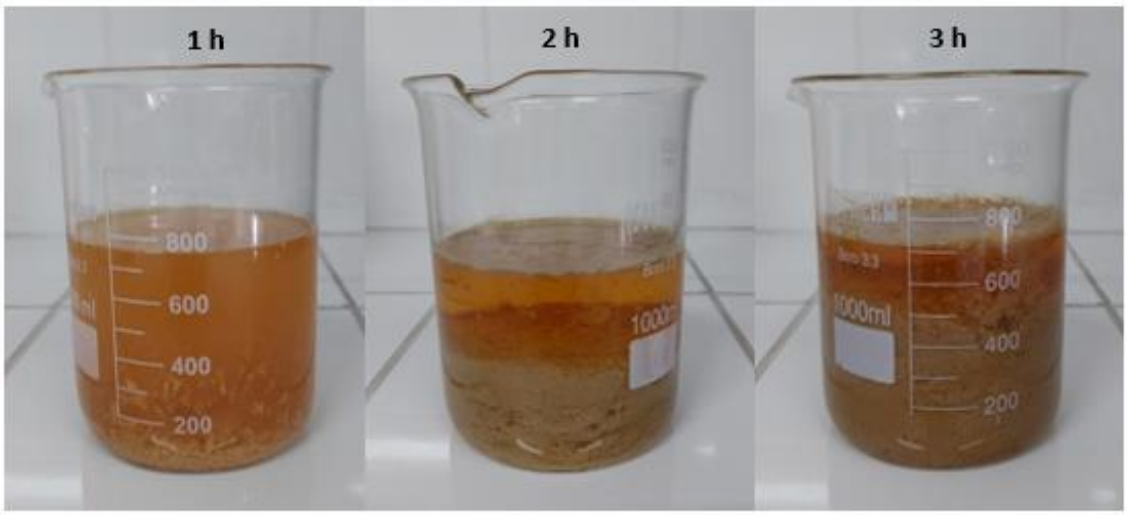

Figure 2. Lignin precipitation

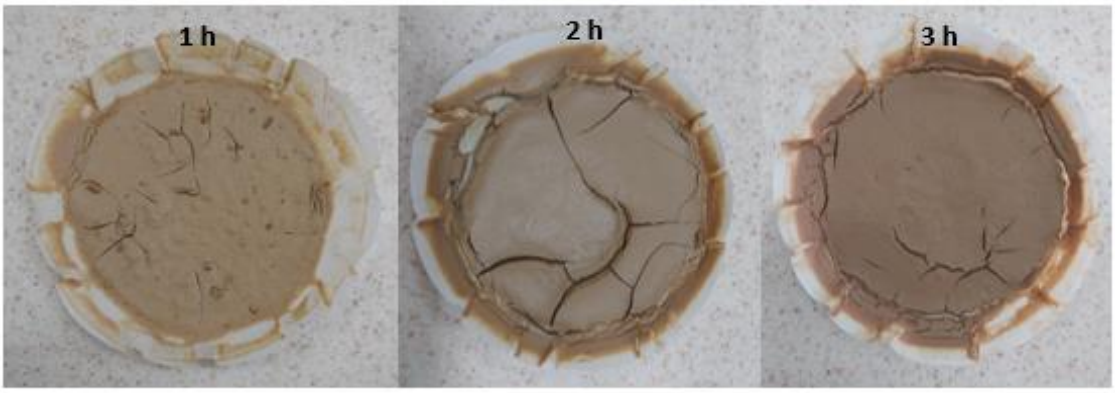

Figure 3. Lignin samples on filter paper

Determination of Wood Chemical Composition

Holocellulose (Wise and Karl, 1962), α-cellulose (TAPPI T 203), and Klason lignin (TAPPI T 222) contents of both control and DES-treated samples were found using appropriate references. The ratio of hemicelluloses was determined by subtracting the -cellulose ratio from the holocellulose. After DES treatment, the solid residue yield was calculated as a percentage of the original weight.

