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Lignin Recovery from Spruce Sawdust: Impact of Catalyst Selection on Delignification Efficiency and Lignin Properties

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Abstract

Aim of study: Forestry residues and wood processing wastes are promising resources for biorefineries due to their abundance and easy accessibility. However, lignin recovery remains challenging in lignocellulosic biorefineries. This study investigates the delignification of spruce sawdust using ethylene glycol organosolv pretreatment, focusing on how catalyst selection affects cellulosic pulp and lignin properties.

Area of study: Spruce sawdust samples were sourced from a wood processing plant in Bursa.

Material and method: Spruce sawdust was delignified using ethylene glycol with phosphoric acid, acetic acid, or sodium hydroxide catalysts at 130 °C under atmospheric pressure. Characterization was done through elemental analysis, FTIR, TGA, Py-GC/MS, and SEC.

Main results: The ethylene glycol-phosphoric acid (EGPA) system showed the highest delignification (41.55%) and lignin recovery (42.87%). The sodium hydroxide system (EGNa) produced lignin with stronger lignin-specific FTIR bands, indicating higher purity. Py-GC/MS analysis showed esterification in both fractions, with EGPAL producing mainly esters, acids and phenols, and EGNaL producing phenols, esters and aldehydes. SEC indicated EGPAL had a lower molecular weight (M_w=2814 g/mol, M_n=828 g/mol) than EGNaL (M_w=4725 g/mol, M_n=1258 g/mol).

Research highlights: Ethylene glycol-based organosolv pretreatment shows promise for biomass valorization, highlighting catalyst effects on delignification, lignin recovery, and characteristics.

Keywords: Organosolv Pretreatment, Delignification, Ethylene Glycol Treatment, Lignin Recovery, Catalyst

Ladin Talaşından Lignin Geri Kazanımı: Katalizör Seçiminin Delignifikasyon Verimi ve Lignin Özelliklerine Etkisi

Öz

Çalışmanın amacı: Orman artıkları ve odun işleme atıkları, bol bulunmaları ve kolay erişilebilirlikleri nedeniyle biyorafineriler için umut verici kaynaklardır. Ancak, lignin geri kazanımı lignoselülozik biyorafinerilerde önemli bir zorluktur. Bu çalışma, etilen glikol organosolv ön işlemi kullanarak ladin talaşının delignifikasyonunu incelemekte ve katalizör seçiminin selülozik hamur ve lignin özelliklerini nasıl etkilediğini araştırmaktır.

Çalışma alanı: Ladin talaşı örnekleri Bursa'daki bir odun işleme tesisinden temin edilmiştir.

Materyal ve yöntem: Ladin talaşı, fosforik asit, asetik asit veya sodyum hidroksit katalizörleri ile 130 °C'de atmosfer basıncı altında etilen glikol kullanılarak delignifiye edilmiştir. Karakterizasyon için elementel analiz, FTIR, TGA, Py-GC/MS ve SEC analizleri uygulanmıştır.

Temel sonuçlar: Etilen glikol-fosforik asit (EGPA) sistemi en yüksek delignifikasyon (% 41.55) ve lignin geri kazanımını (% 42.87) sağlamıştır. Sodyum hidroksit sistemi (EGNa), FTIR spektrumunda lignin-spesifik grupları daha yoğun göstererek daha saf lignin elde edilmesini sağlamıştır. Py-GC/MS analizleri, her iki fraksiyonda da esterleşmeyi göstermiştir; EGPAL esas olarak esterler, asitler ve fenoller üretirken, EGNaL fenoller, esterler ve aldehitler üretmiştir. SEC sonuçlarına göre EGPAL daha düşük moleküler ağırlığa sahiptir (M_w=2814 g/mol, M_n=828 g/mol) ve EGNaL (M_w=4725 g/mol, M_n=1258 g/mol) ile kıyaslandığında bu farklılık belirgin olmuştur.

Araştırma vurguları: Etilen glikol bazlı organosolv ön işlemi, biyokütlenin değerlenmesinde potansiyel taşımakta olup, katalizör seçiminin delignifikasyon verimliliği, lignin geri kazanımı ve özellikleri üzerindeki önemli etkisini vurgulamaktadır.

Anahtar Kelimeler: Organosolv Ön İşlemi, Delignifikasyon, Etilen Glikol İşlemi, Lignin Geri Kazanımı, Katalizör

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Introduction

Among the renewable sources, biomass stands out as the only one capable of producing energy, biofuels, biobased fuel additives, biobased materials, and chemicals through various conversion methods (Amjith & Bavanish, 2022). Lignocellulosic biomass holds great promise due to its abundance, availability and low cost (Yogalakshmi et al., 2022). Derived from plants, lignocellulosic biomass consists of lignin, cellulose and hemicellulose, with a smaller fraction of extractives. Its composition varies significantly based on the source, whether from agricultural residues, energy crops, forestry residues, or softwood/hardwood (Kassaye et al., 2016; Van Spronsen et al., 2011; Deng et al., 2023; Bhatia et al., 2020).

Forestry residues and wood processing wastes are commonly used to generate power through combustion. However, within the framework of green economy, wood processing wastes have much greater potential as resources for biorefineries, capable of producing value-added products beyond just power generation. Wood processing wastes are promising feedstocks for biorefineries because of their abundance, easy accessibility, relatively low cost, and ready to use particle size. Various conversion technologies have been developed to produce value-added products from these wastes in biorefinery systems (Poveda-Giraldo et al., 2021; Paone et al., 2020).

To maximize the benefits of lignocellulosic biomass in biorefineries, pretreatment is essential, as it breaks down the complex structure of the biomass and increases cellulose accessibility for efficient downstream applications (Sidana & Yadav, 2022; Mankar et al., 2021). Pretreatment methods are generally categorized into four types: physical (e.g.,mechanic, radiation, extrusion, ultrasound, microwave), biological (e.g., enzymes, bacteria), physicochemical (e.g., ammonia fiber explosion, steam explosion, hydrothermal, oxidative etc.) and chemical (e.g., acid, alkali, deep eutectic solvents (DES), oxidative, ionic liquid, organosolv) (Ashokkumar et al., 2022; Vu et al., 2020).

