

A Rapid and Tunable Approach for the Fractionation of Technical Kraft Lignin

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Reducing the heterogeneity of technical lignin is essential to obtain predictable and high-performance polymeric materials that are suitable for high-value applications. Organic solvents with different polarities and solubilities can be used to fractionate lignin and reduce the complexity and diversity of its chemical structure. Among the various solvents and solvent mixtures, acetone–water mixtures offer an energy-efficient, cost-effective, and environmentally friendly means of lignin fractionation. In the present study, temperature-induced acetone–water fractionation was investigated to refine the properties of a technical softwood Kraft lignin, i.e., LignoBoost™ lignin. Relatively mild operating conditions were tested, namely, temperatures of 70–110 °C and autogenous pressure. A factorial experimental design was developed using the Design-Expert® software, and three factors (temperature, time, and acetone concentration) were investigated. It was found that temperature-induced fractionation could increase lignin homogeneity and maintain high lignin solubilization with a short processing time (<1 h). It was also possible to tune the properties of the soluble lignin fraction (yield and weight-average molecular weight) based on the factorial models developed. The techno-economic evaluation confirmed the commercial viability of this fractionation process.

1. Introduction

Lignin has been recognized as a biopolymer with useful properties as a renewable feedstock and as a substitute in the industrial production of high-value chemicals, fuels, and materials. Lignin comprises almost 30% of lignocellulosic biomass and is considered the most abundant aromatic biopolymer worldwide (Abdelaziz and Hulteberg, 2017). It is a polyphenolic compound containing valuable monolignols, which have immense potential as chemical building blocks, aromatic chemicals, and/or a feedstock for renewable fuels production (Ajao et al., 2019; Chiamonti et al., 2016; Galanopoulos et al., 2021; Rodrigues et al., 2023; Yadav, 2020). Copious amounts of lignin-containing streams are produced commercially, mainly as a byproduct in the kraft pulping process in the pulp and paper industry. Extraction methods have been developed for lignin isolation, and technologies such as LignoBoost™ and LignoForce™ have been introduced onto the market (Kazzaz and Fatehi, 2020). Lignin-rich streams are, however, underutilized due to their heterogeneity and complex chemical structure (Ji et al., 2022), and are usually combusted on-site to provide energy (Abdelaziz et al., 2022; Wenger et al., 2020). The chemical and physical properties of technically recovered lignin depend greatly on the biomass feedstock, pulping process and extraction method, and process severity (Ajao et al., 2019; Balakshin et al., 2021). The considerable variation in key properties, such as yield, molecular weight, dispersity, and impurities, results in insufficient valorization, limiting its use in strategic applications (Eraghi Kazzaz and Fatehi, 2020). Enhanced control and tuning of these key properties are thus of importance if we are to exploit the enormous potential of technical lignin in value-added applications such as thermoplastics, coatings, and resins.

Several approaches have been investigated to improve the molecular homogeneity of technical lignin, including ultrafiltration and selective precipitation as well as organic solvent fractionation (Quan et al., 2023; Xu et al., 2021). However, organic solvent fractionation is favorable as the properties of the solvent, for example, its

polarity and solubility, can be adjusted, and it is possible to use solvent mixtures, which enables tuning of the resulting yield and lignin properties (Izaguirre et al., 2022; Ponnuchamy et al., 2021).

Solvent fractionation of lignin using a mixture of acetone and water has shown potential in enhancing the homogeneity of key properties of the lignin (e.g., molecular weight and dispersity). A combined experimental and theoretical fractionation study on hardwood kraft lignin revealed increased solubility yield for solvents with higher polarity such as acetone (Ponnuchamy et al., 2021). The addition of water has also been reported to enhance the diffusion of the solvents into the lignin, due to increased hydrogen bonding capacity, hence increasing the solubility capacity (Izaguirre et al., 2022). Homogeneous lignin fractions have been prepared from tetrahydrofurfuryl alcohol lignin using acetone–water system (Xu et al., 2021). The acetone–water system has also been shown to be better than other solvents in terms of its techno-economic viability in a large-scale industrial process and from the environmental health perspective (Ajao et al., 2019). Nevertheless, further investigations of the acetone–water fractionation system are required to improve our understanding of the tuning and acceleration possibilities of the process (Ajao et al., 2021).