XRD Analysis

To assess the crystal structure of the cellulose contained in each sample, XRD was performed on wood samples using a multifunction X-ray diffractometer (Rigaku Smartlab) at 40 kV and 30 mA. The value of CrI was obtained according to the following formula (Equation 1) (Segal et al., 1959):

$$CrI\ (\%) = \left[\frac{I200 - Iam}{I200}\right] * 100 \quad (1)$$

I_{am} denotes the intensity between the 200 and 101 peaks when 2θ = 19.2° and reflects the diffraction intensity of the fiber amorphous region. I_{200} denotes the intensity of the 200 peak when 2θ approximates 22.8° and represents the diffraction intensity of the crystallization region (French, 2014).

BET Analysis

The surface areas of both the control (untreated) samples and the 3-h DES-treated were calculated using the BET technique. Quantachrome Autosorb-iQ equipment was used to detect N2 adsorption at 77 K. The samples were degassed for 4 hours at a temperature of 120 °C prior to the adsorption analysis.

Determination of Lignin Purity, Lignin Yield, and Delignification Ratio

Lignin purity was calculated as a percentage of the mass of the extracted lignin sample using Klason lignin. The lignin yield was calculated as a percentage of the lignin content in Scots pine wood based on the extracted lignin mass.

The following formula (Equation 2) was used to calculate the delignification ratio (Liu et al., 2019b):

$$Delignification\ ratio\ (\%) = \left[1 - \frac{m2 * c2}{m1 * c1}\right] * 100 \quad (2)$$

where *m1* denotes the dry weight of the sample used in the DES treatment (g), *c1* denotes the Klason lignin ratio of the control sample (%), *m2* denotes the dry weight (g) of the remaining sample after DES treatment (g), and *c2* denotes the Klason lignin ratio of DES-treated sample (%).

Color of Lignin

The color of lignin samples was evaluated using a Konica Minolta CM-700d spectrophotometer and three replicates according to the CIE Lab system. L* values are lightness (0: black and 100: white), a* values are redness (negative values: green and positive values: red), and b* values are yellowness (negative values: blue and positive values: yellow).

Statistical Analysis

Statistical analysis was done at a 95% confidence level using analyses of variance (ANOVAs) and the Duncan test. The distinct letter lowercase in Figures 4,5,7 and 9 shows that the difference in the mean values of attributes across the comparison groups was statistically significant (P<0.05).

Results and Discussion

Solid Residue Yield

The influence of DES treatment time on solid residue yield in wood samples is shown in Figure 4. There is a negative correlation between solid residue yield and treatment time. The solid residue yield values were 71.00% after 1 hour, 60.85% after 2 hours, and 54.70% after 3 hours. The removal of lignin and hemicelluloses with DES treatment may explain this result (Figure 5). At the DES (triethylbenzyl ammonium chloride:LA) treatment of wheat straw, Liu et al. (2019a) discovered that cellulose-enriched residues gradually decreased from 66.0% after 2 hours to 48.7% after 12 hours. Chen et al. (2019) found that increasing the treatment time (from 3 to 6 hours) in DES (ChCl:LA) treatment of poplar wood reduced solid residue yield. Kwon et al. (2020) reported that the DES (ChCl:LA, 1:10 mol ratio) treatment of *Pinus densiflora* reduced solid residue production from 70.7% after 2 hours to 56.4% after 12 hours. According to Lu et al. (2022), the residual solid yield of corn stover treated with ternary deep eutectic solvent (TDES, ChCl, formic acid, and maleic acid) reduced with longer treatment times (1 h, 1.5 h, 2 h, 2.5 h, and 3 h).

