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Green Solvents Screening for the Fractionation of LignoBoost Lignin

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Abstract

A new two-step solvent-based lignin fractionation method is proposed in the present contribution. Green solvents are screened for their ability to solubilise and extract LignoBoost lignin and the employed solvents mixtures are selected based on the Hansen solubility parameters (HSPs) theory. Selective extraction of LignoBoost lignin is performed at ambient temperature exploiting solvents mixtures of ethyl acetate/methanol (90:10), ethyl acetate/methanol (60:40), acetone/water (70:30), and acetone/water (30:70). Fractionated lignin samples are characterised using various analytical techniques such as Brunauer–Emmett–Teller N_2 adsorption, gel permeation chromatography, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and liquid chromatography/mass spectrometry. The elucidation of such technical lignin physicochemical properties through a sustainable fractionation approach is crucial towards better understanding its complex molecular structure and fostering technologies for advanced lignin-based materials.

Introduction

Lignin is one of the primary constituents of terrestrial plant biomass, together with the carbohydrate polymers cellulose and hemicellulose. It is considered to be the second most abundant biopolymer available on Earth, representing a promising source of renewable novel materials and value-added products [1]. Despite its considerable potential as a raw material for the chemical industries and future biorefineries, lignin remains the most inadequately utilised in comparison to other lignocellulosic biopolymers [2]. Also, its molecular structure is still not well-defined, creating many challenges for its efficient valorisation [3]. In light of this, lignin refining via fractionation appears to be an effective approach towards producing more homogeneous starting raw materials [4].

Materials and Methods

LignoBoost lignin was obtained from Innventia's pilot plant (Bäckhammar, Sweden) and all other chemicals were purchased from Sigma-Aldrich. Table 1 reports the HSPs for solvents mixtures designed for the fractionation experiments. The fractionated/unfractionated lignin samples were characterised using BET, GPC, FT-IR, 1H -NMR, and LC-MS.

Table 1. Hansen solubility parameters for the solvents mixtures used in the study (where δ_D is the dispersive, δ_P is the polar and δ_H is the hydrogen bonding interactions of HSPs).

Solvent mixture	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})
EtAc/MeOH 90:10	15.7	6.0	8.7
EtAc/MeOH 60:40	15.5	8.1	13.2
Acetone/Water 70:30	15.5	12.1	17.6
Acetone/Water 30:70	15.5	14.3	31.7

Conclusions

A new method for technical lignin selective fractionation has been demonstrated using selected green solvents mixtures with comprehensive characterisation of obtained fractions. The developed approach can readily generate more usable lignin fractions, facilitating its further manipulation in different high-value applications.

References

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Results and Discussion

Table 2 summarises the results generated from the N_2 adsorption-desorption experiments, while Figure 1 shows the gel permeation chromatography curves for the unfractionated/fractionated lignin samples. Figure 2 also presents the FT-IR spectra for the tested samples. The isolation procedure and solvent choice affected the lignin's properties and structure, suggesting notable variations in different obtained lignin fractions.

Table 2. Surface area and pore structure parameters of fractionated LignoBoost lignin samples determined by BET analysis.

Sample	Surface area (m ² /g)				Pore volume (cm ³ /g × 10 ³)			Pore size (Å)	
	S _{BET}	S _{LSA}	S _{BH}	S _{micro}	V _{total}	V _{BH}	V _{micro}	D _{BET}	D _{BH}
Unfractionated	0.40	0.54	0.31	0.26	1.96	1.87	0.11	199.0	240.0
EtAc/MeOH 90:10	3.16	6.96	1.70	0.33	2.33	1.99	0.63	29.53	46.77
EtAc/MeOH 60:40	1.53	2.29	0.03	1.62	0.54	0.54	0.67	14.18	762.98
Acetone/Water 70:30	1.84	2.65	1.98	0.06	7.72	7.44	0.05	167.36	150.62
Acetone/Water 30:70	1.73	2.39	1.89	0.58	6.19	5.98	0.25	142.87	126.57

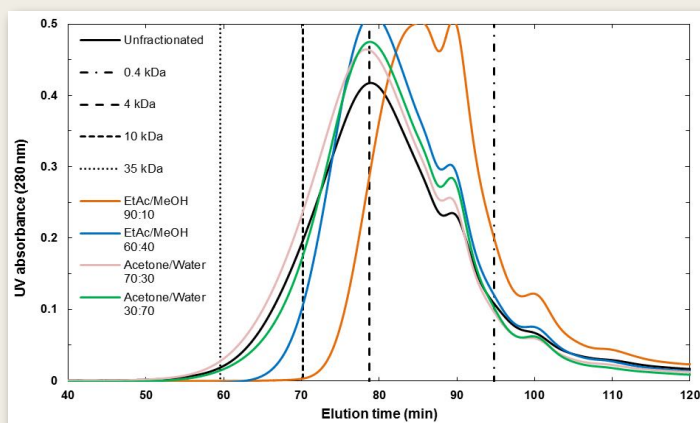


Figure 1. Gel permeation chromatograms for fractionated lignin samples with characteristic UV absorption at 280 nm. The vertical lines indicate the molecular mass (kDa) of the PEG standards that were used for calibration.

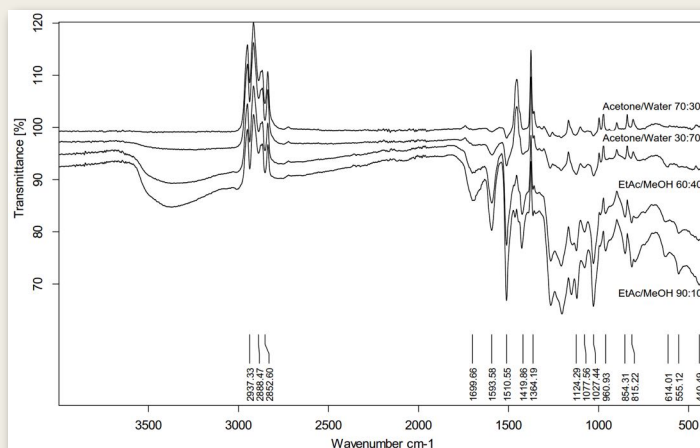


Figure 2. FT-IR spectra of fractionated lignin samples with the wavenumber range 4,000–400 cm⁻¹.

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