The aim of this study was to investigate the acetone–water fractionation system with regard to its sensitivity to process conditions, and to improve our techno-economic knowledge of this process. The aspects investigated were: (i) modeling and analysis of the individual and combined effects of temperature, time, and acetone–water proportions on the fractionated lignin yield and molecular weight using a two-level factorial design; (ii) optimization of the conditions to increase the yield of the soluble lignin fraction; and (iii) assessment of the economic potential of the proposed fractionation approach.

2. Materials and methods

2.1 Chemicals and materials

LignoBoost lignin (LB), a technical softwood kraft lignin, was obtained as a dry powder from the RISE LignoDemo demonstration plant (Bäckhammar, Sweden). Sodium hydroxide (NaOH) pellets (CAS no. 1310-73-2) were purchased from Merck KGaA (Darmstadt, Germany). Acetone (CAS no. 67-64-1) was purchased from VWR Chemicals BDH® (Fontenay-sous-Bois, France). Chemicals were used as received without further purification.

2.2 Fractionation procedure

Elevated-temperature acetone–water fractionation was investigated as a means of refining the LB substrate. Relatively mild operating conditions were tested, i.e., temperatures of 70–110 °C and autogenous pressure. The solvent fractionation experiments were carried out at a concentration of 100 g/L LB in autoclave cookers placed in a temperature-controlled vessel filled with polyethylene glycol. After each experiment, the resultant slurry was filtered (Munktell Filter AB) under vacuum giving soluble and insoluble fractions. The acetone was removed from the soluble LB fraction by rotary evaporation (Heidolph Laborota 4000 efficient, WB eco). The soluble fractions were dried at 40 °C in an oven (Salvis Thermocenter) for yield determination and further analysis.

2.3 Size-exclusion chromatography

The molecular weight distribution (MWD) of LB and fractionated LB samples was determined by size-exclusion chromatography (SEC). The SEC system consisted of a pre-column followed by two analytical columns, PSS MCX 10⁵ and 10³ Å, connected in series. The mobile phase was NaOH at pH 12, and the flow rate was 0.5 mL/min. The samples were dissolved in the mobile phase to suitable concentrations and filtered (syringe filters, 0.2 µm) prior to injection. The injection volume was 100 µL. Detection was performed using a refractive index detector (Shodex RI-101) and a UV detector (Knauer K-2501). The SEC system was calibrated using sulfonated polystyrene standards with molecular weights ranging from 250 to 200,000 Da. MWD, peak molecular weight (M_p), weight-average molecular weight (M_w), number-average molecular weight (M_n), and dispersity index (\mathcal{D} , M_w/M_n) were calculated using Cirrus GPC software version 3.1 by Polymer Laboratories (Agilent). The integration limits used were the elution times for $M_p = 100$ and 100,000. Duplicate samples were analyzed, and the results are presented as the average.

2.4 Design of experiments

The experiments were designed using the response surface methodology (RSM) via a two-level factorial design. RSM implies statistically designed experiments and allows for regression evaluation and the development of accurately validated predictive response models. The methodology and evaluation are based on the conversion of the investigated independent factors to dimensionless coded variables, corresponding to low and high parametric range values. This allows direct comparison and determination of the resulting effect, i.e., the importance of each factor and parameter interactions affecting the process. RSM and the two-level factorial

design allowed simultaneous parametric changes and effects to be investigated, to achieve a true understanding of the whole system. The independent parameters investigated were temperature, time, and acetone–water proportions. The corresponding parametric ranges were 70–110 °C, 20–60 min, and 30–70% acetone in water. Table 1 gives a summary of the investigated parameters, ranges, and corresponding coded levels. The effects of varying the parameters on lignin fractionation were investigated in terms of yield and molecular weight.