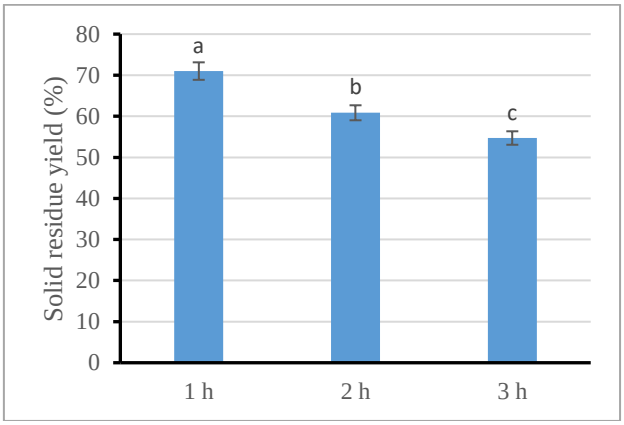

Figure 4. Effect of DES treatment time on solid residue yield in the wood sample

Wood Chemical Composition

Figure 5 depicts the influence of DES treatment time on the chemical composition of a wood sample. The holocellulose content was slightly reduced after 1 hour of DES treatment but increased after extended treatment times (P<0.05). The holocellulose value in the control sample was 74.88%, 73.29% after 1 h of DES treatment, 78.61% after 2 h, and 83.83% after 3 h. The correlation between DES treatment time and α-cellulose content was linear (P<0.05). The α-cellulose content in the control sample was 47.99%, 50.27% in the 1 h treatment, 56.64% in the 2 h treatment, and 62.57% in the 3 h treatment. These results are due to the removal of lignin and hemicelluloses by DES treatment (Figure 5). According to Bai et al. (2022), increased treatment time results in a more thorough penetration of DES into the biomass's cell wall, promoting the dissociation of lignin and the hydrolysis of hemicellulose. With increasing treatment time, hemicellulose and lignin contents decreased (P<0.05). Hemicellulose and lignin contents were 26.89%, 23.02%, 21.97%, 21.26%, and 24.55%, 21.82%, 17.23%, 9.08% in the control, 1 h, 2 h, and 3 h DES-treated wood samples, respectively.

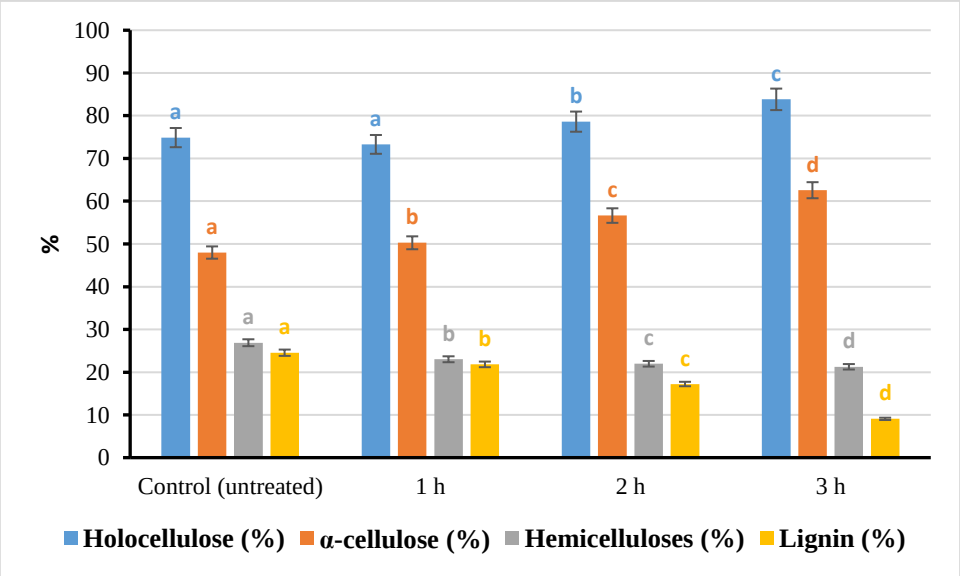

Figure 5. Effect of DES treatment time on the chemical composition of the wood sample

Xu et al. (2018) found that increasing the treatment time (2 h, 4h, and 8 h) with ChCl/glycerol treatment of corn stover enhanced glucose yields by 84%. According to Liu et al. (2019a), xylan and lignin removal rates increased from 43% (2 h) to 78% (12 h) and 48% (2 h) to 74% (12 h) respectively, after DES treatment of wheat straw. Chen et al. (2019) discovered that a 6-hour DES (ChCl:LA) treatment of poplar wood removed more hemicelluloses and lignin than a 3-hour DES treatment. According to Lu et al. (2022), extending the treatment time from 1 hour to 3 hours raised the delignification ratio of corn stover in TDES treatment (130 °C) from 60.4% to 79.4%. Positive correlations were also seen in the DES treatment of rice straw (Pan et al., 2017) and willow (Li et al., 2017).