Recovering lignin remains one of the most challenging issues for lignocellulosic biorefineries. In many biorefinery processes, biomass carbohydrates are targeted for sugar production, leaving behind a recalcitrant lignin-rich residue that is often underutilized. In contrast, emerging "lignin-first" biorefinery approaches aim to actively valorize lignin alongside polysaccharides by incorporating lignin extraction and stabilization into the initial stages of biomass processing. As defined by Abu-Omar et al. (2021), lignin-first processing refers to solvent-based strategies that intentionally prevent lignin condensation through catalytic or protection-group chemistry. Importantly, lignin-first is an integrated strategy that seeks to derive value from both lignin and carbohydrates, enabling a more efficient and sustainable utilization of lignocellulosic biomass. Depending on the process design, the goal can either be the preservation of native-like lignin structures, such as β-O-4 linkages, or the catalytic depolymerization of lignin into valuable chemical building blocks (Mullen et al., 2023; Dong et al., 2022; Abu-Omar et al., 2021).

One of the most effective pretreatment processes for recovering lignin while obtaining high-purity cellulose in biorefineries is the organosolv method (Rabelo et al., 2023). In this method, biomass is mixed with an organic solvent (or a solvent mixture), and heated to a temperature range of 100-250 °C. The system can be self-pressurized or sometimes operate at atmospheric pressure, depending on the type of the solvent used. The organosolv pretreatment employs various solvents, including low-boiling solvents like ethanol (Meng et al., 2020; Schmatz & Brienzo, 2022), methanol (Sun et al., 2022; Weerasai et al., 2021), as well as high-boiling-point solvents such as glycerol (Song et al., 2023), and ethylene glycol (EG) (Ling et al., 2022; Wei et al., 2021; Tang et al., 2019), gamma valerolactone (GVL) (Trevorah et al., 2020; Giannoni et al., 2021; Gelosia et al., 2017), organic acids like formic acid, lactic acid and acetic acid (Liu et al., 2022), acetone, n-butanol, n-propanol (Vaidya et al., 2022), tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MTHF) (Xu et al., 2023).

In organosolv pretreatment, the use of catalyst plays a critical role in enhancing the efficiency of the process. Catalyst significantly influences the hydrolysis rate of hemicellulose and the cleavage of lignin bonds, which is essential for effective biomass fractionation (Ferreira & Taherzadeh, 2020). By facilitating these reactions, catalyst reduces the required retention time and operating temperature, making the process more energy-efficient and cost-effective (Mateo et al., 2021). The β-O-4 aryl/alkyl-ether linkage, due to its abundance and sensitivity, is often targeted in lignin depolymerization, where catalysts can greatly improve the rate of hydrolysis between glycosidic bonds, depending on the catalyst type and ratio used.

The choice of catalyst is particularly important, as it can influence not only the efficiency of lignin depolymerization but also the formation of new lignin-lignin bonds, which can impact the overall quality of the resulting lignin (Thoresen et al., 2020). With the addition of appropriate catalyst, delignification and hemicellulose solubilization efficiency can be significantly increased, facilitating the extraction of high-purity lignin and cellulose (Wei Kit Chin et al., 2020). Catalysts such as H_2SO_4, (Xu et al., 2023; Gelosia et al., 2020; Momayez et al., 2022), and HCl (Farid et al., 2023) are widely used in organosolv pretreatment due to their high efficiency. However, they are corrosive, difficult to handle, and they may produce inhibitors (Park et al., 2010). Their corrosive nature can shorten the cycle life of industrial facilities, prompting research into alternative catalysts like organic acids (such as acetic acid, formic acid etc.) and weaker inorganic acids like H_3PO_4 (Sar et al., 2022). Alkaline catalysts, which produce fewer inhibitors than acid catalysts, degrade more lignin, and better preserve the structure of cellulose and hemicellulose, have also attracted increasing attention in recent years (Zhang et al., 2020).

Most studies utilize an ethanol-water mixture in the organosolv process under pressurized conditions. However, the risks associated with high pressure and the costs of high-pressure systems limit the widespread use of low- boiling-point solvents. In contrast, high-boiling-point solvents, such as ethylene glycol, glycerol, and γ-valerolactone, can be used at milder conditions without the need for high-pressure reactors.

Ethylene glycol (EG) is a high-boiling point (198 °C) polyhydric alcohol that has been successfully used for delignification, offering moderate lignin removal with minimal cellulose degradation (see in Table 1). The presence of -CH and -OH groups in EG enhances its effectiveness in the fractionation of lignin and hemicellulose. According to Hansen Solubility and Hildebrand Solubility parameters, studies have shown that ethylene glycol has higher lignin solubility compared to many other solvents (Wei Kit Chin et al., 2020). Additionally, its medium vapor pressure allows for operation at high temperatures without the need for high-pressure conditions (Thoresen et al., 2020; Jiang et al., 2018). These characteristics, combined with its low cost and ability to operate under atmospheric conditions, make EG a particularly attractive candidate for organosolv treatment.

The degree of delignification and the structure of the precipitated lignin are significantly influenced by the catalyst used with EG. While the EG organosolv method can be applied with or without catalyst, lignin and hemicellulose removal is markedly higher when an acid or alkali catalyst is used. This approach also results in higher cellulose recovery and greater purity of the cellulose compared to non-catalyzed processes (Shang et al., 2017; Yu et al., 2019; Lee et al., 2010; Chin et al., 2019; Zhang et al., 2013).

In this study, we investigated the delignification and lignin recovery from spruce sawdust using an ethylene glycol-water system, incorporating three distinct catalysts -phosphoric acid, acetic acid, sodium hydroxide- under atmospheric pressure at 130 °C. This research represents the first application of phosphoric acid and acetic acid catalysts together with an ethylene glycol-water system for the delignification of woody biomass. The novelty of this approach highlights the need to explore alternative catalysts that can enhance lignin recovery while operating at milder conditions. Furthermore, the study examines the influence of retention time on both delignification and lignin recovery, providing valuable insights into optimizing these processes. The importance of this study lies in its potential to contribute to the development of more efficient and cost-effective biorefinery processes, particularly in the context of sustainable lignin valorization and biomass utilization.

