OPTIMIZED LIGNIN RECOVERY FROM BLACK LIQUOR FOR ENHANCED MECHANICAL PROPERTIES OF ACRYLONITRILE BUTADIENE RUBBER COMPOSITES

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ABSTRACT

Due to climate change, the transition from petroleum-based materials to renewable sources is essential. Lignin, a complex aromatic polymer derived from lignocellulosic biomass, offers a promising alternative. This study is focused on optimizing lignin recovery from black liquor based on the LignoBoost™ process and evaluating its application in acrylonitrile butadiene rubber (NBR). The optimized conditions (80 °C, pH 2.0) yielded lignin with significantly lower phenolic hydroxyl group concentrations compared to lignins prepared according to the design of the experiment (DoE). Surface property analysis revealed a high surface free energy of 55.3 mJ/m², indicating potential for interaction with various substances. A DoE approach to investigate the influence of precipitation conditions on lignin properties is employed in the study. NIR spectroscopy and surface property measurements were used for lignin characterization. The results demonstrated that hydroxyl group concentrations, influenced by black liquor freshness and filtration temperature is significantly affected by the preparation method. Notably, pilot lignin (PL) application in NBR composites resulted in a more than twofold increase in tensile strength and elongation at break compared to NBR without additives or with commercial lignin. These findings suggest that lignin recovered through optimized processes can enhance the mechanical properties of NBR, offering a sustainable alternative to traditional additives. This research provides valuable insights for further exploration of lignin's potential in industrial applications, particularly in the context of lignin recovery and utilization in pulp mills.

Keywords: lignin recovery; acrylonitrile butadiene rubber (NBR); design of experiment (DoE); kraft lignin; renewable resources.

INTRODUCTION

The use of renewable sources to replace petroleum-based materials is crucial, primarily due to climate change. Among the potential renewable resources, lignocellulosic biomass stands out for its potential to replace fossil-based sources. Lignin, a complex aromatic polymer abundantly found in plant cell walls, is particularly noteworthy. In the pulp and paper industry, lignin is mainly obtained during the pulping process and is often used as a low-value fuel burned in recovery boilers to produce heat and power.

Kraft Process

The Kraft process is a leading chemical pulping method that converts wood chips into nearly pure cellulose fibers using a highly alkaline solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) (SJÖSTRÖM, 1993; Worku *et al.,* 2023). This process, known for its high selectivity in delignification, operates in very alkaline conditions (pH above 12) at temperatures of 160–180 °C for 1–3 hours (Biermann, 1996; Sjöström, 1993). The main active reagents are hydroxide and hydrosulfide anions, with hydrosulfide ions accelerating delignification (Sixta *et al.,* 2008).

Kraft pulping is versatile, processing both hardwood and softwood, and is less dependent on debarking compared to the sulfite process (Sjöström, 1993). However, it emits malodorous chemicals like methyl mercaptan and hydrogen sulfide, posing environmental and safety hazards (Hansen, 1962; Taylor *et al.,* 1961). Modern mills use recovery boilers and scrubbers to mitigate these impacts. Tab. 1 summarizes the most frequent advantages and disadvantages of Kraft pulping.

Tab. 1 Advantages and Disadvantages of the Kraft Pulping Process (Patt *et al.*, 2000).

Advantages	Disadvantages
Universal raw material basis	Small process flexibility
High insensitivity to bark	Low yields for softwood
Fast pulping process, short cover-to-cover times	High residual lignin content and poor bleachability of the pulps
High yields for hardwoods	High bleaching chemicals demand
Good pulp strength	Indispensable use of chlorine-containing bleaching agents; high water pollution
Low extract content of the pulps	Offensive smell due to volatile reduced sulfur compounds

Considering that lignin content in hardwood and softwood ranges from 25 % to 30 %, the annual lignin supply is estimated to be between 67 and 81 million tons. Alternatively, based on projections by Keyoumu *et al.,* (2004), lignin production from chemical pulping alone in 2025 is expected to be between 44 and 66 million tons (Nadányi *et al.*, 2022).