XRD Analysis

The determination of CrI level in the control and pretreated samples can give an idea for the evaluation of the pretreatment of lignocellulosic biomass (Xu et al., 2019). The elimination of hemicelluloses and lignin, as well as alterations in the crystalline structure of cellulose, all have an effect on the CrI (Hou et al., 2018). In this study, samples treated with DES had considerably higher CrI values than that of the control sample, and the CrI values of samples had a positive correlation with treatment time (Figure 6, Table 1). This finding can be explained by removing of amorphous components (hemicelluloses and lignin) and a rise in α-cellulose concentration (Figure 5). The peaks for the I_{200} and I_{am} are located at 2θ = 22.64°-22.68° and 19.04°-19.72°, respectively (Table 1). Chen and Wan (2018) discovered that ChCl:LA treatment improved the CrI in corn stover (from 43% to 65%), switchgrass (from 54% to 67%), and miscanthus (from 56% to 68%). Kwon et al. (2020) discovered that pretreatment with ChCl-LA raised CrI in red pine sapwood and heartwood.

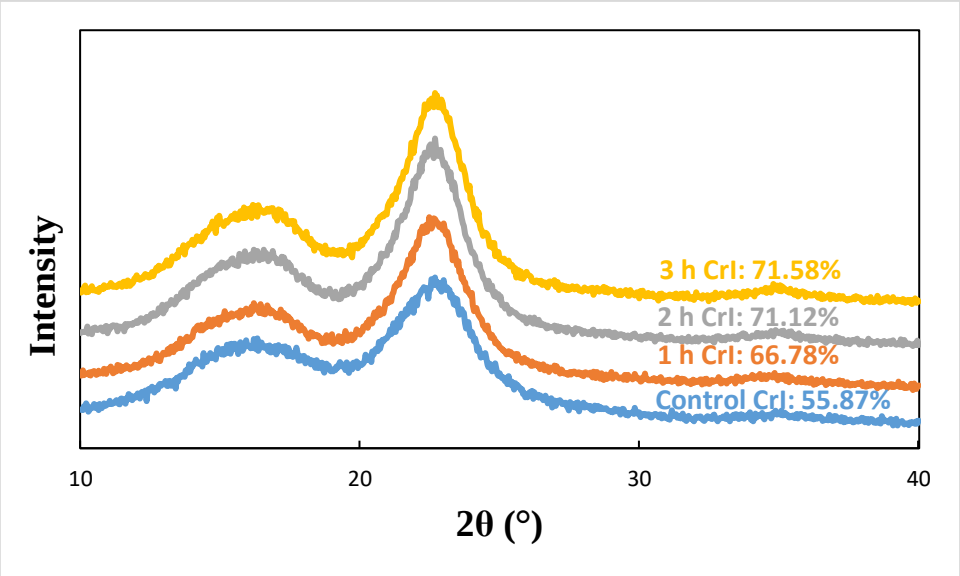

Figure 6. XRD spectra of control and DES-treated wood samples

Table 1. 2θ, intensity, and CrI values of control and DES-treated wood samples

Sample	I_{200}		I_{am}		CrI (%)
	2θ (°)	Intensity	2θ (°)	Intensity	
Control	22.68	1634	19.60	721	55.87
1 h	22.64	1800	19.04	598	66.78
2 h	22.68	2164	19.24	625	71.12
3 h	22.68	2199	19.72	625	71.58

