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Effect of Amine Type on Lignin Modification to Evaluate Its Reactivity in Polyol Construction for Non-Isocyanate Polyurethanes (NIPU)

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ABSTRACT

Polyols are groups of organic compounds which contain carbon and are randomly linked to other atoms, especially carbon-carbon and carbon-hydrogen. These compounds are mainly used as reactants to make other polymers. Among biopolymers, lignin is regarded as the base of a new polymer in polyol construction. The present study aimed to investigate the effects of amine type (diethylenetriamine and ethylenediamine) on the modification of lignin-based polyols, so as to provide an alternative to petroleum polyols and, in turn, increase functional groups and reduce their harm to humans' health and the environment. To this aim, first, lignin was extracted from raw liquor. Next, the extracted lignin was reacted with diethylenetriamine (DETA) and ethylenediamine (EDA). Finally, the Mannich method was used for the reaction between amine lignin and propylene carbonate. The results of the Fourier Transform Infrared (FTIR) spectroscopy analysis showed that modification with DETA led to more structural change in lignin and peak 1100 indicates the presence of C–O bond related to urethane bonds in modified lignin. Moreover, adding propylene carbonate to aminated lignin did not result in much change in the results of the FTIR analysis. Additionally, urethane bonds can be seen in the results of GPC at 400°C–500°C. Furthermore, a slight decrease in thermal stability was observed in lignin modified with amine and propylene carbonate, compared to the raw lignin sample.

KEYWORDS

Polyol; lignin; diethylenetriamine; ethylenediamine; propylene carbonate; polyurethanes; NIPU

1 Introduction

Polyols belong to the group of organic compounds which contain carbon and are randomly attached to other atoms, especially carbon-carbon and carbon-hydrogen. These compounds, with several hydroxyl functional groups, are available for organic reactions and are principally used as reactants to make other polymers.

They can be categorized according to their ultimate application. Polyols with higher molecular weights (between 2000 and 10,000 g/mol) are applied to make more flexible polyurethanes, whereas polyols with



lower molecular weights are used to make stiffer products. Luo et al. [1] and Chen et al. [2] stated in their research that lignin is a good candidate for polymerization and chemical modification to prepare stable polyurethane materials.

Gondaliya et al. [3], in their research, used lignin as a partial polyol substitute in flexible polyurethane foam. In the research of Saražin et al. [4] non-isocyanate polyurethane a wood adhesive was produced from organosolv lignin, which is a bio-sourced raw material, produced in large quantities as a by-product of the paper industry.

The use of polyols has several advantages: a) high solubility of simple metal salts (similar to water) which are used as raw materials for the synthesis of many nanomaterials; b) high boiling points up to 320°C; c) utilization of coordination properties to functionalize the surface or create colloidal stability in different nanoparticles; d) very high adaptability, which means that they can be used for some specific syntheses, from the lower molecular weight polyols such as ethylene glycol to the higher molecular weight compounds such as polyethylene glycol.

Noteworthy is the fact that some polyols also have low toxicity, high biodegradability, and biocompatibility. Some polyols are FDA-approved, and some others are known as green solvents [5].

Biodegradable polyols are polymers that decompose after serving their purpose through a bacterial decomposition process. This decomposition leads to the formation of by-products such as CO₂, N₂, water, biomass, and mineral salts. These polymers form either naturally or are synthesized and are mainly composed of esters, amides, and ethers functional groups. Their properties and decomposition mechanisms are determined based on their exact structures. It should also be stated that these polymers are often synthesized through compression reactions, open-ring polymerization, and metal catalysts. There are many examples and applications of degradable polymers.

Biodegradable polymers are classified into four main categories based on their source of production:

- A) Agricultural biomass products such as starch, cellulose, chitosan, lignin, and proteins are major sources of renewable biodegradable polymers that can be extracted directly;
- B) Biodegradable polymers produced from the activity of micro-organisms such as polyhydroxy alkanoates;
- C) Polymers resulting from biotechnological processes such as polylactides, which are widely used in medicine and pharmacy; and
- D) Polymers derived from petrochemical monomers such as caprolactones [6,7].

Of the above-mentioned biopolymers, lignin is considered to be a polymer source in the production of polyols. Lignin, as a very important renewable material, is the second most abundant biopolymer on earth after cellulose and has a heterogeneous and amorphous structure, with many hydroxyl groups and aromatic rings.

Based on known lignin properties, among the various methods for its chemical modification, amination is one of the most promising ones because amino groups can be ionized under acidic conditions [8]. Amines are organic bases, to which a central nitrogen atom and one, two, or three alkyl groups are attached, named type one amine, type two amine, and type three amine, respectively. Amines are usually extracted from ammonia replacing the hydrogens linked to alkyl groups. Diethylenetriamine (DETA) and ethylenediamine (EDA) are among the amines used to aminate organic compounds, including lignin. The formation of amine groups is rather simple and increases the structural strength and resistance to hydrolysis of polyols.

The second method used to modify lignin is to react it with propylene carbonate. Due to its high vapor pressure, toxicity, flammability, and carcinogenicity, the use of propylene oxide in lignin modification

reactions are not advisable. Therefore, with these considerations in mind, the organic five-membered ring of propylene carbonate is instead preferable to propylene oxide for its use in reactions. This organic material is known as a compound with low toxicity, and low vapor pressure, biodegradability, solubility, and a high boiling [9].

The purpose of the two-stage modification of lignin with propylene carbonate is to improve its solubility and increase its reactivity. In this reaction, lignin is first reacted with the amine. The aminated product is next reacted with propylene carbonate and end hydroxyl groups are developed [10].

Xue et al. [11] proposed an innovative type of solvent-free and catalyst-free process to obtain a hybrid non-isocyanate polyurethane (HNIPU). The researchers used ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) in reaction with ethylene carbonate (EC) to obtain four bi(hydroxyethyloxycarbonylamine)alkane (BHA)s. The results of TGA thermal analysis and DTG derivative thermogravimetry showed that the obtained HNIPUs had good thermal stability and can, thus, be considered heat resistant coatings.