Table 1. Comparative results of ethylene glycol-water organosolv pretreatment on lignocellulosic biomass

Biomass	EG:H_2O (v/v)	Catalyst	S:L[(1)]	T[(2)]	RT[(3)]	LR[(4)]	GR[(5)]	XR[(6)]	Reference
Sugarcane bagasse	90:10	NaOH	1:10	110	60	61.3	99.2	14.9	Wei et al., 2021
				130		85	95.2	27.1	
				150		90.9	91	28.8	
	90:10	HCl	1:10	110	60	40.6	98.4	75	
				130		60	93.7	96	
				150		67.1	80.5	99.3	
Fruit bunch	50:50	NaOH	1:10	80	45	75.1	90.4	81.5	Chin et al., 2021
Sugarcane bagasse	90:10	HCl	1:20	120	75	57.3	78.4	87.5	Ling et al., 2022
	75:25					61.2	71.4	83.5	
Rice straw	90:10	$AlCl_3$	1:20	150	30	88	100	90	Tang et al., 2019
Sugarcane bagasse	100:0	HCl	1:20	120	60	48.5	96.9	78.8	Lv et al., 2022
				130		52.5	94.6	96.6	

(1)Solid: Liquid Ratio, (2)Temperature (°C), (3)Retention Time (min), (4)Lignin removal (%), (5) Glucan Retention (%), (6)Xylan Removal (%)

Material and Methods

Material

Spruce sawdust samples were obtained from a wood processing plant in Bursa (Marmara Region). The samples were sieved to 250 µm (60 mesh), and dried at 105 °C before organosolv pretreatment. Ethylene glycol (Extra pure, TK.010101.05001 Tekkim), phosphoric acid (85%, Merck), sodium hydroxide (Merck), acetic acid (100%, Merck) and sulfuric acid (95-97%, Sigma-Aldrich) were used as received without further purification.

Methods

All pretreatments (ethylene glycol-water-phosphoric acid system: EGPA; ethylene glycol-water-acetic acid system: EGAA; ethylene glycol-water-sodium hydroxide system: EGNa) were performed in a two-necked glass reactor (500 ml) equipped with a reflux condenser and a thermocouple. In each pretreatment, 10 g spruce sawdust is mixed with ethylene glycol-water system (80:20, v/v) with a certain amount of catalyst. In EGPA, H_3PO_4 was added to solvent system to have a final catalyst concentration as 0.1 M. In EGAA, CH_3COOH was added to solvent system to have a final catalyst concentration as 0.8 M. In EGNa, the final NaOH concentration in the solvent system was 0.1 M. In this study, the organosolv treatment was conducted at 130 °C for 60 min, where the parameters were chosen based on the findings of Farid et al. 2023. Their research identified 132 °C as an optimal temperature for lignin solubilization.

After each treatment, the cellulose-rich pulp was separated from the liquor, washed with water, and then dried at 105 °C for 24 h. The solution in which lignin was dissolved was diluted up to 1 L with pure water (at 55 °C) to precipitate the lignin. The pH of solution was measured, and in cases where the pH was high, the pH was reduced to 2-2.5 using 0.1M H_2SO_4. After precipitation, lignin was separated by centrifugation, then washed with distilled water. Then, it dried at 105 °C for 24 h. The entire organosolv treatments were repeated more than twice. Each organosolv solvent-catalyst combination was evaluated based on its delignification efficiency and lignin recovery (Eq. 1,2):

$$\text{Delignification (\%)} = \frac{(m_{L,B} - m_{L,P})}{m_{L,B}} \times 100 \qquad (1)$$

$$\text{Lignin Recovery (\%)} = \frac{m_L}{m_{L,B}} \times 100 \qquad (2)$$

where $m_{L,B}$ is the lignin in biomass, $m_{L,P}$ is the the lignin in pulp, and m_L is the lignin precipitate.

The nomenclature of the fractions in the organosolv process of spruce sawdust is as follows: cellulose-rich pulp and lignin obtained from EGAA system: EGAAP and EGAAL; cellulose-rich pulp and lignin obtained from the EGPA system: EGPAP and EGPAL; cellulose-rich pulp and lignin obtained from EGNa systems, EGNaP and EGNaL.

Analyses

Extractive content was identified according to ASTM E1690-08 Standard Test Method for Determination of Ethanol Extractives in Biomass (ASTM, 2016). Elemental carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content were quantified using an elemental analyzer (LECO CHN628). The lignin content of each sample was determined gravimetrically following the NREL protocol NREL/TP-510-42618 (Sluiter et al., 2012).

Fourier Transform Infrared (FTIR) spectra of EGPAL and EGNaL samples were recorded on a Perkin Elmer Spectrum 100 spectrometer equipped with a universal attenuated total reflectance (ATR) accessory featuring a diamond crystal. Spectra were collected over the wavenumber range of 400-4000 cm^{-1} with a spectral resolution of 4 cm^{-1}.

Thermal degradation behavior of the pulp and lignin samples was evaluated using a simultaneous thermogravimetric analysis and differential scanning calorimetry system (TGA/DSC, TA Instruments SDT Q600). Measurements were carried out from 25 °C to 800 °C at a constant heating rate of 15 °C $\cdot min^{-1}$ under a nitrogen atmosphere with a flow rate of 100 $mL \cdot min^{-1}$.

Fast pyrolysis experiments were conducted using a Frontier PY-2020iS pyrolyzer coupled to a Shimadzu QP 2010 Ultra GC/MS system. Each analysis was performed at 600 °C with a heating rate of 10 $°C \cdot ms^{-1}$ and a residence time of 15 s. The pyrolysis vapors were transferred by helium (1 $mL \cdot min^{-1}$) into a GC capillary column (Teknokroma, 30 m × 0.25 mm × 0.25 μm). The GC oven temperature was initially maintained at 40 °C for 2 min, ramped to 200 °C at 5 $°C \cdot min^{-1}$ and held for 2 min, then increased to 280 °C at 10 $°C \cdot min^{-1}$ and held for an additional 2 min. Mass spectrometric detection was performed under electron impact ionization at 70 eV, scanning over a mass range of m/z 30-600 amu. The ion source and interface temperatures were set to 230 °C and 280 °C, respectively. Compound identification was achieved by comparison with the NIST mass spectral library integrated into the GC/MS.