Table 1: Experimental independent parameters with respect to RSM symbols and coded levels

Parameter	Symbol	Coded levels		
		-1	0	+1
Temperature (°C)	A	70	90	110
Time (min)	B	20	40	60
Acetone (%)	C	30	50	70

Design-Expert® software (version 13, Stat-Ease, Inc., Minneapolis, MN, USA) was used to evaluate the experimental response data. This software allows regression modelling, statistical analysis of parametric significance, system optimization, and graphical plotting. Analysis of variance (ANOVA) is the fundamental statistical tool used, and the calculation of *F*- and *p*-values provides measures of the significance of the factors, the model generated, and the model fit. The *F*-value is a measure of the chance that the resulting effect is due to the model rather than system noise. The statistical significance is obtained by comparing the observed *F*-value to specific confidence interval (CI) critical tabulated reference distribution values. The *p*-value represents the probability, for a specific CI, that the model terms have a statistically significant effect on the response. A 95% CI was used, given that *p*-values less than 0.05 indicate statistical significance. Parametric optimization analysis was performed to maximize the yield of the soluble lignin fraction. Optimization was performed in accordance with the corresponding resulting regression equation and in terms of minimization of parametric severity of the process.

2.5 Modeling and techno-economic analysis

Process simulation using Aspen Plus® software was performed to assess the techno-economic performance of the proposed lignin fractionation concept. The resulting mass and energy balances were used to calculate the fractionation solvent losses, and the requirements of power, heat, and cooling of an industrial-scale plant processing 50 t/d of kraft lignin. The choice and description of property method, unit operations, operating conditions, and breakdown of the capital and operating expenditures are similar to those previously reported in a comparison of different green solvents (Ajao et al., 2019). The reference costs were updated to 2021 values using the Chemical Engineering Plant Cost Index (CEPCI), and all costs are provided in US dollars. The cost of the chemicals was updated using the producer price index by commodity industrial chemicals. The raw lignin feedstock purchase price was assumed to be \$750 per dry tonne. Benchmarking against untuned acetone–water mixtures was also conducted in order to determine the incremental cost of tuning the process. One of the purchased equipment cost drivers for the process was the dryer (35–50%), depending on the fractionation yield.

3. Results and discussion

3.1 Model development and statistical analysis

The two-level factorial experimental test matrix generated, and the resulting lignin fractionation yield and molecular weight of the soluble fraction are given in Table 2.

Table 2: Experimental matrix for lignin fractionation with respect to temperature, time, and proportion of acetone for each experimental run. The resulting yield of the soluble fraction and M_w are given for each run.

Run number	Temperature [°C]	Time [min]	Acetone [%]	Yield [%]	M_w [kDa]
1	110	20	70	96.6	5.1
2	110	20	30	9.6	3.0
3	70	20	70	96.2	5.0
4	70	20	30	3.8	1.4
5	70	60	30	5.8	1.5
6	110	60	30	10.8	2.1
7	110	60	70	96.8	4.8
8	70	60	70	94.6	4.9
9	90	40	50	51.2	3.1

Coded regression models with statistically significant fits were generated for both the yield and molecular weight of the soluble lignin fractions, as represented in Eqs. (1) and (2). The coded model terms A, B, and C represent temperature, time, and acetone proportion, respectively.

$$Yield = 51.71 + 1.68 \times A + 44.28 \times C - 1.03 \times A \times C \quad (1)$$

$$M_w = 3.43 + 1.48 \times C \quad (2)$$

Regression modeling and the ANOVA evaluation indicated that the proportion of acetone had the most significant effect on the resulting yield and molecular weight of the lignin fractionation at the temperatures studied. The resulting yield was also influenced by the temperature and the combined effect of temperature and acetone proportion. However, the large factorial model term of C in Eq. (1) confirmed that the acetone proportion had the greatest influence on the yield in this system.

Figure 1 shows the observational analysis of the model generated for yield in terms of the correlation between predicted values and actual experimental data (a), and the externally studentized residuals (b). A strong linear correlation can be seen between the predicted values and actual data. The adequate precision of both the models generated indicates their suitability in predicting the outcomes for this system. The adequate precision provides an estimate of the ratio of signal-to-noise, and values greater than 4 indicate a predictive model for the specific system. The adequate precision was 148.4 for the model representing the yield, and 12.4 for that predicting the molecular weight.