In another study, Hu et al. [12] investigated an environmentally-friendly and non-toxic route for the synthesis of lignin-based non-isocyanate polyurethane networks. Specifically, the NH_2 -terminated polyhydroxy urethane prepolymer was first synthesized from the 6-membered cyclic bicarbonate BCC and diamine through a ring-opening reaction. Subsequently, lignin-based non-isocyanate polyurethanes were synthesized. The structural, mechanical, and thermal properties of NIPU were determined. DMA analysis and TGA thermal analysis results showed that tensile strength, Young's modulus, toughness, storage modulus, glass transition temperature, and thermal stability of lignin-based NIPUs gradually increased in parallel with the increase in lignin content.

Non-isocyanate polyurethanes (NIPU) have been in the spotlight of many researchers for quite some time now [13–17]. The more established route to prepare them is through the preparation and use of cyclic carbonates [18–22]. More recently a rather easier route using a simple aliphatic carbonate, namely dimethyl carbonate, has been found [23–27]. All of these routes are different from the classical approach using isocyanates, even if using natural polyols [28]. The dimethyl carbonate route has led to applicable NIPUs as adhesives and coatings and has been pursued with some success, and moreover by using a number of biomaterials [29–33]. The route presented in this paper is another, different, alternative approach to preparing NIPUs from biosourced materials such as lignin.

With respect to the above-mentioned points, the present study investigated the modification of lignin with DETA, EDA, and propylene carbonate in the manufacture of basic lignin polyols to provide an alternative to petroleum polyols and finally to find an alternative route to the preparation of non-isocyanate polyurethanes (NIPU). This can increase the number of functional groups and reduce the harmful effects on health and the environment.

2 Experimental

2.1 Extraction of Lignin from Liqueur

First, some liqueur was supplied from Mazandaran Wood and Paper Factory. The production method of paper pulp in this factory was a mechanical pulping process. Next, to prepare the required lignin, the researchers added 20-percent sulfuric acid to a liter of liqueur with a PH of about 12 to 13, which resulted in a mixture with a PH of 2–3, causing the lignin to precipitate. This precipitated lignin was then dried in an oven at a temperature of about 40°C. Finally, the resulting powder was washed three times again with methanol. The residual amount and lignin extraction efficiency were measured according to the method introduced in [34].

2.2 Modification of Lignin with Amine (DETA and EDA)

To aminate lignin, the researchers first heated 10 g of the extracted lignin and 3 g of the DETA in 50 cc of methanol solution and 50 cc of xylene solution at a ratio of 1:1 at 75°C for 6 h. After the completion of the reaction, the reaction mixture was cooled to ambient temperature, and the resulting precipitate was first passed through the polyester sulfone membrane with a pore size of 0.22 μm and then washed with methanol. The solid residue, the aminated lignin, was then washed 4 times with methanol solution and was finally dried in a vacuum oven at 30°C. The same steps were repeated to modify the lignin with ethylenediamine.

2.3 Modification of Amino Lignin with Propylene Carbonate (PC)

The Mannich method was used for the reaction between amino lignin and propylene carbonate. As shown in Figs. 1 and 2. In this process, 9 g of amino lignin was dissolved with 10 g of PC and 150 cc of chloroform. Subsequent to this, a certain amount of DBTDL catalyst was added to the reaction mixture. The reaction proceeded for 6 h at 65°C at atmospheric pressure. When the reaction was completed, the reaction mixture was cooled to ambient temperature and the precipitate was first passed through the polyester sulfone membrane with a pore size of 0.22 μm and then washed with methanol. The product was next dried in a vacuum oven at 30°C. All the chemicals used in this research were obtained from the German brand Merck Schuchardt.

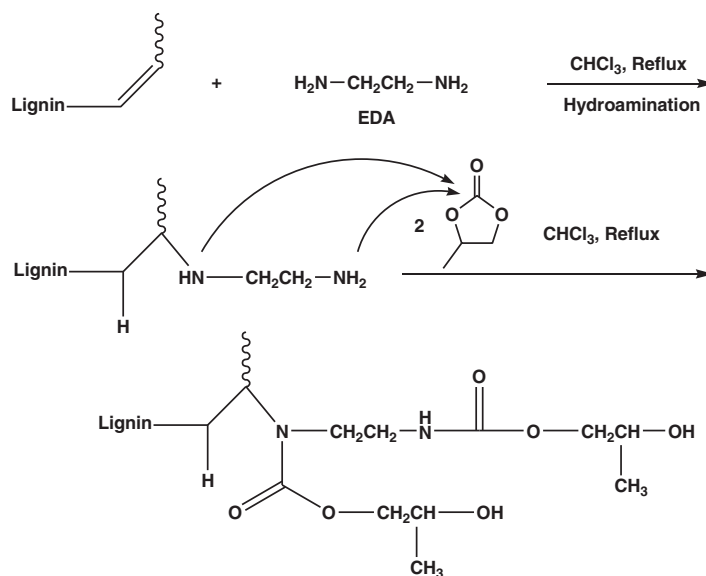


Figure 1: The first step is the reaction of ethylene diamine with unsaturated areas on lignin and the second step is the reaction of propylene carbonate with the amines formed in the first step

2.4 Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared analysis was performed using the Bruker Vertex 80 system, manufactured by Arvin Bonyan Tajhiz according to ASTM D8036-16 to study changes in lignin functional groups [35]. KBr tablet samples were prepared with a concentration of 1% of the weight of lignin extracted from liqueur (L1), amino lignin (L2), and amino lignin of propylene carbonate (L3). To remove moisture from the samples, they were first dried in the open air and then for 6 h at 100°C in the oven. Next, by irradiating electromagnetic waves in the range of 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1} , the researchers recorded the FTIR sample spectrums.