The number average molecular weight (M_n), the weight average molecular weight (M_w), and polydispersity index (PDI) of the lignins were determined by size exclusion chromatography (SEC) (Waters 600E chromatography system, Waters 2414 refractive index detector, Waters 486 UV absorbance detector). Each sample was dissolved in 0.1 M NaOH (1 mg/mL) and filtered through a syringe filter. 0.1 M NaOH (0.5 mL/min flow rate) was used as an eluent. For the calibration, polyethylene glycol standards were used, (0.2 to 35 kDa, Merck). The absorbance of 280 nm was used for detection.

Result and Discussion

Delignification Efficiency and Lignin Recovery

Table 2 presents the proximate, ultimate and compositional analysis of spruce sawdust. The major elements in spruce sawdust are carbon (47.57%), oxygen (48.36%), and hydrogen (3.64%), with no detectable nitrogen or sulfur, which aligns with the typically low nitrogen and sulfur content found in coniferous woods (Sulg et al., 2021). The proximate analysis reveals a moisture content of 9.84%, volatile matter at 76.98%, fixed carbon at 12.75%, and ash at 0.43%. These values are generally consistent with literature data for softwood sawdust, which typically reports volatile matter content between 70-77%, fixed carbon around 19-27% and ash content below 1% (Sulg et al., 2021). The low ash content is particularly favorable as it suggests minimal inorganic residues in downstream applications. As a softwood, spruce sawdust contains 27.33% lignin, which mainly comprises guaiacyl units (90-95%) with a small fraction of p-hydroxyphenyl units (0.5-3.4%). Given the significant lignin content in spruce sawdust, its efficient removal and recovery are critical factors in optimizing the delignification process.

Table 2. Characterization of spruce sawdust

Proximate analysis (wt. %)	
Moisture	9.84
Volatile matter	76.98
Fixed carbon	12.75
Ash	0.43
Elemental analysis (wt. %), dry basis	
C	47.57
H	3.64
N	0
S	0
O*	48.36
Composition (wt. %), dry basis	
Extractives	6.39
Lignin**	27.33

Calculated from difference O%= 100-ash-(C+H+N+S)
Klason lignin

Calculated from difference O%= 100-ash-(C+H+N+S) —

Figure 1 shows the comparison of the delignification rates and lignin recovery percentages observed in EGPA, EGAA and EGNa systems. Using spruce sawdust as the feedstock, the EGPA system achieved the highest delignification rate of 41.55% and lignin recovery of 42.87%. Conversely, EGAA system resulted in the lowest delignification rate (26.64%). When comparing these results to similar study utilizing pine wood-softwood like spruce-significant differences are observed. De Santi et al. (2020) employed higher temperatures (140 °C), extended retention times (120 min), and an effective catalyst (H_2SO_4), achieving a markedly higher delignification rate of 77%. The lower delignification rates observed in the current study may be attributed to the milder reaction conditions and the use of weaker acids. The differences observed in delignification rates between EGPA and EGAA systems can be partly explained by the correlation between acid strength and organosolv treatment efficacy (Farid et al., 2023). The use of phosphoric acid, which has a higher acidic strength than acetic acid, likely contributed to the increased delignification rate and lignin recovery in the EGPA system compared to the EGAA system. Despite achieving partial delignification, no lignin recovery was observed in EGAA system. Acetic acid is frequently preferred as a solvent or catalyst in delignification processes due to its ability to break down lignin linkages. However, it can also modify lignin through esterification and acetylation reactions. Wang et al. (2021) reported that acetic acid pretreatment led to acetylation and a reduction in molecular weight of lignin. The absence of lignin precipitation in the EGAA system might be due to increased solubility of acetylated lignin in the solution.

The studies regarding the use of NaOH as catalyst in ethylene glycol-water systems are rare. This is mainly due to hemicellulose, which retains in the biomass during delignification in alkaline environment. In our study, the delignification efficiency and lignin recovery rates of EGNa system were 30% and 34.63%, respectively. It is much lower as compared to Wei et al. (2021), who delignified sugarcane bagasse with an efficiency 85%. Since the final NaOH concentration in the solution, reaction temperature (130 °C) and solid/liquid ratio are same for both studies, the difference in delignification efficiencies might be due to type of biomass and ethylene glycol/water ratio. With milder reaction conditions (ethylene glycol/water ratio: 1; NaOH: 3% (v/v), 80 °C, 45 min), Chin et al. (2021), carried out organosolv treatment with a delignification efficiency of 75.1%. Although the highest delignification rate in the solvent-catalyst systems we studied was seen in the EGPA system (41.55%), the result obtained is lower compared to the studies given in Table 1. One of the reasons for this is that organosolv delignification of softwood is less selective than that of hardwoods and herbaceous crops. Similar observation was done by Uraki and Sano (1999), where propylene glycol and ethylene glycol with HCl catalyst gave very low delignification efficiencies for softwoods even at 170 °C. Zheng et al. (2018) used microwave- assisted organosolv with ethylene glycol (94.4g)-water (5.6 g) with H_2SO_4 as catalyst (1%) for delignifying Eucalyptus waste (at 108 °C, for 90min, under reflux). In their study, a low amount of organosolv lignin was obtained, between 15-18%, and they attributed this to the degradation of oligomeric lignin, which could not be captured by filtration, and the dielectric loss factors of the solvent in microwave- assisted organosolv process.