LignoBoost™ process

Lignin recovery is essential in the pulp and paper industry, transforming a significant waste product into a valuable resource. The LignoBoost™ process, developed by Inventia AB and Chalmers University, marks a significant advancement in producing high-purity lignin from black liquor (Tomani, 2010). Before this innovation, lignin typically contained high levels of impurities and ash. The LignoBoost™ process addresses these issues by yielding high-purity lignin with low ash content. The process includes several key steps: lignin precipitation, filtration, re-slurrying of the lignin cake, a second filtration, and final washing (Zhu and Theliander, 2015). LignoBoost™ was the first to achieve high yields and exceptional quality in lignin precipitation and purification.

In the LignoBoost™ process, black liquor from the kraft process is treated with CO_2 to lower the pH, causing lignin to precipitate. Key factors include temperature (60–80 °C), final pH (9–10), and CO_2 concentration. After initial precipitation and filtration, the lignin filter cake is resuspended and acidified with sulfuric acid to pH 2–4, then filtered and washed to remove impurities. This process reduces ash content, making the lignin suitable for high-value applications (Öhman *et al.,* 2007; Tomani, 2010; Ziesig *et al.,* 2014).

Lignin-rubber applications

Natural rubber (NR) is widely used and often reinforced with carbon black for mechanical strength. However, due to sustainability concerns, lignin is being explored as an

alternative. Lignin is sustainable, produced on a large scale, and has high structural rigidity, making it suitable for industrial applications (Jiang *et al.,* 2020; Mohamad Aini *et al.,* 2020).

Lignin can enhance the mechanical properties of rubber, such as tensile strength and heat resistance, and acts as an antioxidant. Blending lignin with synthetic polymers improves mechanical and thermal properties and biodegradability. However, lignin's polar functionalities can affect its compatibility with NR (Gregorová *et al.,* 2006; Intapun *et al.,* 2021; Makhalema *et al.,* 2021; Mohamad Aini *et al.,* 2020). Lignin is particularly promising for use with acrylonitrile butadiene rubber (NBR) due to its opposite polarity to NR. It can replace half the carbon black in NBR, enhancing strength, modulus, thermal stability, and oil resistance (Wang *et al.,* 2018).

This study aims to optimize lignin recovery from black liquor and explore its use in NBR to replace carbon black, comparing it with commercially available lignin.

MATERIALS AND METHODS

Materials

Alkali lignin used to produce acid washed lignins was provided by Mondi SCP, Ružomberok. Sulfuric acid (96 %) from Centralchem (Bratislava, Slovakia) and carbon dioxide from Messer Tatragas (Bratislava, Slovakia). The commercial softwood kraft lignin (UPM BioPiva™ 100) is provided by UPM Biochemicals (Helsinki, Finland).

The materials used to prepare lignin-NBR composites are as follows: NBR (SKN3345) (Sibur International, Russia), sulfur (Siarkopol Tarnobrzeg, Poland), zinc oxide (Slovzink a.s., Košeca, Slovakia), Stearic Acid III (Setuza, Ústí nad Labem, Czech Republic), N-cyclohexyl-2-benzothiazole sulfenamide CBS (SULFENAX CBS/MG) (Duslo a.s., Šaľa, Slovakia).

Methods

Design of experiment (DoE) was used to study the influence of precipitation conditions on lignin properties. Specifically, a two-factor, five-level DoE was applied to prepare a total of 13 samples of acid-washed lignins. The specific conditions are listed in Tab. 2.

Tab. 2 Conditions for Design of Experiment – Lignin Purification.

	1	2	3	4	5	6	7	8	9–13
T [°C]	33.1	72.0	33.1	72.0	25.0	80.0	52.5	52.5	52.5
pH	2.4	2.4	4.1	4.1	3.3	3.3	2.0	4.5	3.3

Lignin recovery involved resuspending 100 g of alkali lignin in water (8:1 ratio), heating, and acidifying with 50 % sulfuric acid to the desired pH and temperature. The slurry was aged for 30 minutes, filtered, washed with hot water, and air-dried. Optimization used the Equation (1) to find optimal conditions (80 °C, pH 2.0).

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 \qquad (1)$$

Pilot lignin production at Mondi SCP's pulp mill involved processing black liquor, cooling, acidifying, aging, and filtering to produce alkali lignin cakes. These were further processed to obtain acid lignin, which was diluted, filtered, and air-dried.

DoE lignins and Pilot Lignin (PL) were analyzed using Near-Infrared (NIR) spectroscopy, Thermogravimetric analysis (TGA), and surface property measurements. NIR spectra were obtained using a Multi-Purpose Analyzer FT-NIR, and functional groups were

analyzed with a Partial least squares regression (PLS) calibration model by Sumerskii *et al.* (2024). Surface properties were determined using contact angles with water and α-bromonaphthalene, calculated with See System software based on the Owens-Wendt model.