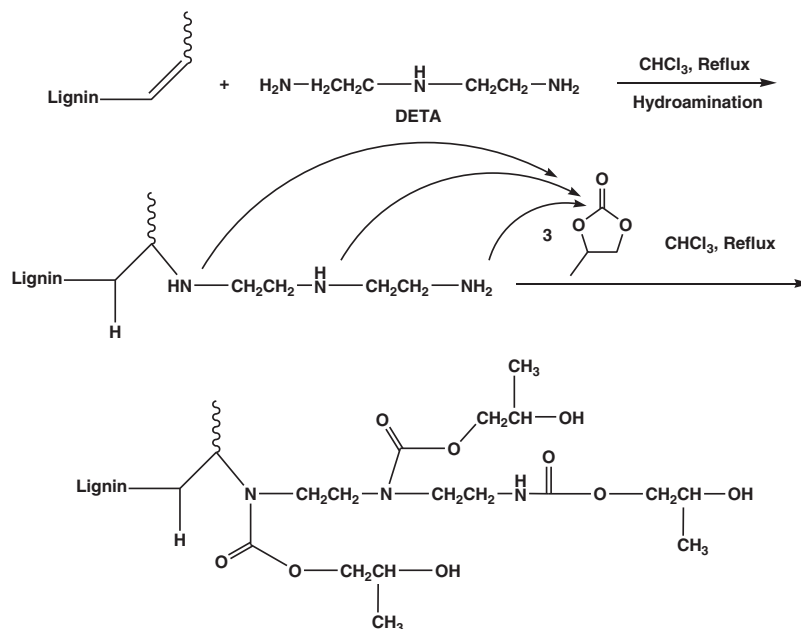


Figure 2: The first step is the reaction of diethylenetriamine with unsaturated areas on lignin and the second step is the reaction of propylene carbonate with the amines formed in the first step

2.5 Gel Permeation Chromatography (GPC)

The gel permeation chromatography test was performed according to ASTM D6579-11 to determine the molecular mass and separate the molecules of the amino carbonate lignin powder sample (L3) [36]. The separation of amino lignin polymers modified with polycarbonate in the organic solvent tetrahydrofuran (THF) was conducted through the stationary phase of polystyrene. Lignin was dissolved in THF and injected into the column. Tetrahydrofuran was used as the mobile phase at a rate of 1 min/mL.

2.6 Measurement of Acid Number

The acid number of lignin was determined according to ASTM D4662-08 [37]. To this aim, the researchers dissolved 2 g of lignin in 50 ml of ethanol solution. The mixture was then titrated with a normal solution of 0.1 N sodium hydroxide. The acid number of the sample was then calculated using the following equation:

$$\text{Acid value} = \frac{(C - B)n \times 5.611}{W} \quad (1)$$

where C represents the titration volume of sodium hydroxide solution at the equivalence point (mL), B denotes the bulk solution volume (mL), n is the normality of sodium hydroxide solution (mL), and W refers to the sample weight (g).

2.7 Hydroxyl Number Test

The hydroxyl number of lignin modified with amine and polycarbonate was determined according to ASTM D4274-05 [34,38]. One gram of modified lignin and 10 ml of sterilization reagent (150 g of anhydridaphthalic, 100 g of pyridine, and 900 g of dioxane) were poured into Erlenmeyer, covered with aluminum foil, and then placed in a 100°C hot water bath for 30 min. After cooling the solution to room

temperature, the researchers added 20 ml of dioxane and 5 ml of distilled water to it. Using a pH meter, the researchers titrated the mixture with a standard solution (sodium hydroxide 1 N). The hydroxyl number of the sample was then calculated using the following equation:

$$\text{Hydroxyle value} = \frac{(a - b)n \times 56.1}{W} + \text{Acid value} \quad (2)$$

where b is the volume of sodium hydroxide solution required for sample titration (mL), a represents the bulk solution volume (mL), n is the normality of sodium hydroxide solution (mL), and W denotes the sample weight (g).

2.8 TGA-DTA Thermal Analysis

TGA-DTA thermal analysis (Thermal Gravimetric Analysis-Differential Thermal Analysis) is one of the widely used methods in material analysis. TGA-DTA thermal analysis measures the changes, due to heat, in the sample and provides the user with a graph. Thermal analysis was performed by Perkin Elmer Pyris Diamond device with a thermal gradient of 5 °C/min.

By interpreting TGA-DTA thermal analysis, one can find out the thermal stability, i.e., reaction content in a chemical substance.

3 Results and Discussion

3.1 FTIR Analysis

Structural changes of lignin, extracted from raw liquor, before and after its reaction with DETA and EDA are shown in Figs 3 and 4. In order to study the resulting FTIR spectra more accurately, the total amine depletion index of lignin was determined using the method of El-Mansouri et al. [39] and according to Eqs. (3) to (5) below.

$$\text{KOH} = \frac{\frac{T_{3401}}{T_{1510}} + \frac{T_{1364}}{T_{1510}} + \frac{T_{1371}}{T_{1510}}}{3} \quad (3)$$

$$\text{KOH}_{\text{ar}} = \frac{T_{1377}}{T_{1510}} \quad (4)$$

$$\text{Amine index} = \frac{\text{KOH}}{\text{KOH}_{\text{ar}}} = \frac{\text{KOH}_{\text{al}}}{\text{KOH}_{\text{ar}}} \quad (5)$$

where KOH shows the total amount of hydroxyl groups, KOH_{ar} indicates the amount of aromatic phenolic hydroxyl groups, KOH_{al} refers to the amount of aliphatic hydroxyl groups, and Amin index is the amination index. The assignment of the different FTIR signals are shown in Table 1 and the calculated results are given in Tables 2 and 3

Fig. 3 shows that in lignin aminated with DETA, the wave intensity at peaks of 3200–3400 cm^{-1} , which are related to the hydroxyl groups of lignin, is reduced, and the wavelength of 1460 cm^{-1} , which belongs to the hydrocarbon groups, has somewhat increased.

Fig. 4 reveals that in lignin aminated with EDA, unlike its modification with DETA, the wave intensity at peaks of 3200–3400 cm^{-1} does not change significantly.