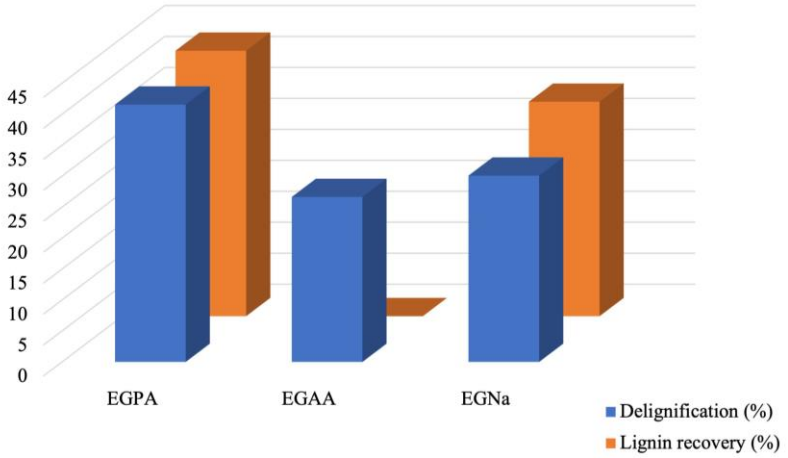

Figure 1. Delignification and lignin recovery in EGPA, EGAA and EGNa system

Figure 2 presents the delignification efficiency and lignin recovery percentages for the EGPA and EGNa systems as a function of retention time. Due to absence of lignin precipitation and a low delignification rate in the EGAA system, its time dependence was not further investigated. In both the EGPA and EGNa systems, the duration of organosolv treatment had minimal impact on delignification efficiency and lignin recovery. For the EGPA system, extending the treatment time from 60 min to 90 min slightly increased delignification efficiency from 41.6% to 45.2%. However, the highest lignin recovery rate was achieved with a 60 min treatment (42.9%), while the lowest recovery was observed with a 90 min treatment (34.3%).

In the EGNa system, delignification efficiency ranged from 28.86% (at 90 min) to 30% (at 60 min), indicating that the duration of organosolv treatment had minimal impact on delignification. Similarly, lignin recovery percentages varied only slightly with treatment time, ranging from 34.63% (at 60 min) to 41.3% (at 90 min). Compared to EGPA system, the NaOH experiments yielded slightly lower delignification and lignin recovery rates. In a related study, Alves-Ferreira et al. (2021) applied ethylene glycol organosolv treatment to *Cistus ladanifer* plant with 2% and 4% NaOH catalyst at 130 ˚C for 1 and 2 hours. They reported delignification efficiencies of 68.8% and 68.7% for the 1 and 2 h treatments with 2% NaOH catalyst, and 77.7% and 78.3% for the corresponding treatments with 4% NaOH.

Given the minimal impact of pretreatment duration on delignification efficiency and lignin recovery, characterization was conducted on the lignin and cellulose fractions of the EGPA and EGNa systems with a 60 min treatment period.

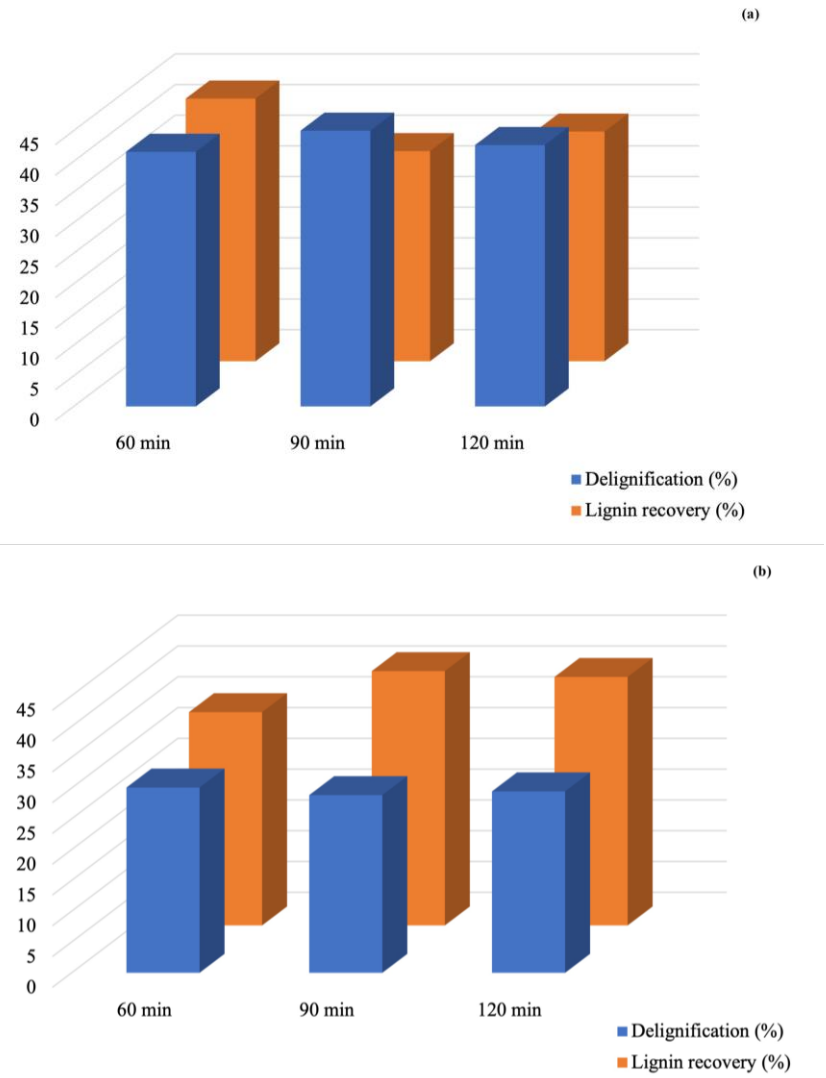

Figure 2. (a) EGPA, (b) EGNa delignification and lignin recovery depending on retention time

Characteristics of Cellulose-Rich Pulps

Delignification disrupts the structure of biomass, resulting a change in chemical structure in both pulp fraction and lignin. FTIR is a useful tool to describe the functional groups in the structure. Table 3 was used for describing common functional groups in wood components. The FT-IR spectra of EGPAP and EGNaP (Figure 3) were similar, showing similar structure with same functional groups of different intensities. In both EGNaP and EGPAP, the stretching vibration of hydroxyl (-OH) groups (due to absorbed water, aliphatic primary and secondary alcohols) appeared at 3293 cm^{-1} (Chen et al., 2019). C-H stretching of alkyl groups appearing at 2947 and 2821cm^{-1} (Ruiz cm^{-1}.and aromatic skeleton vibration at 1430 cm^{-1}. C-O-C skeletal vibration of pyranose rings was observed in both spectra at 1028 and 895 cm^{-1} (Klaai et al., 2022).