RESULTS AND DISCUSSION

NIR analysis provided a detailed evaluation of lignin characteristics, including concentrations of aliphatic and phenolic hydroxyl groups, methoxyl groups and syringyl and guaiacyl (S and G) units concentrations. This chemical characterization helps identify how pH and temperature variations during precipitation affect lignin. NIR analysis offers a comprehensive understanding of lignin properties, guiding the adjustment of precipitation conditions to tailor lignin for specific uses. The measured characteristics are shown in Tab. 3.

Tab. 3 NIR Structural Characterization of Lignins Prepared According to the DoE.

Sample	Ph-OH [mmol/g]	R-OH [mmol/g]	OCH_3 [mmol/g]	S-Unit [mmol/g]	G-Unit [mmol/g]
1	3.60	1.44	5.53	2.60	1.10
2	3.92	1.45	5.93	2.77	1.19
3	3.67	1.47	5.62	2.64	1.15
4	3.96	1.54	6.05	2.80	1.18
5	3.82	1.47	5.83	2.71	1.19
6	3.82	1.43	5.72	2.68	1.23
7	3.60	1.26	5.22	2.55	1.28
8	3.55	1.46	5.47	2.55	1.14
9	3.39	1.36	5.17	2.46	1.11
10	3.41	1.46	5.30	2.47	1.10
11	3.46	1.45	5.32	2.49	1.11
12	3.60	1.46	5.54	2.59	1.14
13	3.48	1.44	5.37	2.52	1.11

The structural characterization of PL, UPM BioPiva 100™, and DoE lignins reveals notable differences in their functional group concentrations and monolignol content. These variations primarily reflect the impact of preparation methods, such as temperature, pH, and other processing conditions like the freshness of black liquor and filtration temperature. The relationship between the structural characteristics of lignin and process parameters (temperature and pH) is illustrated in for phenolic hydroxyl groups (Ph-OH) and in for aliphatic hydroxyl groups (R-OH). For Ph-OH, the dependence exhibits a local minimum at approximately 3.46 ± 0.23 mmol/g and a maximum at around 4.13 ± 0.23 mmol/g. These values were calculated based on a thorough evaluation of the measured results. In contrast, R-OH demonstrates a different trend compared to Ph-OH. The concentration does not exhibit a distinct local minimum, as the curve does not change its directional pattern. However, the minimum and maximum concentrations can still be determined, with values of 1.32 ± 0.11 mmol/g and 1.55 ± 0.11 mmol/g, respectively.
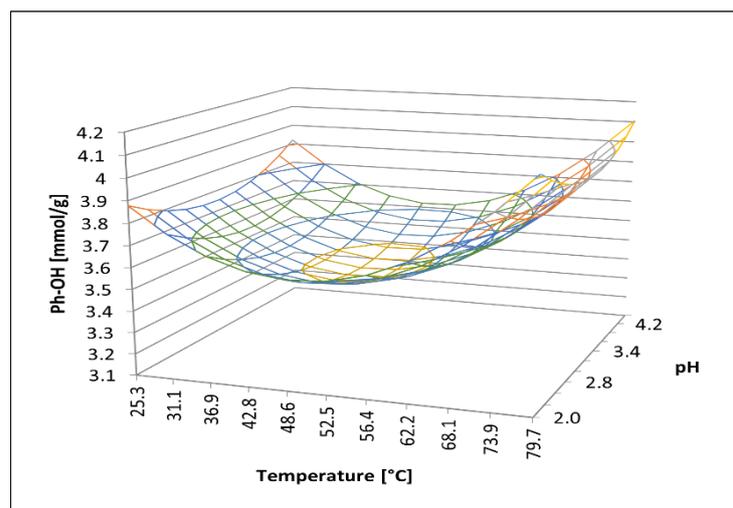
Fig. 1 Dependence of phenolic hydroxyl groups concentration from process parameters calculated using DoE.
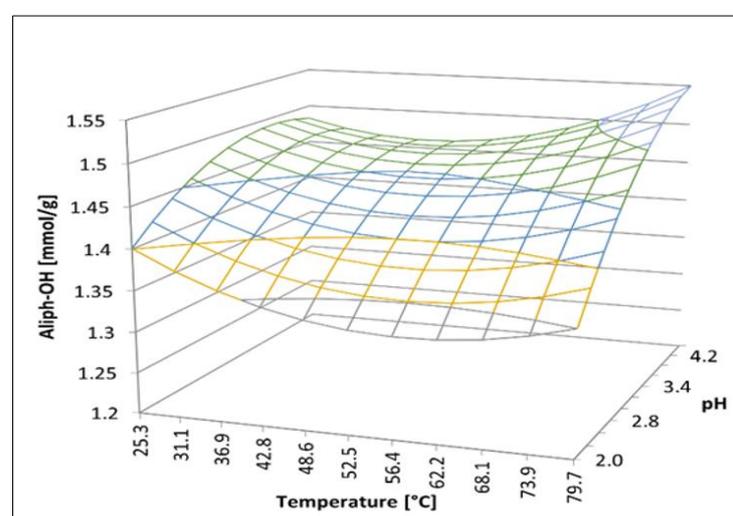
Fig. 2. Dependence of aliphatic hydroxyl groups concentration from process parameters calculated using DoE.