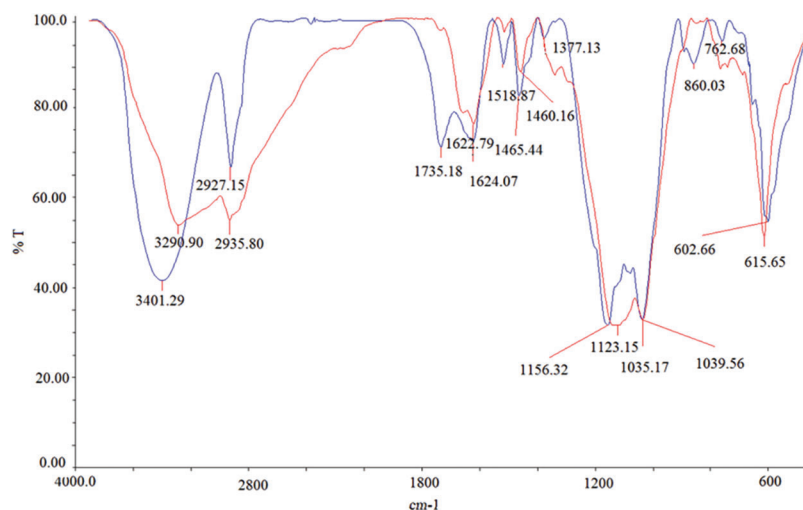


Figure 3: FTIR spectrum of lignin (blue: before amination with DETA and red: after amination with DETA)

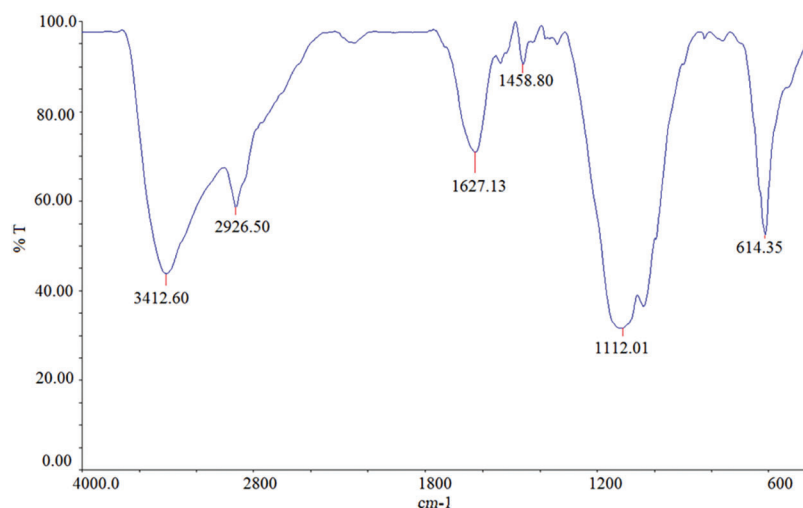


Figure 4: FTIR spectrum of lignin after amination with EDA

The results of the FTIR test of lignin aminated with DETA and EDA indicate that the wave intensity at $1710\text{--}1715\text{ cm}^{-1}$ peaks, relating to the carbonyl and carboxylic groups, and the peaks in the $700\text{--}800\text{ cm}^{-1}$ range, which belong to the aromatic rings and alkene hydrocarbons of methylene groups, are completely eliminated.

The results also show that the peaks in the range of $1035\text{--}1130\text{ cm}^{-1}$, which belong to the groups of hydrocarbons in syringyl and carbon monoxides in secondary alcohols and aliphatic ethers, the wave intensity in the peaks of $1425\text{--}1605\text{ cm}^{-1}$, belonging to the aromatic ring, the peaks in the range of $1330\text{--}1340\text{ cm}^{-1}$, relating to the carbon monoxide and hydroxide groups, and the $1035\text{--}1130\text{ cm}^{-1}$ peaks, which belong to the carbon monoxide group in aliphatic ethers, have been completely removed after the modification of lignin with DETA and EDA.

The wave intensity at $1710\text{--}1715\text{ cm}^{-1}$ peaks in the lignin modified with both amines belonging to the carbonyl and carboxylic groups is reduced and almost eliminated. Reducing the adsorption intensity ratio of the carbonyl group is a measure of crosslink density. Decreased carbonyl group uptake indicates an increase

in adverse reactions [38]. It can be said that with decreasing crosslinking in polyols, their solubility increases [40] In parallel, peaks of 1035–1130, which belong to the carbon monoxide group in aliphatic ethers, decrease. The reduction of ether junctions reduces the molecular weight of lignin, which ultimately improves the reactivity potential of lignin [41].

As can be seen in the spectra, the integrals and peak positions of the alcoholic and phenolic hydroxyl groups in the 3200–3400 cm^{-1} spectra of DETA-modified lignin differ from those of unmodified lignin. These spectra reveal the reaction of DETA amines with lignin. The main drawbacks of this method are related to the amination reaction of lignin, which is often incomplete and in which a small number of hydroxyl groups remain unaminated [39]. Although this behavior has been observed by other researchers, it has been ignored [39].

As is shown in Table 1 [42], the total number of hydroxyl groups of lignin decreases after reaction with DETA. The amination index is 1.75, while the total number of hydroxyl groups after modification with EDA remains unchanged; El Mansouri et al. [43] proved that increasing the lignin modification time to more than 10 h slightly reduces the number of aromatic hydroxyl groups, possibly due to secondary reactions of lignin condensation.

Table 1: FTIR table of lignin

Bond type	Adsorption site cm^{-1}
OH Alcoholic and phenolic	3100–3500
C–H methoxyl group and methyl and methylene groups of side chains	2935–3848
C=O in position β as well as COOH	1710–1715
C=O in δ and α	1655
C–H methylene group	1461
Aromatic ring	1425–1605
Vibration of OH-syringyl phenolic and C-O	1330–1340
Vibration of OH syringyl guaiacyl and C-O	1220–1272
C–H in guaiacyl	1150
C–H in syringyl	1125
C–O in secondary alcohols and aliphatic ethers	1035–1130
C–H attached to ring	780–945

Table 2: Relative percentage of functional groups and amination index of lignin

Type of lignin	Total amount of aromatic hydroxyl	Total amount of hydroxyl	Lignin amination index
DETA lignin	0.9	1.58	1.75
EDA lignin	–	2.26	–

Table 3: Relative percentage of functional groups and amino lignin carbonation index

Type of lignin	Aromatic hydroxyl	Total amount of hydroxyl	Amino lignin carbonation index
DETA lignin	–	2.1	0
EDA lignin	–	2.26	0

The amination of lignin with DETA significantly reduces the amine content of aliphatic hydroxyl groups, which indicates that lignin has been aminated. One of the increasing applications of lignin is its use in the structure of synthetic polymers and in the manufacturing of various composites; if lignin is used as part of polyols, the more amino groups it has, the better and stronger the reaction will be with the formation of C–N bonds. The reaction of amino lignin with polycarbonate, while producing hydroxyl groups, also leads to the production of amide bonds, which can play an important role in improving polyol properties.