et al., 2011) was more intense in EGPAP. C=C and C-H stretching vibration of terpenoids in wood appears at 2150 and 2030 cm^{-1}, both in the FTIR spectra of pulps and FTIR of spruce sawdust (see in Supplementary Material, Fig. S1). The presence of terpenes was also observed in Py-GC/MS results. C-H deformation in cellulose and hemicellulose at 1375 cm^{-1}, C-O stretching of aromatic units in cellulose and hemicellulose at 1317 cm^{-1}, C-O-C stretching in cellulose and hemicellulose at 1160 cm^{-1} and 896 cm^{-1} were observed in both pulps. Due to partial delignification there was still lignin remaining in the pulp, which was observable by the presence of C-O stretching vibration of the acetyl group in lignin at 126

Table 3. Functional groups from FTIR spectral library (Ferrer et al., 2016; Chen et al., 2015; Md Salim et al., 2021; Volli et al., 2021; de Oliveira Brotto et al., 2023; Zhuang et al., 2020; Schulz & Baranska, 2009; Alzagameem et al., 2018)

Wavenumber (cm^{-1})	Assignment
3412-3460	O-H stretching
2940-3000	C-H vibration in methyl and methylene groups in hemicellulose, lignin and cellulose
3000-2000	C-H stretching vibration of the volatile terpenoids
1700-1710	C=O vibration of unconjugated carbonyl, ester and ketone groups in lignin and hemicellulose
1605-1593	C=O stretching of aromatic skeletons in lignin
1515-1505	Aromatic skeleton vibrations in lignin
1470-1445	C-H deformation in lignin ($-CH_3$, $-CH_2$)
1430-1420	Aromatic skeleton vibration in lignin
1370-1365	Symmetrical deformation, $-CH_3$
1335	O-H bending in cellulose
1330-1325	Condensed S and G units in lignin
1317	C-O stretching of C5 substituted aromatic structures
1270-1263	C=O vibrations in G chains of lignin
1245	C-C, C-O, C=O stretching in cellulose
1230-1209	C-C, C-O and C=O stretching in G units
1167-1156	C=O stretching (ester) (HGS)
1169-1160	C-O-C vibrations in cellulose and hemicellulose
1140	C-H aromatic deformation (lignin)
1128-1115	C-H aromatic in-plane deformation (S)
1110	Aromatic C-H deformation of the anhydroglucose ring in cellulose
1086-1080	C-O deformation in aliphatic ethers and secondary alcohols
	C-O-C ring skeletal vibration in cellulose
1038-1028	C-H aromatic in-plane deformation
990-966	-HC=CH- out of plane deformation
925-915	C-H out of plane in aromatic chains
903-895	Glycosidic C-H deformation
896	C-O-C stretching in cellulose and hemicellulose
858-853	C-H out of plane deformation in G units of lignin
835-834	C-H out of plane deformation in S units of lignin
832-817	Plane bending -CH in G units in lignin

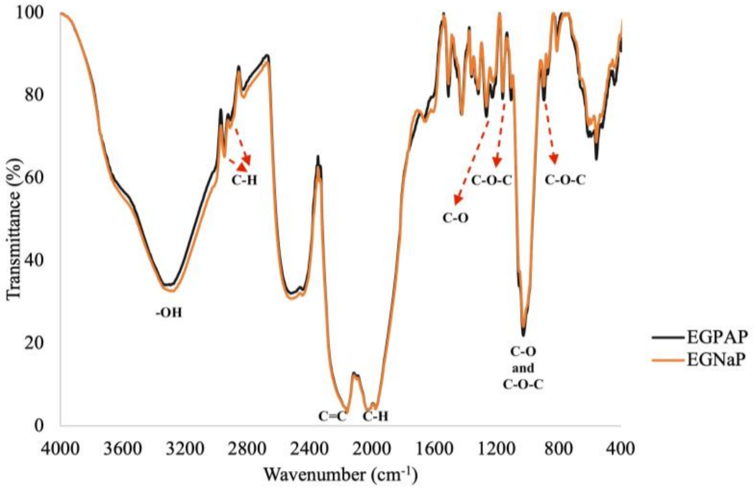

Figure 3. FTIR spectra of EGPAP and EGNaP

TGA and DTG of EGPAP and EGNaP are given in Figure 4. Both EGPAP and EGNaP show similar thermal degradation trends with two main DTG stages: first stage (centered at 60 °C and 61 °C for EGNaP and EGPAP respectively) is due to moisture and light gases (such as CO, CO_2) removal, second stage is due to thermal degradation of cellulosic fraction. The temperature at which the mass loss rate is maximum (T_{max}) appears in second stage, and T_{max} is 339 °C and 338 °C for EGPAP and EGNaP, respectively.

Thermal decomposition of cellulose is observed at a temperature range of 315-400 °C (Chen et al., 2015), which is consistent with our observations. In DTG of original spruce sawdust (see in Supplementary Material, Fig. S2), a shoulder before the main degradation peak, which is due to hemicellulose degradation, is observed. In DTG of EGPAP, this shoulder is missing due to hemicellulose hydrolysis under acidic organosolv conditions. In DTG of original spruce sawdust, lignin degradation has a small peak centered at 440 °C, which is missing in both EGPAP and EGNaP. Due to the reason that lignin is partially removed, both EGPAP and EGNaP have tail-ends after 400 °C (ending around 650 °C). Although they represent similar thermal stability, EGPAP is more reactive, which is observable from the intensity of the peak. Mass loss due to thermal degradation is 85.84% and 81.53% for EGPAP and EGNaP, respectively.

