IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

Development Of Resin From Liquefied Wood By Solvolysis And Its Applications

[1]Neelam Patil Radhika, [2*]Shobha G, [3]Malini S, [4]Shwetha K C, [5]Shylaja K R, [6]Madhuri Bhat S, [7]Rakshitha H S, [8]Varsha Prakash, [9]Jai Karthik J
[1]Department of Chemistry, K. S. Institute of Technology, Bangalore - 560109, India
[2*]Department of Applied Science and Humanities, K. S. Institute of Technology, Bangalore, India
[3]Department of Chemistry, B.M.S College of Engineering, Bangalore -560019, India
[4]Department of Chemistry, K. S. Institute of Technology, Bangalore - 560109, India
[5]Department of Chemistry, K. S. Institute of Technology, Bangalore - 560109, India
[6]Department of Biotechnology, Sapthagiri College of Engineering, Bangalore - 560057, India
[7]Department of Biotechnology, Sapthagiri College of Engineering, Bangalore - 560057, India
[8]Department of Biotechnology, Sapthagiri College of Engineering, Bangalore - 560057, India
[9]Department of Biotechnology, Sapthagiri College of Engineering, Bangalore - 560057, India

Abstract: In this study, polyethylene glycol (PEG) in various ratios was used to solvolyze renewable biomass, yielding polyol. The presence of functional groups including -CO, C=O, esters, and ethers was revealed when the liquefied wood was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The resultant polyol was employed to make resin and then polymerized with different proportions of methylene diphenyl diisocyanate (MDI) to create adhesives, wood composites, and polyurethane foam. The FTIR analysis confirmed the successful incorporation of functional groups essential for polyurethane formation. An analysis of the mechanical characteristics of the generated polyurethane foams showed that the NCO/OH ratio has a major impact on the foam's mechanical strength and thermal stability. Higher NCO/OH ratios led to higher glass transition temperature and degradation temperature, which indicated increased rigidity in the polyurethane films. This study advances the evolution of bio-based polyurethane materials made from renewable resources, providing a sustainable substitute for petroleum-based products.

Key words: FTIR Liquefaction, Resin, Solvolysis

I. INTRODUCTION

The development of bio-based substitutes made from renewable resources has attracted a lot of attention due to the growing environmental issues around petrochemical-based products [1]. Wood is a vital natural resource that is essential to sustainable development initiatives because of its renewable nature and capacity to retain CO2 [2]. Wood is a viable feedstock to produce sustainable materials like resins because it is renewable and easily available biomass. wood is made up of four chemical components: cellulose, lignin, hemicellulose, and extractives [3]. One approach of using wood components is to chemically derivative the wood components and thus increase their solubility in selected solvents. The solubilized macromolecules are then used in preparing useful polymeric materials.

A promising technique for producing bio-based polyurethane adhesives for wood composites is wood liquefaction with polyethylene glycol (PEG) and methylene diphenyl diisocyanate (MDI). Through the process of solvolysis, lignocellulosic biomass is transformed into liquid polyols, which can subsequently react with isocyanates such as MDI to produce polyurethane networks. This strategy has been shown to be beneficial in recent investigations. For instance, bio-polyols with high biomass conversion and hydroxyl numbers ranging from 238 to 815 mg KOH/g were produced by liquefying forestry wastes, such as sawdust, in solvents like glycerol and PEG at temperatures of 120, 150, and 170 °C. Polyurethane materials with a bio-polyol content of more than 80 %weight were effectively synthesized using these bio-polyols. Depending on the reaction conditions, the final materials showed a modulus of elasticity ranging from 62 to 839 MPa [4].

In this study, polyethylene glycol (PEG) in various ratios was used to solvolyze renewable biomass, yielding polyol. The presence of functional groups including -CO, C=O, esters, and ethers was revealed when the liquefied wood was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The resultant polyol was employed to make resin and then polymerized with different proportions of methylene diphenyl diisocyanate (MDI) to create adhesives, wood composites, and polyurethane foam. The FTIR analysis confirmed the successful incorporation of functional groups essential for polyurethane formation. An analysis of the mechanical characteristics of the generated polyurethane foams showed that the NCO/OH ratio has a major impact on the foam’s mechanical strength and thermal stability. Higher NCO/OH ratios led to higher glass transition temperature and degradation temperature, which indicated increased rigidity in the polyurethane films. This study advances the evolution of bio-based polyurethane materials made from renewable resources, providing a sustainable substitute for petroleum-based products.