Furthermore, structural changes of lignin aminated with DETA before and after modification with propylene carbonate are displayed in Fig. 5. As can be seen, the spectral patterns of both samples before and after modification are very similar to propylene carbonate. Fig. 5, in turn, shows that the structure of DETA-aminated lignin remains almost unchanged after modification with propylene carbonate. However, the intensity of the 1330–1340 cm^{-1} peak belonging to the hydroxide and hydrocarbon groups in aminated lignin reacted with propylene carbonate increases slightly.

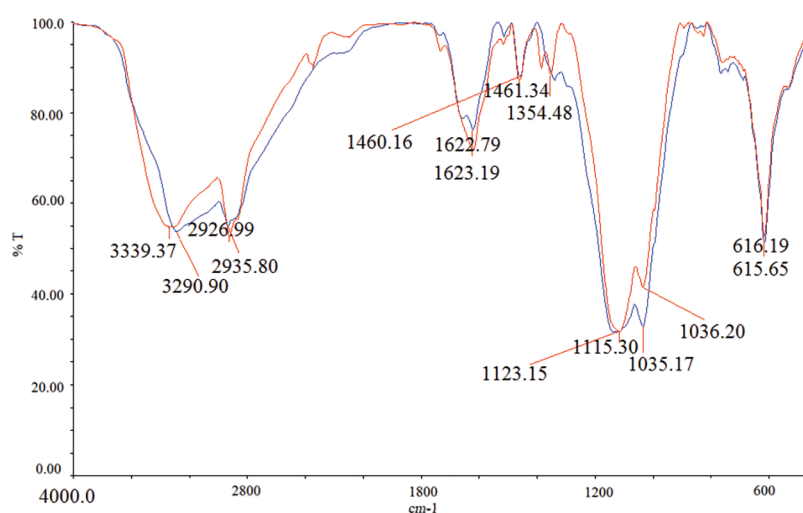


Figure 5: FTIR spectrum of DETA-aminated lignin with propylene carbonate (blue: before modification with propylene carbon and red: after modification with propylene carbon)

Fig. 6 indicates the structure of EDA-aminated lignin after the reaction with propylene. According to this figure, the intensity of the 1458 cm^{-1} wave in the amino lignin modified with propylene carbonate, corresponds to the C–H groups of the methylene group.

As stated above, the bonding of propylene carbonate with does confirm the presence of these bonds and the CO_2 resulting from this reaction. Peak 1100 also indicates the amine in lignin causes the formation of urethane bonds. The presence of the 1650–1750 cm^{-1} peaks does indicate the presence of C–O groups belonging to urethane bonds. Moreover, the peak 3200 cm^{-1} shows NH tensile vibrations, and the 1350 cm^{-1} peak indicates NH flexural vibrations in lignin modified with both amines and PC.

3.2 GPC Analysis

The large hydrodynamic volume of the lignin molecule can be determined using gel permeation chromatography (GPC). Next, using the calibrated column, one can compute the number average molecular weight (M_n) and the weight average molecular weight (M_w). As a result, the molecular weight distribution can also be calculated. When working with GPC, it is very important to prevent the accumulation of lignin molecules in the solvent, which constitutes a serious challenge [44].

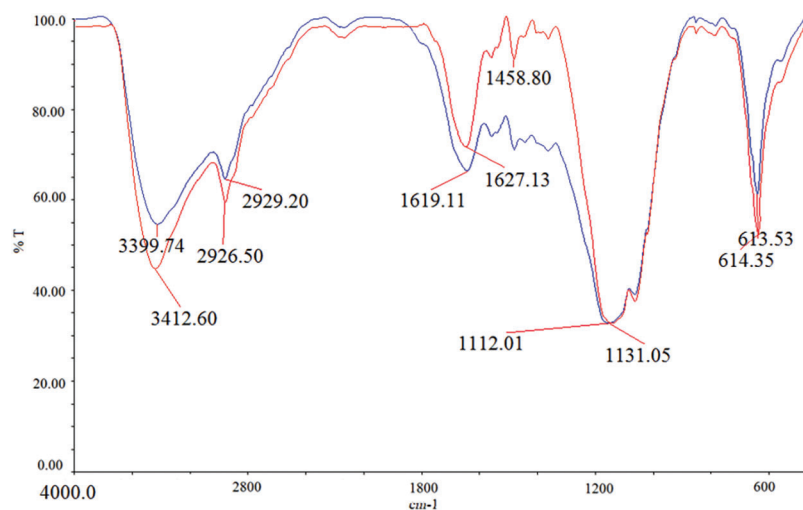


Figure 6: FTIR spectrum of EDA-aminated lignin with propylene carbonate (red: before modification with propylene carbonate and blue: after modification with propylene carbonate)

The results of GPC analysis of lignin modified with DETA and propylene carbonate are shown in [Table 4](#) and [Figs. 7 and 8](#). Also, [Table 5](#) shows the molecular weights of conifer and broadleaf lignin obtained from the GPC analysis [45].