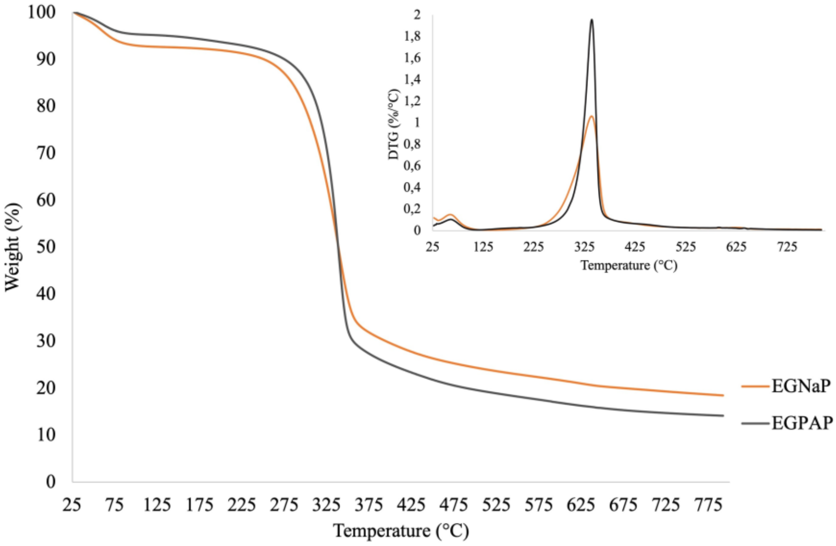

Figure 4. Thermogravimetric analysis curve of EGPAP and EGNaP

The Py-GC/MS was used for qualitative analysis to thoroughly examine the composition and distribution of pyrolysis products from EGPAP, EGNaP, EGPAL and EGNaL. To easily analyze the pyrolysis products, it is essential to categorize the pyrolysis products according to their chemical structures. As depicted in Figure 5, the main pyrolysis products of EGPAP and EGNaP are not similar, indicating that catalyst used in ethylene glycol-water system alter the pulp structure. While terpenes (limonene) are the main pyrolysis product of EGPAP, esters are the main fast pyrolysis product of EGNaP. Appearing in both pulps, terpenes can be present in a pulp after organosolv treatment due to their natural occurrence in wood, mainly in the bark (Pinto et al., 2018; Santos et al., 2022). Although soluble in organic solvents, terpenes may remain in the pulp depending on their solubility in ethylene glycol and the effectiveness of washing steps to remove solvent system.

Esters (39.23%), acids (17.07%), ketones (9.56%), terpenes (9.17) and phenols (8.14) are the main pyrolysis products of EGNaP. The high ester content can be explained with the formation of esters during treatment. In NaOH-catalyzed organosolv delignification with ethylene glycol-water solvent systems, esters can be formed through esterification reactions between carboxylic acids and ethylene glycol under basic conditions. Since the delignification is low in EGNa system, more phenols are detected in EGNaP compared to EGPAP. Because, the fast pyrolysis of lignin, which involves the thermal cleavage of inter-unit linkages and char formation, ends up with phenolic compounds including phenols, methoxyphenols and dimethoxyphenols (Carrier et al., 2017). Carbohydrate derivatives, including ketones and acids, are also detected in both pulps, relatively higher in EGNaP.

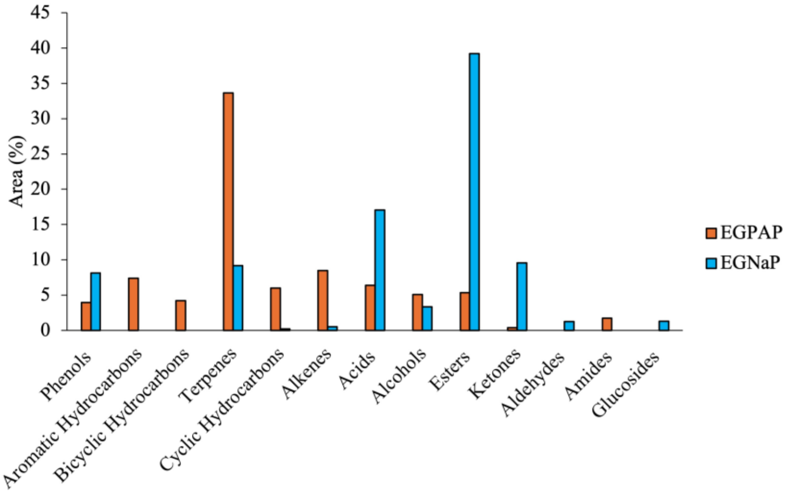

Figure 5. Fast pyrolysis product distribution of EGPAP and EGNaP

Characteristics of Lignins

FT-IR spectra of EGPAL and EGNaL are depicted in Figure 6. Published studies on lignin in Table 3 are used to identify FT-IR bands. FT-IR analysis of EGPAL and EGNaL revealed notable differences in their spectra. While both samples exhibited common lignin bands (Wang et al., 2015), a distinct and strong absorbance in the 800-1040 cm^{-1} region was observed in phosphoric acid catalyzed lignin. This region corresponds to C-O-C stretching vibration, suggesting partial glycolation of lignin through etherification between ethylene glycol and benzylic positions under acidic conditions (Hassanpour et al., 2020; Dong et al., 2022; Jasiukaitytė-Grojzdek et al., 2012). In contrast, the base catalyzed lignin, EGNaL, displayed more intense peaks in the 1200-1700 cm^{-1} region, particularly associated with aromatic skeletal vibrations (1603 cm^{-1}, 1509 cm^{-1} and 1424 cm^{-1}) and carbonyl stretching (G unit of lignin at 1263 cm^{-1} and 1209 cm^{-1}). These features indicate the cleavage of β-O-4 linkages, generating more free aromatic structures and phenolic groups, which are characteristics of alkaline lignin depolymerization pathways (Li et al., 2025).

Fast pyrolysis product distribution of EGPAL and EGNaL are given in Figure 7. The pyrolysis products of EGPAL mainly consists of esters, acids and phenols. The chromatograms were different from that of native lignin, which end up with mainly phenols and carbonyls, alcohols and aromatics (Qian et al., 2023). The difference is mainly related with how the lignin isolated (because it also affects the purity of lignin) and the biomass type. The pyrolysis products of EGNaL consist of phenols, esters and aldehydes. Phenol and acid units were seen less in EGNaL than in EGPAL. The phenol content of lignins was found to be lower than the organosolv studies in the literature (Başakçılardan Kabakcı & Tanış, 2021; Wang et al., 2021; Soongprasit et al., 2020). The existence of ketones and acids denote that precipitate also includes carbohydrates along with lignin.

Lignins obtained by the EGNa solvent-catalyst pair would be a more profitable option to use as platform chemicals rather than using them traditionally as a low-value energy source (Zhang & Wu, 2015). The excessive esterification was caused by the combination of alkyl groups from the solvent and alkanoate groups from the biomass. Phenolics can be converted into low-value energy and phenolic bio-oils or used as fuel additives (Tahir et al., 2021; Kim, 2015). Esters are often used in plasticizers, resins, adhesives, coatings, polyols, oil drilling fluids and plant protection products (Almeida et al., 2022).