Lignin Purity, Lignin Yield, and Delignification Ratio

The influence of DES treatment time on lignin purity, lignin yield, and delignification ratio can be seen in Figure 7. With increasing treatment time, lignin purity, lignin yield, and delignification ratio improved. Lignin purity was 82.34% after 1 hour, 84.44% after 2 hours, and 86.43% after 3 hours. Lyu et al. (2018) obtained similar results; the purity of DES-lignin is favorably associated with treatment time. While the lignin purity value was 90.02% after 6 hours of DES treatment, it increased to 95.40% after 24 hours. The lignin yield of DES-treated samples after 1 h, 2 h, and 3 h were 40.22%, 64.66%, and 82.48%, respectively. Delignification ratio was 36.90% after 1 hour, 57.29% after 2 h, and 79.78% after 3 h. Chen et al. (2019) discovered that extending the DES treatment period from 3 h to 6 h enhanced the amount and purity of lignin recovered from poplar wood. Bai et al. (2022) noted that delignification ratio at the DES treatment of poplar wood was 71.5% after 1 h and 96.3% after 3 h. They also demonstrated that the lignin yield peaked at 95.2% after 3 h and subsequently slightly declined with the extended treatment time. According to Lu et al. (2022), lignin purity and lignin yield in TDES treatment of corn stover were favorably correlated with treatment time.

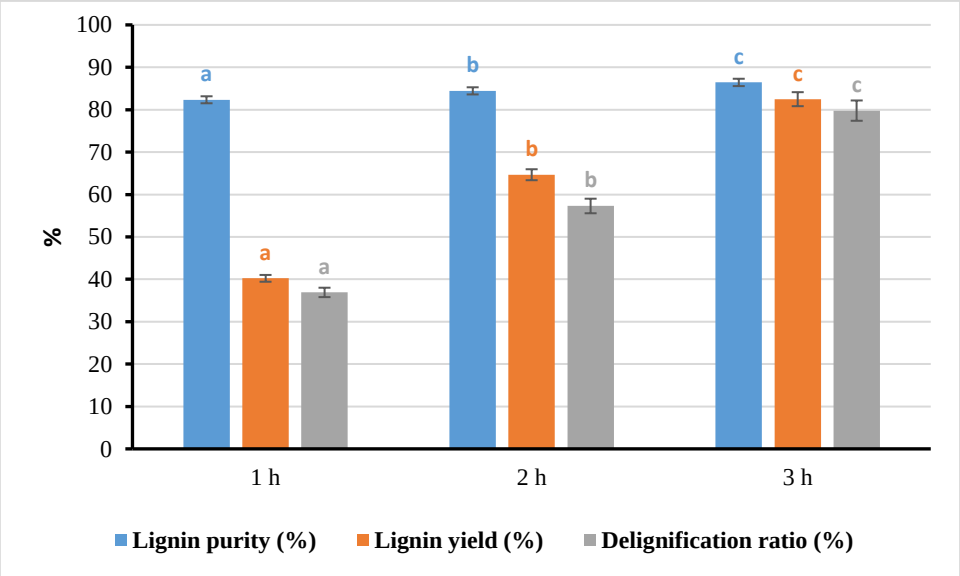

Figure 7. Effect of DES treatment time on lignin purity, lignin yield, and delignification ratio

BET Analysis

BET measurement is commonly used in biomass pretreatment studies to look at lignocellulose's pore structure and surface area (Gong et al., 2022). A porous, loose structure frequently has a larger specific surface area (Ho and Wu, 2020; Tang et al., 2023). The surface area of the sample increased with DES treatment. The surface area values of control and 3-h DES-treated samples were 3.095 m^2/g and 3.621 m^2/g, respectively. This finding is explained by the elimination of lignin and hemicelluloses from samples using DES treatment. Ong et al. (2019) reported that the surface area of oil palm frond samples increased from 0.3566 m^2/g to 0.4215 m^2/g with DES (ChCl:Urea) treatment. In another study, Tang et al. (2023) noted that surface area values of control and DES-treated (acetic acid and cetyltrimethylammonium bromide) samples of rice hull were 0.85 m^2/g and 62.3 m^2/g, respectively.