Table 4: Results of GPC test of lignin modified with DETA and propylene carbonate

Components	Mn (g/mol)	Mw (g/mol)	MP (g/mol)	Mz (g/mol)	Mz + 1 (g/mol)	Polydispersity	Mz/Mw	Mz + 1/ Mw	Mw/ Mn
Modified lignin	15765	16652	17230	17532	18398	1.056257	1.052861	1.104828	1.05

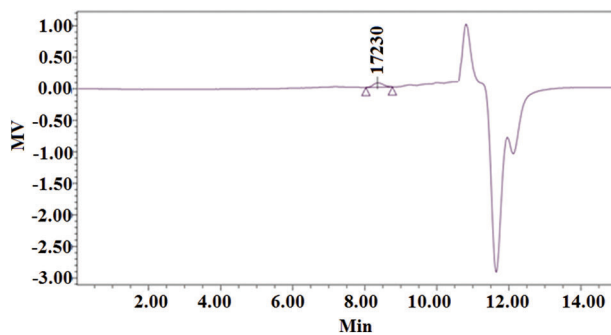


Figure 7: GPC test diffusion spectrum of lignin modified with DETA and propylene carbonate

The number average molecular weight of amino lignin modified with propylene carbonate was found to be 16652 Daltons, while the weight average molecular weight was 15765 Daltons, and the polydispersity index of modified lignin was calculated to be 1.05 (see [Table 5](#)) [43,44,46].

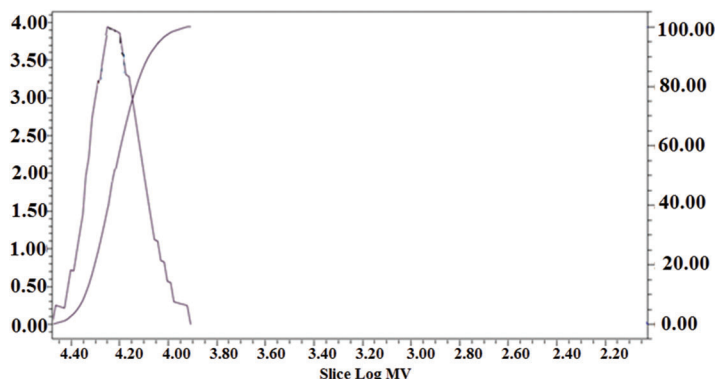


Figure 8: Normal distribution of GPC test diffusion spectrum of lignin modified with DETA and propylene carbonate

Table 5: Molecular weight of conifer and broadleaf lignin, obtained from GPC test

Kind	Mw (g/mol)	Mn (g/mol)	Mw/Mn
Conifer	398000	115000	3.46
Broadleaf	33000	15000	2.2
Paper mill	1851	954	1.94

To obtain the molar value of hydroxyl groups per gram of modified lignin, it is necessary to calculate the weight of the groups (M_{AP}) added to lignin, namely DETA and propylene carbonate [21].

$$\frac{n_{OH}}{m_L} (\text{mol/g}) = \frac{1}{\frac{1}{\frac{n'_{OH}}{m_{APL}}} - (M_{AP} - 1)} \quad (6)$$

In Eq. (6), the molecular weight of propylene carbonate amine groups is added, which equals 112.17 + 102.09 g/mol. The number 1 in ($M_{AP}-1$) indicates the proton removed from OH lignin during the amination reaction.

M_{PAL} is the weight of propylene-carbonated amino lignin, and N'_{OH}/m_{AP} is the molar of hydroxyl groups per weight of lignin amine propylene carbonate. By rearranging Eq. (1), one arrives at Eq. (2). In this case, the molar of hydroxyl groups is calculated per gram of propylene-carbonated amino lignin:

$$\frac{n'_{OH}}{m_L} (\text{mol/g}) = \frac{\frac{n_{OH}}{m_L}}{1 + \frac{n_{OH}}{m_L} - (M_{AP} - 1)} \quad (7)$$

Using N'_{OH}/m_{AP} , as well as Eqs. (6) and (7), the researchers calculated the number of hydroxyl groups of lignin per 1 mol of chain and the mean numerical molecular weight of lignin:

$$\frac{n_{OH}}{n_L} (\text{mol/mol}) = \frac{n_{OH}}{m_L} (M_{n.AP}) = \frac{n'_{OH}}{m_{AP}} (M_{n.AP}) \quad (8)$$

$$m_{n.L} = \frac{\frac{n'_{OH}}{m_{APL}} \times (M_{n.APL})}{\frac{n_{OH}}{m_L}} \quad (9)$$

In Eqs. (6) and (7), $M_{n.AP}$ represents the molecular weight of propylene-carbonated amino lignin, n_{OH}/n_L is the molar of lignin hydroxyl groups per 1 mol of lignin chains, and $M_{n.L}$ is the mean numerical molecular weight of lignin. Table 6 shows the weight average molecular weights, the number average molecular weights, and molecular weight distributions of propylene-carbonated amino lignin, together with the results of calculations for the numerical molecular weight of lignin and moles of lignin hydroxyl groups per mole of lignin chains.

Table 6: Number average and weight average molecular weights of modified lignin, molecular weight of lignin, and molars of hydroxyl groups per 1 mol of lignin chains

Lignin				Lignin modified with DETA and propylene carbonate		
PDI	n_{OH}/n_L	Mw (g/mol)	Mn (g/mol)	PDI	Mw (g/mol)	Mn (g/mol)
1.18	9.46	16814.16	14149.66	1.056	16652	15765

Rajendran et al. [47] mixed a combination of adipic acid with different glycols four times for polyol synthesis and used zinc acetylacetonate as a catalyst. The reaction was carried out for 3 h at 220 mmHg until the acid number dropped below 1. The obtained polyol had an acid number of 0.2, a hydroxyl number of 56, and a mean molecular mass of 2000.

Murayama et al. [48] synthesized a type of polyester polyol using adipic acid and 2, 4-diethyl-1 and 5-pentane diol in an inert nitrogen atmosphere. The obtained polyester polyol had an acid number of 0.2, a hydroxyl number of 56, and a mean molecular mass of 2000.

Allauddin et al. [49] synthesized a polyol with a hydroxyl number of 240 using the reaction of adipic acid and isophthalic-anhydride. In this reaction, a 2-liter 4-port reactor, a mechanical stirrer, and a nitrogen source were used. The reaction continued for several hours until the acid number dropped below 5. The obtained polyol molecular mass was 2687.

To prepare a polyurethane, Cook [50] synthesized a linear polyol using dimethylglutarate and diethylene glycol. The reaction was performed under nitrogen-free atmosphere, and the reaction temperature rose from 170°C to 215°C. In this reaction, the catalyst was tin-2-ethylhexanoate. The obtained polyol was black and viscous and had an acid number of 0.25, a hydroxyl number of 53.9, and a molecular mass of 2072.