Another study examined by varying the ratios of NCO/OH on bio-based polyurethane films derived from liquefied Acacia mangium wood. The findings demonstrated that as NCO/OH ratios increased the degradation temperature from 275°C to 286°C and the glass transition temperature increased from 50°C to 84°C. A higher crosslinking density, which resulted in more rigid and less soluble films, was credited with this improvement [5,6,7,8,9].

These studies shows that it is possible to combine liquefied wood with PEG and MDI to produce effective polyurethane foams and adhesives, offering eco-friendly alternatives for wood composite applications.
Lantana camara is an important non edible lignocellulosic biomass, which grows widely throughout India Lantana is very easy to grow and will adapt to most soil types.

The leaves and stem were separated from the collected raw material (Lantana camara) and the stem was subjected to chipping, pulverizing, and sieving was used for liquification.

II. Materials and Methods

Collection of Raw Material:

***Collection of Lantana camara*:**
The lantana camara plants were collected and sun-dried for three days and stored at room temperature for further use.

***Preparation of Wood Flour*:**
The dried Lantana camara stems were separated from the leaves and subjected to chipping using a mechanical chipper, producing wood chips of various sizes. With particle sizes ranging from fine powder to grains roughly the size of rice, these chips were then pulverized to fine wood flour. In accordance with British Standards Institution (BSI) guidelines, the wood flour was sieved using strainers with mesh sizes of 52, 60, 80, 100, and 150. To stop moisture absorption, the sieved wood flour was oven-dried at 105°C and then cooled in desiccators over calcium chloride.

Liquefaction of Wood

Liquefaction of wood refers to the process in which the solid wood material is converted into a liquid phase through chemical reactions, often facilitated by heat and a solvent. In this study, wood was liquefied using polyethylene glycol solvent.

A 250 mL flask with a reflux condenser was used for the liquefaction procedure, and it was set up in a constant temperature oil bath over a magnetic stirrer. 30 mL of polyethylene glycol (PEG), ten grams of dried Lantana camara wood meal, and three percent sulfuric acid (H_2SO_4) were mixed. After 30 minutes of stirring-free heating to 140°C, the mixture was vigorously stirred for 90 minutes. Two hours was kept as the overall liquefaction time. The resulting product was diluted with excess methanol to obtain a highly viscous liquefied wood solution. The residue was thoroughly washed with methanol to remove any un-reacted PEG and was filtered. The Filtration is carried out using Whattman filter paper and is kept overnight for completion of filtration. The product after filtration is subjected to distillation to recover methanol and to obtain pure liquefied product. The residue that is left after filtration is subjected to oven drying at 105ºC for 24hrs and the liquefied product obtained can be further utilized for various applications. The dried wood meal sieved from mesh sizes 150, 80 and 52 were used and liquefaction was done at the ratios 1:3 and 1:4 for all the samples using the same above procedure [9]. The dried residual was weighed and liquefaction efficiency (LE%) was calculated as:

$$LE = 100(w_1-w_2)/w_1$$

Where, w_1 is the wood meal's starting weight and w_2 is the residue's weight upon liquefaction.
The full factorial experimental analysis was employed to understand the interaction of temperature, liquid ratio, and catalyst content on liquefaction efficiency.

III. Characterization of Liquefied Wood

***Acid Value Determination*:** Titration was used to determine the acid number, which is the milligrams of potassium hydroxide (KOH) needed to neutralize one gram of the sample. To find the endpoint, a pH meter was used to titrate a mixture of 0.03 g of liquefied wood sample and 20 mL of isopropanol–water solution (4:1 v/v) with 1 mol/L KOH to pH 8.3. The acid value was computed as follows:

$$Acid\ value\ (mg\ KOH/g) = \frac{56.1\ \times\ V \times N}{W}$$

Where, W is the sample weight (g), N is the KOH solution's normality, and V is the volume of KOH solution consumed at the neutralization point (mL).