Optical Properties of Lignin

Figure 8 indicates lignin samples taken from DES-treated Scots pine wood. Optical characteristics of lignin samples are shown in Figure 9. The L*, a*, and b* values of lignin samples decreased as treatment time increased ($P<0.05$). The L* values of lignin samples after 1 hour, 2 hours, and 3 hours of treatment were 71.62, 59.76, and 55.59, respectively. The a* values of lignin samples were 7.07 after 1 hour, 6.71 after 2 hours, and 5.49 after 3 hours. The b* values of lignin samples after 1 hour, 2 hours, and 3 hours of treatment were 15.61, 14.27, and 14.04, respectively. According to Lu et al. (2022), the L* value of lignin extracted from corn stover after TDES treatment was adversely correlated with treatment time. They discovered that the L* values of lignin samples (TDES treatment temperature 110 °C) were 62.96, 57.66, and 52.14 for 1 h, 2 h, and 3 h TDES treatment times, respectively. Wu et al. (2023) recently investigated the influence of organic solvent type (methanol, ethanol, and acetone) on alkali lignin fractionation. They discovered that alkali lignin (control) has L*, a*, and b* values of 46.09, 10.27, and 17.84, respectively. In addition, the lightest colored lignin (L*: 59.27) was obtained from lignin fractions extracted with acetone.

Figure 8. Lignin samples obtained from DES-treatment of Scots pine wood

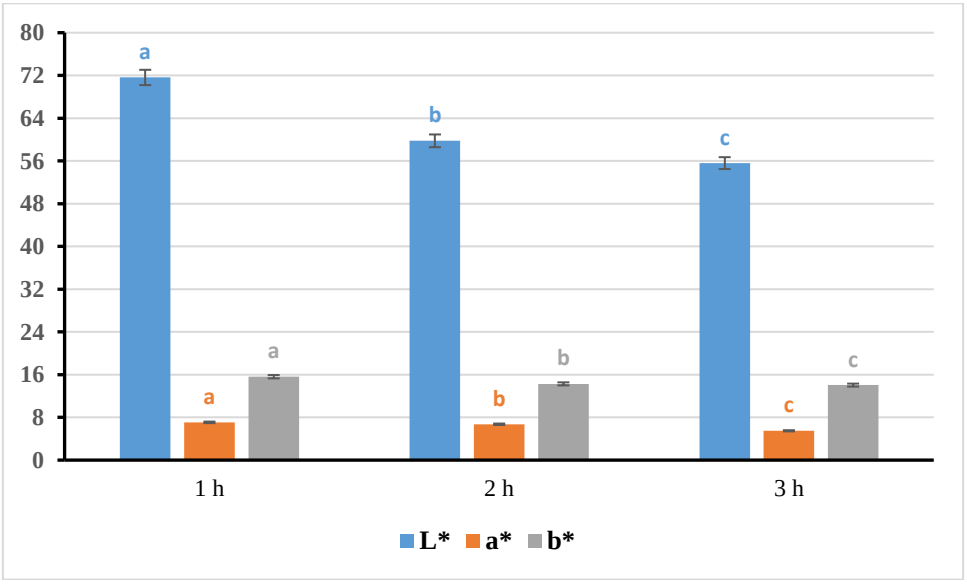

Figure 9. Optical properties of lignin samples

Conclusions

The results demonstrated that the treatment time has an effect on the main compounds of Scots pine wood during DES treatment. In addition, it has a significant impact on the yield, purity, and optical characteristics of extracted lignin. The CrI and surface area (BET) of wood samples increased considerably after DES treatment. However, shorter treatment periods resulted in lighter-colored lignin samples. Obtaining light-colored lignin in less time is critical, particularly for lignin uses in the cosmetic sector. As a result, it is preferable to base treatment time on the balance between energy consumption and treatment performance (color, yield, and purity of lignin).

Ethics Committee Approval

N/A

Peer-review

Externally peer-reviewed.

Author Contributions

Conceptualization: S.K.G., A.K.P.; Investigation: S.K.G., A.K.P.; Material and Methodology: S.K.G., A.K.P.; Supervision: S.K.G., A.K.P.; Visualization: S.K.G., A.K.P.; Writing-Original Draft: S.K.G., A.K.P.; Writing-review & Editing: S.K.G., A.K.P. All authors have read and agreed to the published version of manuscript.

Conflict of Interest

The authors have no conflicts of interest to declare.

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