In the present work, the results of gel permeation chromatography of modified lignin and the mean molecular weight of lignin extracted from liquor showed that lignin was converted into a lower molecular weight after modification. Comparison of the results with previous research also indicated that the basic lignin polyol prepared in this work had a lower molecular weight than the existing synthetic and natural polyols, which can be due to the mechanical degradation of lignin during its preparation and modification. Due to alkaline hydrolysis and rupture of aryl ether bonds during de-lignification, the lignin in the black liquor resulting from the pulping process had a lower molecular weight and a higher number

of active functional groups, such as phenolic and aliphatic hydroxyl groups, in comparison with the lignocellulosic raw material. Therefore, they had acquired a greater potential for reaction [51].

3.3 Hydroxyl Number Analysis

The first characteristic of polyols is the presence of terminal hydroxyl groups for the reaction and production of various products. The hydroxyl number is a standard measure for quality control of polyols. This number is also used in determining the polymer formulation of polyurethane systems [52].

In this work, the hydroxyl number was determined through the modification of lignin with DETA and propylene carbonate and through the modification of lignin with EDA and propylene carbonate. In the former case, the hydroxyl number was calculated to be 848 (mgKOH/g), and in the latter case, this number was 2220 (mgKOH/g), which showed an increasing trend.

Mahmood et al. [53] research project involved producing polyols based on lignin kraft (KL) with a relatively high hydroxyl number. In this study, they prepared polyols with a hydroxyl number of 352 (mgKOH/g) and a molecular weight of 3310 (g/mol). These polyols were derived from lignin kraft by direct hydrolysis using NaOH as a catalyst and without any organic solvents.

In another study, Perez-Arce et al. [54] prepared and analyzed a family of lignin-based polyols using a new synthetic approach. This approach involved the polymerization reaction of the cationic ring opening of oxidants in the presence of tetrahydrofuran, as a solvent and a monomer, and organosol lignin. The hydroxyl number ranged from 53 to 253 (mgKOH/g), and the mean molecular weight ranged from 2730 to 30258 g/mol.

Li et al. [55] used alkaline lignin as a by-product manufactured during bioremediation in the production of polyurethane foams. The results indicated that the produced polyester had better thermal stability and higher compressive strength than petroleum-based polyurethanes. The hydroxyl number of these polyols was 420 (mgKOH/g).

Cross et al. [56] prepared polyester polyol using 1, 2-propylene glycol, trimethylol propane, phthalic anhydride. The resulting product had an acid number of about 5 and a hydroxyl number of 78.

Vogt et al. [57] using adipic acid and diethylene glycol, synthesized polyols that were linear. In this reaction, taking 14 h, a tetraalkyl titanate-tin-alkanate catalyst was used. The resulting polyol had an acid number of 0.6 and a hydroxyl number of 46.

As can be seen, the lignin-based polyols prepared in this process had a much higher hydroxyl number than the petroleum-based polyols, as well as other similar lignin-based polyols, the same as in Tables 7 to 8 [58,59]. Therefore, it can be said that the lignin-based polyols modified with DETA and polypropylene carbonate has a higher reactivity potential than other polyols used for the same purpose (Table 9).

Table 7: Hydroxyl number of conifer leaf and broadleaf lignin

Functional groups	Conifer lignin/100 units	Broadleaf lignin/100 units
Phenolic hydroxyl	20–30	10–20
Aliphatic hydroxyl	115–120	110–115
Methoxy	90–95	140–160
Carbonyl	20	15

Table 8: Test results of hydroxyl number for lignin aminated with amine and propylene carbonate

Functional groups	Lignin aminated with DETA and propylene carbonate/100 units (mgKOH/g)
Total hydroxyl number of phenolic, methoxy, aliphatic and carbonyl DETA	848
Total hydroxyl number of phenolic, methoxy, aliphatic and carbonyl EDA	2220

Table 9: Hydroxyl number data for acetylation method

Test material	Average hydroxyl number
PTME glycol	111
Glycerin based on protected polyol	54.5
Glycerin/sucrose (based on propoxylated polyol)	492.6

3.4 Thermogravimetric Heat Analysis (TGA)

The amount of weight loss of the samples is displayed in the following figures and Table 10. As can be seen, the graphs of crude lignin and lignin modified with amine and propylene carbonate are almost identical in both forms. Moreover, the thermal degradation of crude lignin and modified lignin takes place in one step, which can be divided into three regions. In the first and second regions, the degradation and weight loss in crude lignin starts at about 100°C and then increases. In turn, the third region, which starts at 600°C, involves the complete degradation of unmodified lignin to ash.

Table 10: Temperature drop steps obtained from the diagram

	Primary degradation temperature (°C) T _i	Initial weight loss	Final degradation temperature (°C) T _F	Remaining coal W _{550°C}
Lignin	100–250	24%	623	9%
Amino lignin (TEDA)	0–150	23%	600	12%
Amino lignin (EDA)	0–150	16%	580	5%

The first stage of weight loss of lignin is attributed to the evaporation of water and other volatile compounds, and the second stage of thermal decomposition is attributed to the disintegration of syringyl, guaiacyl, and p-hydroxyphenyl polymer units [60]. It should also be noted that the degradation and weight loss in modified lignin starts from the very beginning. However, its rate decreases slightly, compared to that in crude lignin. As stated previously, aminated lignin is completely reduced to ash at 600°C.

When lignin is pure or carbohydrate-free, losses occur due to water evaporation, and light gases because of the separation of β -O-4 bonds in the lignin structure and CO₂ release because of the disintegration of weak ester bonds in the aminated propylene-carbonate lignin [60].

The abundance of these bonds in lignin determines its thermal stability [61]. In fact, the higher the ratio of β -O-4 bonds, the greater its stability. C-C bonds are also degraded at 200°C to 400°C in modified lignin,

and the propylene glycol structures are removed. Also, urethane bonds formed through the combination of PC and amine with lignin are destroyed at a temperature of 400°C–500°C.