***Fourier Transform Infrared Spectroscopy (FTIR)*:**
FTIR spectroscopy was used to examine oven-dried residues to determine their chemical structures and functional groups. Using a Tensor series FTIR spectrometer and the KBr pellet method, spectra were acquired at a spectral resolution of 4 cm^{-1}.

Preparation of Polyurethane (PU) Foams

The pH of liquefied wood sample obtained was adjusted by adding 50 wt% of sodium hydroxide aqueous solution. 40grams of liquefied wood and 40grams of MDI (4,4-Methylene diphenyl diisocyanate) were added in the ratio of 1:1 (liquefied wood: MDI). After 10 to 15 seconds of constant stirring, the mixture was put into a mould and let to rise at room temperature. After being taken out of the mould, the resulting foam was allowed to dry for two days at room temperature. To maximize the qualities of the foam, this process was repeated using various ratios of liquefied wood to MDI.

Preparation of Adhesives

40grams of liquefied wood sample was mixed with 40grams of MDI that is in a ratio 1:1. This mixture was subjected to continuous stirring for 10-15seconds. The obtained product was spread on a small board of wood and another board of same size and thickness was manually pressed on it. After that, it was let to cure for two days at room temperature.

Preparation of Wood Composites

40grams of liquefied wood sample was mixed with equal amount of powdered wood (wood flour) and MDI. After ten seconds of constant stirring, the fluid was placed into a mould. After being taken out of the mould, the composite was allowed to cure for two days at room temperature.

IV. Results:

***Preparation of Wood Flour*:**
The plant was dried and brought to fine powder using standard biomass preparation techniques, ensuring uniformity and efficiency in subsequent liquefaction processes. In a study by Yue et al., waste pine wood underwent a similar preparation process, involving chipping, pulverizing, and sieving to achieve desired particle sizes for liquefaction. This standardization is crucial, as particle size influences the efficiency of the liquefaction process (Fig 1).

Pulverizer Wood chips Wood flour

Figure 1 – Preparation of wood flour

Liquefaction of Wood

The liquid products were subsequently extracted with polyethylene glycol by solvolysis, result in formation of thick blackish –brown colour liquid. The obtained liquid was subjected to filtration and distillation after treating with excess of methanol to recover methanol. At the end of distillation process pure liquefied wood was obtained Figure 2.

Depending on the conditions of the reaction, liquefaction efficiency ranged from 40% to 86.4%. Because the solvent and wood interacted better and the process had greater surface area, efficiency rise with higher liquid ratios and smaller particle sizes.

Mahmood et al. used a water-ethanol mixture and a hydrolytic liquefaction method to liquefy hydrolysis lignin at 250°C for one hour. The efficiency and characteristics of the liquefied product are strongly influenced by the solvent selection and reaction circumstances.

Yue et al. also found that waste pine wood was effectively liquefied at an ideal liquefaction temperature of 160°C, highlighting the significance of reaction parameter optimization for high efficiency.