When comparing PL to DoE lignins, the most striking difference lies in the concentration of phenolic hydroxyl groups. PL has a significantly lower Ph-OH content of 0.45 mmol/g, while DoE lignins range from 3.39 to 3.96 mmol/g. This suggests that the conditions under which PL is prepared result in a much lower availability of phenolic hydroxyl groups, which could affect its reactivity and application potential. Similarly, the aliphatic hydroxyl group concentration in PL (0.71 mmol/g) is also lower than in DoE lignins, which range from 1.26 to 1.54 mmol/g. These differences indicate that the preparation of PL, particularly the combination of temperature and pH, leads to a reduced presence of hydroxyl groups, which are crucial for lignin's chemical interactions. In terms of methoxyl (OCH_3) groups, PL also shows a lower concentration (4.65 mmol/g) compared to DoE lignins (5.17 to 6.05 mmol/g). The higher methoxyl content in DoE lignins is likely due to differences in the syringyl (S) and guaiacyl (G) unit ratios, which play a critical role in determining lignin's reactivity and structural properties. Interestingly, while the syringyl content in PL (2.48 mmol/g) is comparable to that in DoE lignins (2.46 to 2.80 mmol/g), PL exhibits a slightly higher concentration of guaiacyl units (1.59 mmol/g) compared to DoE

lignins (1.10 to 1.28 mmol/g). This suggests that PL has a somewhat higher G-unit content, which could impact its overall chemical behavior and reactivity.

When comparing PL to UPM BioPiva 100™, further differences emerge (refer to Tab. 4). The Ph-OH concentration in UPM (2.9 mmol/g) is considerably higher than in PL, again highlighting the reduced reactivity of PL in this regard. UPM also shows a higher aliphatic hydroxyl group concentration (1.02 mmol/g) than PL (0.71 mmol/g), though the difference here is less pronounced than that between PL and DoE lignins. On the other hand, PL has a significantly higher methoxyl group concentration (4.65 mmol/g) compared to UPM (2.4 mmol/g), which can be attributed to the higher syringyl content in PL. This distinction in methoxyl content suggests different applications for each type of lignin, with PL potentially being more suitable for uses that require higher methoxyl group functionality.

In terms of monolignol content, PL contains more syringyl units (2.48 mmol/g) than UPM (1.31 mmol/g), while UPM has a higher guaiacyl unit content (2.48 mmol/g) compared to PL (1.59 mmol/g). This reversal in the S/G ratio between the two lignins could have significant implications for their reactivity and structural properties, with the guaiacyl-rich UPM likely being more suited to applications that benefit from higher G-unit concentrations, such as adhesives or resins.

Tab. 4 Structural Characterization and Surface Properties of Pilot Lignin and UPM BioPiva 100™.