3.5 DTG Lignin Mass Loss Derivative

The derivative curve of lignin mass loss as a function of temperature, obtained at a heating rate of 15 °C/min, is displayed on the TGA curve in the figure which is shown in Figs. 9 and 10.

In the temperature range studied, the DTG diagram shows several peaks. The first case, at very low temperatures, is related to dehydration. The peak is relatively sharp at a maximum of 340°C. The peak is surrounded on both sides by shoulders.

Most of the research works reported in the literature generally show two peaks in the DTG [62–64]. To the researcher's best knowledge, only Watkins et al. [65] reported the presence of combs at 450°C, and Manara et al. [66]. They reported the presence of peaks at higher temperatures in the form of a broad band. Kim et al. [62] stated that these peaks are formed due to dehydration. In these peaks, β -O-4 bond breakage, C-C bond breakage, β - β bond breakage and polymerization reactions take place. The clarity and intensity of the peak related to the decomposition of β -O-4 bonds depend on the ratio of these bonds in lignin [21].

In modified lignin, degradation started at lower temperatures and lignin has completely lost its weight at 600 degrees.

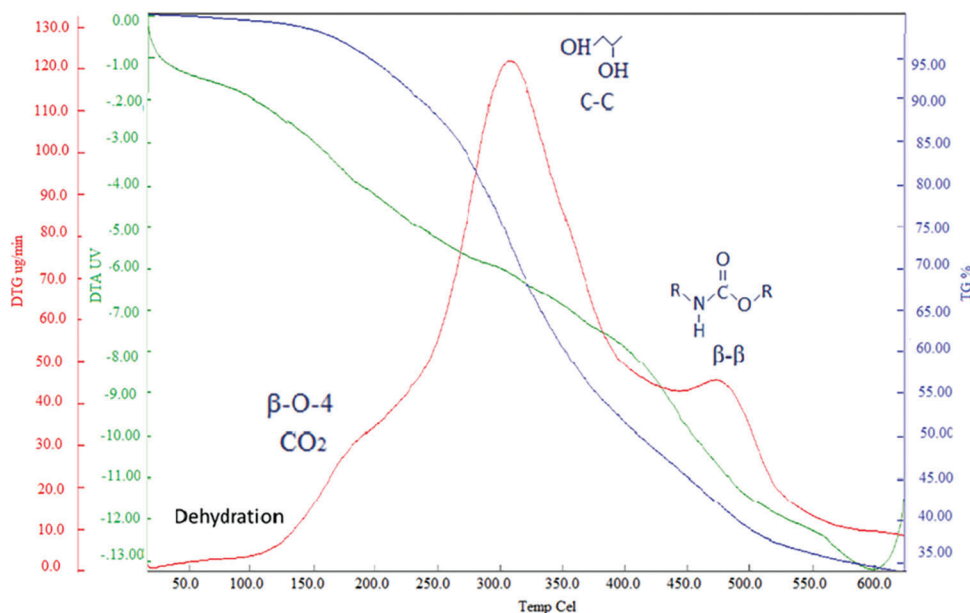


Figure 9: Thermogravimetric spectrometry test: blue (lignin), green (lignin modified with DETA and propylene carbonate)

They also showed that lignin without β -O-4 completely decomposed at 200°C–300°C. However, lignin with a lower frequency of β -O-4 bonds compared to C-C bonds is more resistant. In the case of lignin, where the ratio of β -O-4 bonds is equal to C-C bonds, peaks occur with relatively equal intensities.

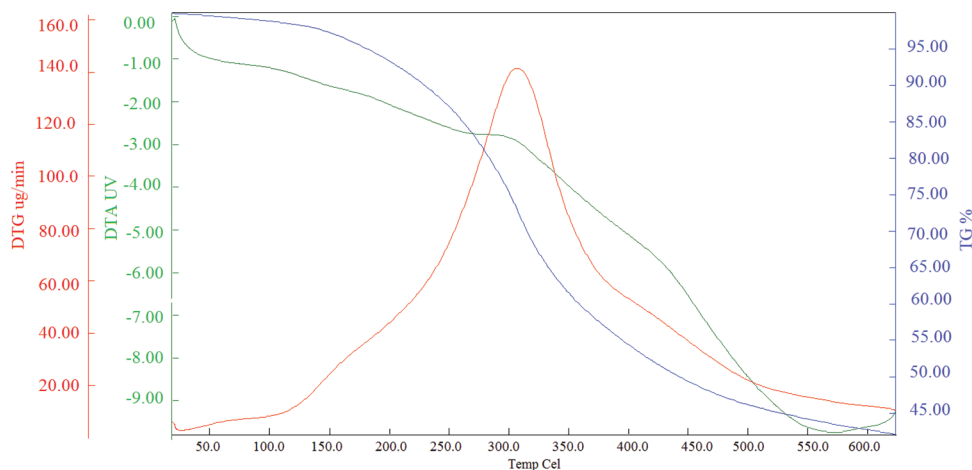


Figure 10: Thermogravimetric spectrometry test: blue (lignin), green (lignin modified with EDA and propylene carbonate)

In modified lignin, however, degradation begins at lower temperatures, and lignin completely loses its weight at 600°C. With the addition of amine and propylene carbonate, a slight decrease in thermal stability is observed for modified lignin samples, compared to crude lignin samples. These results can be attributed to the low molecular weight of modified lignin. The presence of oligomers in the modified lignin samples and the absence of significant intermolecular interactions in this case cause the samples to degrade at lower temperatures. The results obtained from GPC also confirm the reduction of molecular weight of the copolymers in the modified lignin samples, compared to the pure polymer.

4 Conclusions

1. The results of the FTIR analysis showed that peak 1100 indicates the presence of C-O bond related to urethane bonds in modified lignin.
2. The results of GPC of lignin modified showed that lignin was converted to a lower molecular weight after modification. This could be due to the mechanical degradation of lignin during its preparation and modification.
3. The lignin-based polyol prepared in this process has a much higher hydroxyl number than oil-based polyols. Therefore, it can be said that it has a high reactivity potential.
4. Urethane bonds formed by the combination of PC and amine with lignin can be seen in the results of GPC at 400°C–500°C.

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