Calculation Efficiency of Liquefaction

Liquefaction efficiency is calculated by using the below Formula

$$LE = 100\,(w_1 - w_2) / w_1$$

Where, w_1=weight of wood meal

w_2=weight of residue

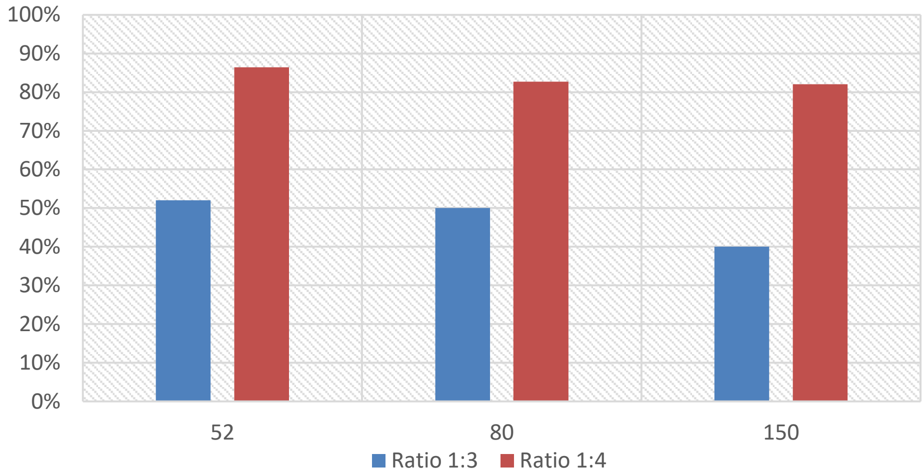
Liquefaction efficiency was found between 40% to 86.4% depending upon reaction conditions. When wood meal is reacted with PEG (polyethylene glycol) in the presence of H2SO4, glycol derivaties of lignin are produced due to cleavage of lignin carbohydrate bonds and ether linkages in the lignin side chains. This results in dissolution of wood into glycol. At a lower liquid ratio, initially only a part of wood wetting by solution takes place. As the reaction proceeds breakdown of lignin is initiated by liquefaction. As the liquid ratio increases efficiency increases because there is more interaction between the solvent and wood. As the particle size increases there is increase in liquefaction because there is more surface area for the process to occur. Percentage liquefaction efficiency is shown in Figure 3.

Dried wood flour *Wood flour + PEG (1:3 and 3% H_2SO_4* *Conventional glass flask*

Filtered *Filtration* *Residue*

Distillation Pure liquefied wood

Figure 2: The Liquefaction of wood process



Particle size [mesh number]

Figure 3: Liquefaction Efficiencies of Different Samples

Characterization of Liquefied Wood

Acid Value

As particle size increased, the liquefied wood's acid value decreased, ranging from 14.49 to 18.23 mg KOH/g. This implies that more thorough liquefaction is made possible by smaller particles since they offer a greater surface area for acid contact. Table 1 and Fig 4.

According to Mahmood et al., the liquefied hydrolysis lignin's total hydroxyl number was roughly 442 mg KOH/g, indicating a high availability of reactive sites for subsequent polymerization procedures.

Sample	Acid value
150 (3:1)	18.23
80 (3:1)	16.83
52 (3:1)	15.425
150 (4:1)	17.29
80 (4:1)	16.36
52(4:1)	14.49

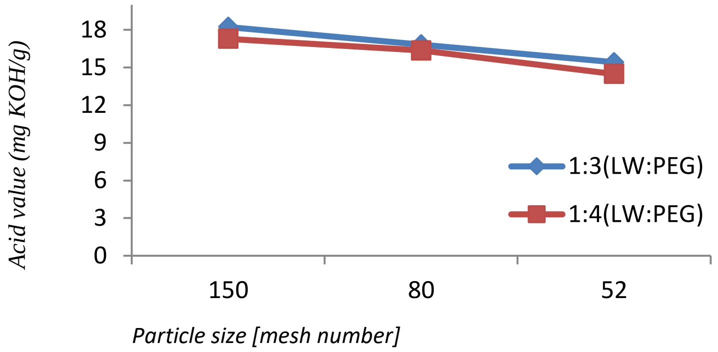


Figure 4: Acid Values of Liquefied Wood Sample

Fourier Transform Infrared Spectroscopy (FTIR)

The liquefied wood samples FTIR spectra showed a variety of functional groups. Around 3328–3500 cm⁻¹, a wide peak represents the O–H groups of lignin or carbohydrates. The methyl and methylene groups are indicated by the peak that lies between 2800 and 3200 cm⁻¹. Carbonyl (C=O) stretches in unconjugated ketone, ester, or carboxylic groups in carbohydrates are the source of absorption bands ranging from 1710 to 1740 cm⁻¹. The C=C connections are responsible for the peak at 1644.67 cm⁻¹. These peaks' varying intensities show how the samples' bond topologies differ from one another.

Similar functional groups were found by Yue et al. using FTIR analysis on liquefied pine wood, confirming that complex lignocellulosic structures break down into simpler compounds during liquefaction. Fig 5.