	Ph-OH [mmol/g]	R-OH [mmol/g]	OCH_3 [mmol/g]	S-unit [mmol/g]	G-unit [mmol/g]	CA H_2O [°]	CA BN [°]	SFE [mJ/m^2]
PL	0.45	0.71	4.65	2.48	1.59	54.39	29.14	55.30
UPM	2.9	1.02	2.4	1.31	2.48	-	-	-

CA = contact angle; BN = a-bromonaphtalene; SFE = surface free energy

UPM and PL lignins were tested in NBR applications, revealing significant differences in mechanical properties (see Fig. 3). As the concentration of the lignin increases, PL consistently outperforms UPM. At 10 phr, UPM slightly improves elongation at break to 448 %, while PL significantly enhances it to 711 %. This trend continues, with PL reaching 946 % at 30 phr and over 1000 % at 40–50 phr, compared to UPM's 670 % and 787 %, respectively. We hypothesize that intense mixing allows lignin molecules to exfoliate from the hydrogen-bonded network into smaller domains. The renewed surface provides additional sites for interaction with nitrile rubber, leading to an increase in the number of interactions. This greater number of interactions would ensure excellent toughness at large deformations (Tran *et al.,* 2016), as evident from the results, where PL again outperforms UPM at every concentration. At 10 phr, UPM drops to 3.8 MPa, while PL increases to 7.0 MPa. This gap widens further at 20–50 phr, where PL reaches a tensile strength of 10.5 MPa, nearly double that of UPM in some cases. Even at 60 phr, PL remains superior in both characteristics, though both lignins experience a decline.

In conclusion, PL lignin enhances both the elongation and tensile strength of NBR more effectively than UPM, especially at higher concentrations, making it a superior choice for applications demanding better flexibility and mechanical strength.
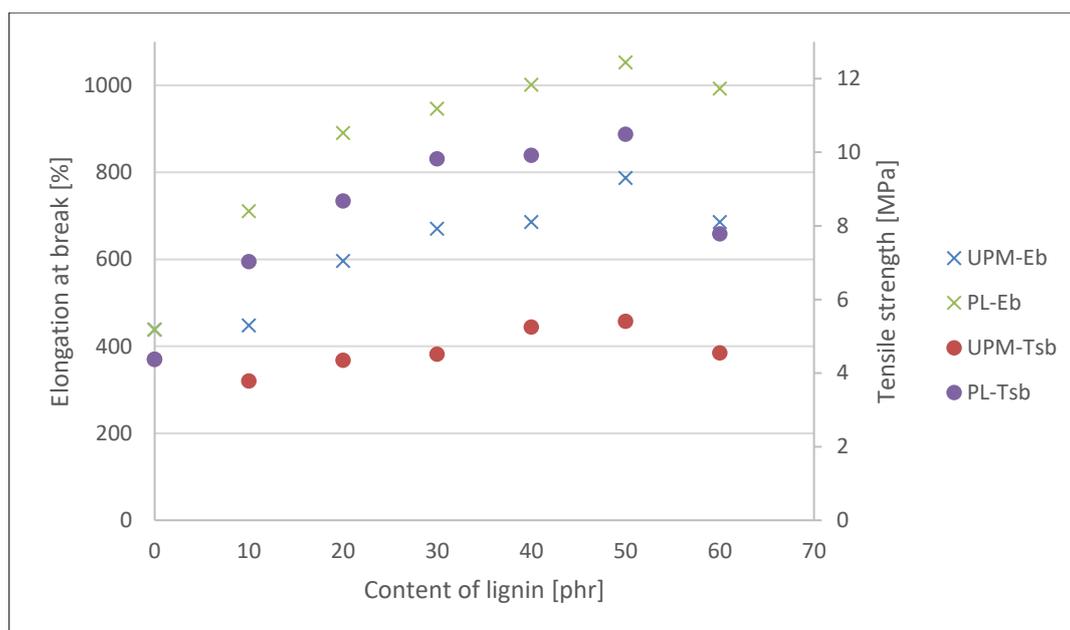
Fig. 3 Mechanical properties of NBR produced using different kraft lignins.

CONCLUSION

In this study, the influence of precipitation conditions on lignin properties and their application in NBR was explored, focusing on the structural differences between pilot lignin, UPM BioPiva 100™, and DoE lignins. The results showed that PL lignin consistently outperformed UPM in both elongation at break and tensile strength, especially at higher concentrations. PL's lower phenolic hydroxyl content and higher methoxyl concentration appear to enhance its performance in NBR, making it more suitable for applications requiring improved flexibility and mechanical strength. Overall, this research highlights the importance of lignin's preparation conditions in determining its suitability for industrial applications, such as rubber reinforcement, and demonstrates PL's superior potential over UPM for such purposes.

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