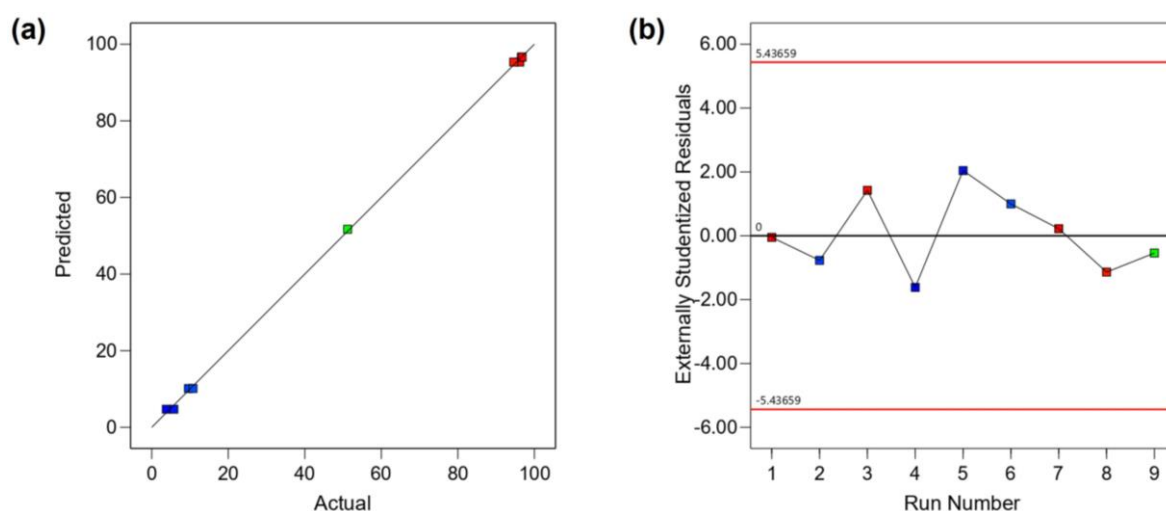


Figure 1. Observational analysis of the model generated for the yield in terms of: (a) predicted values vs. the experimental data, and (b) externally studentized residuals.

Optimization analysis revealed a maximum yield of the soluble LB fraction at a temperature of 97 °C with an acetone proportion of 50%, after 20 min. The regression models were experimentally validated at these conditions, and relative errors between the measured and predicted values were calculated to be 9% and 3.5% for the yield and M_w , respectively, indicating good agreement between the models and the experimental data.

3.2 Techno-economic evaluation

Economic analysis in our previous study indicated that one of the drivers for the investment cost of this lignin fractionation process is the dryer, which will need to be operated in batch mode for the low- and high-molecular weight fractions (Ajao et al., 2019). The focus of the economic evaluation in the present study was, therefore, on run #9, which represents the lowest minimum selling price of the fractionated lignin, under the assumption that both fractions can be utilized directly. Ratios of low to high molecular weight mass fractions deviating from 1 lead to disproportionation of the capital investment influenced by the batch unit operations, including the dryer. As can be seen from Table 3, a capital investment of about \$33.5 M is required to realize the suggested process. The cost of installed equipment is attributed mainly to feedstock handling (3.7%), solvent handling (5.1%), the solubilization reactor (3.2%), wash liquor preparation (1.7%), the washing systems for the high-molecular weight fraction (19.1%) and low-molecular weight fraction (20.7%), the vapor recompression system for heat recovery (9.5%), and the dryer (36.1%) (all percentages are rounded off).