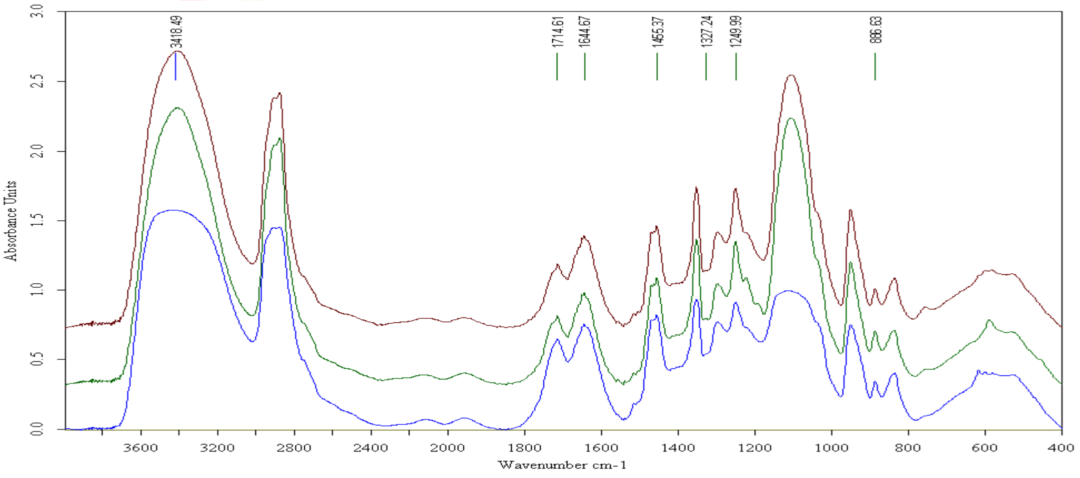


Figure 5: FTIR Absorption spectrum for liquefied wood obtained from various particle sizes.

Figure 6: PU foams

Figure 7: Adhesive used to bind wooden blocks

Figure 8: Wood composite

Preparation of Resins

Preparation of Polyurethane (PU) Foams

The PU foams are obtained by the reaction of MDI (4,4-Methylene diphenyl diisocyanate) with liquefied wood. The foams were prepared at two different ratios of 1:1(LW: MDI) and 0.8:1(LW: MDI). The Foam obtained from the ratio 0.8:1(LW: MDI) was found to be more efficient as the foam formation in this sample was better compared to the 1:1 ratio (LW: MDI). This variation was done to optimize the product and to obtain the product with maximum efficiency (Fig 6).

Preparation of Adhesives

Forty grams of liquefied wood and forty grams of MDI (1:1 ratio) were combined and agitated for ten to fifteen seconds. A wooden board was coated with the mixture, and then another board of the same size was pressed onto it. The hardwood blocks formed a solid adhesive bond after the assembly was left to cure for two days at room temperature.

The adaptability of liquefied biomass in adhesive applications was demonstrated by Wang and Chen's creation of biodegradable PU adhesives using liquefied wheat straw, which demonstrated mechanical qualities similar to those of traditional adhesives (Fig 7).

Preparation of Wood Composites

Equal parts MDI and wood flour were combined with forty grams of liquid wood. After ten seconds of constant stirring, the fluid was placed into a mould. A hard, non-porous wood composite that could be used for boards and handles was produced after two days of curing at room temperature (Fig 8).

Similarly, Yue et al. expanded the possible uses of these composites by adding melamine phosphate to PU foams based on liquefied pine wood, improving their thermal stability and flame retardancy.

The product obtained after curing was a hard block of wood. This could be used for making boards, handles etc. This was a thick, hard block which was non porous. This composite can be moulded in any shape and used according to requirements Fig 8.

V. Conclusion

This study shows how to successfully use the invasive plant Lantana camara as a raw material for liquefaction, which creates bio-based polyols. The liquefaction efficiency was greatly impacted by the process parameters, such as the liquid ratio and particle size; the efficiency was increased by higher liquid ratios and smaller particle sizes. The liquefied wood's characteristics, which matched the chemical structure of lignocellulosic biomass, verified the presence of functional groups appropriate for further reactions. The successful conversion of liquefied wood into polyurethane foams, adhesives, and composites highlights the material's promise as a sustainable substitute for goods derived from petroleum. These discoveries support sustainability in material production by aiding in the creation of environmentally friendly materials and the value-adding of invasive species.

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