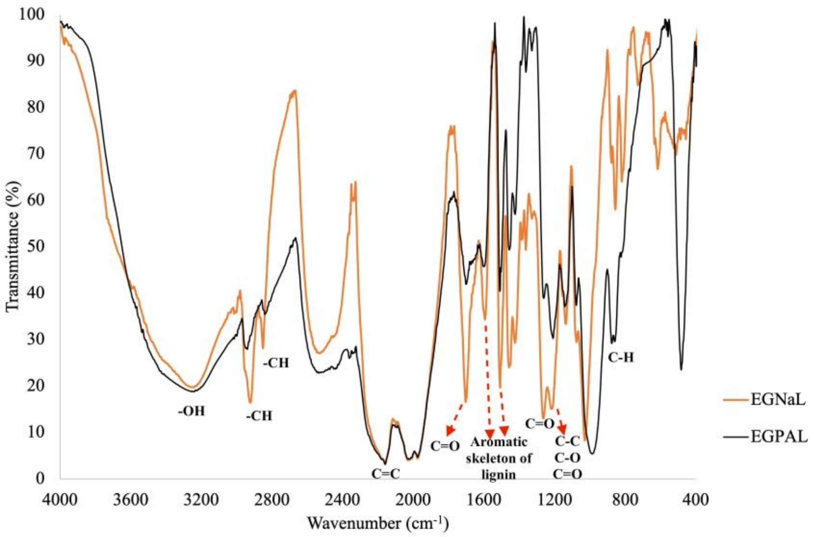

Figure 6. FT-IR spectra of EGPAL and EGNaL

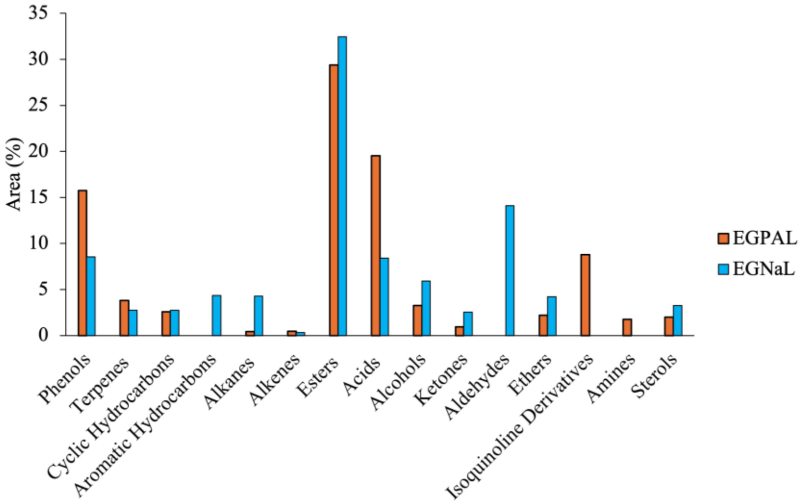

Figure 7. Fast pyrolysis product distribution of EGPAL and EGNaL

The SEC analysis of the two lignin samples, EGPAL and EGNaL, shows significant differences in molecular weight, which can be attributed to the different catalytic systems used for their extraction. EGPAL has a M_w of 2814 g/mol, while EGNaL exhibits a much higher M_w of 4725 g/mol. Similarly, the M_n of EGPAL is lower (828 g/mol) compared to 1258 g/mol for EGNaL. The PDI was found to be 3.40 for EGPAL and 3.76 for EGNaL, indicating a broader molecular weight distribution in the alkali-catalyzed system. The higher M_w observed in the EGNaL sample can be explained by the selective depolymerization in alkaline environment. NaOH primarily cleaves β-O-4 linkages (Rabelo et al., 2023) while preserving more resistant C-C bonds in lignin, resulting in the formation of larger molecular fragments. Additionally, alkaline environments are known to promote condensation reactions, where smaller lignin fragments recombine, further increasing the molecular weight. In contrast, acidic conditions lead to more aggressive depolymerization of lignin by cleaving both ether and ester bonds, producing smaller molecular fragments and a lower M_w (Zhu et al., 2023). Although acidic environments are conducive to condensation, the presence of ethylene glycol plays a critical role in suppressing this pathway (Deuss et al., 2015).

Conclusions

In this study, spruce sawdust was pretreated using ethylene glycol with catalysts -phosphoric acid, acetic acid, sodium hydroxide- at 130 °C under atmospheric pressure. After pretreatment, the resulting mixture was separated into a cellulose-rich pulp and a lignin precipitate, both of which were characterized. The delignification efficiency and lignin recovery percentages were found to be highly dependent on the specific solvent-catalyst system employed. Key findings include:

-The EGPA solvent-catalyst system achieved the highest delignification efficiency (41.55%) and lignin recovery (42.87%) for spruce sawdust.

-The acetic acid catalyst did not facilitate lignin recovery, indicating the need for further research to optimize conditions.

-Pretreatment period had minimal impact on delignification efficiency and lignin recovery in the EGPA and EGNa systems.

-The FTIR spectra of lignins reflect the distinct reactivity of lignin under acid and base catalyzed EG systems. While acidic conditions promote etherification, basic conditions favor cleavage and formation of more aromatic rich structures.

-Partial delignification had little effect on the thermal stability of the pulps.

-Py-GC/MS analysis revealed evidence of esterification in both pulp and lignin fractions. Additionally, the presence of limonene in pulps needs further investigation to determine whether it is a result of the organosolv conditions or fast pyrolysis pyrolysis. While the EGPAL sample contained a higher concentration of phenols, further optimization of precipitation conditions or changes in the solvent system are recommended to enhance its purity.

-EGPAL had a lower weight-average molecular weight (M_w=2814 g/mol) and number-average molecular weight (M_n=828 g/mol) compared to EGNaL (M_w=4725 g/mol, M_n=1258 g/mol), with a polydispersity index of 3.40 for EGPAL and 3.76 for EGNaL, indicating a broader molecular weight distribution in the alkali-catalyzed system

Ethics Committee Approval

N/A

Peer-review

Externally peer-reviewed.

Author Contributions

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

Conflict of Interest

The authors declare that they have no conflict of interest.

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