Table 3: Capital investment costs

Component	Cost (\$ M)
Cost of installed equipment	9.9
Direct costs (instrumentation and control, piping, electrical, building, and facilities)	8.8
Indirect costs (engineering, legal expenses, construction expenses, contingency)	9.2
Other capital costs (land, working capital, start-up)	5.6

If this process were to be implemented on-site and integrated with an existing commercial lignin recovery process such as the LignoBoost™ system, the total capital investment would fall to \$29 M due to the cost savings in buildings and auxiliary installations. Regarding operating expenditure, the major cost drivers were determined to be the costs of raw kraft lignin and make-up solvent (Figure 2). This is consistent with the results reported by Jiang and co-workers on the scalability and techno-economics of lignin fractionation (Jiang et al., 2020). The minimum selling price of the fractions was calculated to be \$2060 per tonne, based on the current inflation-adjusted costs for utilities and an expected return on capital employed of 20%. This current minimum selling price includes a 28.6% increase compared to the pre-pandemic level, which was \$1602 per tonne.

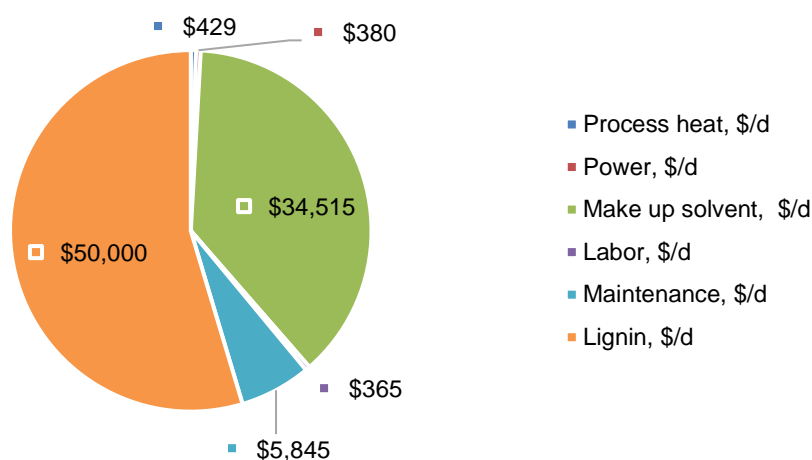


Figure 2. Breakdown of operating costs for the tunable lignin fractionation process.

Overall, the techno-economic evaluation confirms that this tunable process for lignin fractionation is economically viable and competitive with the previously studied process, which utilized a lower fraction of acetone and a lower temperature in a comparison of 12 green solvent fractionation systems (Ajao et al., 2019). However, the minimum selling price in the present study was 24% higher than that for the lower-temperature process. Given that the solubilization reactor represents less than 5% of the cost of installed equipment, the increase in cost for a higher-temperature reactor was counteracted by the shorter residence time.

4. Conclusions

A rapid and tunable approach for the fractionation of technical kraft lignin has been described. Temperature-induced fractionation could provide high lignin solubilization in a short processing time (<1 h), while generating soluble lignin fractions with tunable properties. The relative errors between the measured and predicted values, according to the statistical model, were 9% and 3.5% for the yield and *M_w* of the soluble LB fraction, respectively, which are deemed acceptable from an engineering perspective. The resulting yield from acetone–water fractionation was influenced by the acetone proportion, the temperature, and the combined effect of temperature and acetone proportion; the acetone proportion having the most significant effect. It was also found to be imperative to perform filtration directly after lignin solubilization in order to maintain high yields of soluble LB fractions. The techno-economic evaluation confirmed that this tunable process for lignin fractionation is economically competitive with a lower-temperature counterpart. Comprehensive physicochemical characterization will be required to elucidate the properties of the lignin fractions obtained to allow the development of molecularly tailored high-value applications of LB.

Acknowledgments

This work was supported by the Swedish Foundation for Strategic Environmental Research, MISTRA (F2019/1822) within the framework of the research program STEPS – Sustainable Plastics and Transition Pathways at Lund University. Omar Abdelaziz acknowledges the Troëdsson Paper Engineering grant (P111639) supporting his research stay at the RISE Research Institutes of Sweden AB. Marzouk Benali is grateful for financial support from the Program on Energy Research and Development (PERD-3A03-003) and the Forest Innovation Program of the Canadian Forest Service at Natural Resources Canada.

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