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Turning Invasive Biomass into Value: Biopolyol Synthesis from Prosopis juliflora Via Four Liquefaction Techniques

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ABSTRACT

Global warming and depletion of non-renewable resources like fossil fuels, escalating the need for the development of environmentally acceptable and sustainable product by utilizing the naturally available renewable biomass. Prosopis juliflora (PJ), a highly ecological disruptive species was considered to a be a renewable biomass that was utilized in the production of biopolyol under four different liquefaction methods such as solvolytic, hydrothermal, phenol and microwave assisted liquefaction method. The wood and bark of Prosopis juliflora (biomass) were subjected to grinding, pretreatment and finally analysed using FTIR, TGA, DSC. After the liquefaction of both the biomass, the liquefied biopolyol was initially underwent solubility checking, identification of hydroxyl and acid number, measurement of initial pH value. Then to identify the functional group, structure, thermal properties of biopolyol, it was put through the characterisation like FTIR, NMR, TGA and DSC. This study highlights the importance of waste to resources approach by transforming an ecologically prevalent species into renewable chemical feedstocks, which supports green initiatives alongside industrial innovation.

KEYWORDS: Prosopis juliflora (PJ), lignocellulosic biomass, liquefaction, biopolyol, solvolytic, hydrothermal, phenol, microwave assisted, FTIR, TGA and DSC.



GRAPHICAL ABSTRACT



1. INTRODUCTION

Increasing use of fossil fuel for industrial development and post-industrial development paved way for higher risk of pollution as well the serious environmental ill-effect. Also, the global warming caused by emission of CO₂ during the depletion of fossil fuel resulted in serious threat, that needs to be controlled. Currently the worldwide society trying to override the issues by replacing the former non-renewable fossil fuels with renewable resources which is abundant and environmentally friendly. The green chemistry principle about the utilization of renewable resources states that, "A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable". Renewable resources consist of wind energy, solar energy, water (hydro) energy, biomass and geothermal energy. Consideration of variety of alternative energy resources, biomass plays a crucial role in renewable energy source. The European union has a strong desire for biomass which has the ability in conservation of environment and protection. Biomass classification includes microbial, agricultural residues, wood and bark waste, herbaceous waste, animal waste and aquatic waste [1,2].

Among the classification of biomass, lignocellulose biomass is considered to be the most abundant material in the earth. The lignocellulose biomass classified into trees, bushes, agricultural residue, stover, bagasse and grasses. These renewable materials are generated by utilizing the CO₂, sunlight and water under photosynthesis process. Lignocellulose materials mainly consist of three essential compounds includes, cellulose, hemicellulose and lignin, rather than this, ash and other extractive components are also present. The cellulose 30-35wt%, hemicellulose 15-35 wt%, lignin 20-35 wt% are present in the biomass related to wood and bark. The bark contains a greater number of extractives and lignin than the wood. Also, the softwood contains high amount of lignin than hardwood whereas hardwood contains high amount of hemicellulose. Also 60-70% of water content will present in fresh biomass and for dried biomass the water content will be less that is 10-15%. The conversion of biomass into a valuable material



involves several conversion technologies, such as direct combustion; thermochemical conversion (pyrolysis, gasification, direct liquefaction); indirect liquefaction; physical extraction; biochemical conversion (anaerobic conversion, ethanol synthesis); electrochemical conversion [3,4,5,6].

The thermochemical conversion of biomass plays a crucial role in the conversion of biomass that has higher capability in reducing the conversion time shorter and also degrade the organic components rapidly. In the thermochemical conversion, direct liquefaction is superior than other methods like pyrolysis and gasification. Generally, liquefaction of biomass reaction involves low temperature a(200-400°C) and high pressure (5-20 MPa). The liquefaction process takes place by initially depolymerisation of biomass-tobiomass monomers, then the biomass monomers are decomposed by cleavage, dehydration, decarboxylation and deamination results in the formation of unstable and active small molecules. Then finally the rearrangement of small molecules by condensation, cyclization and polymerisation leads to the formation of new compounds [7]. A xerophyte tree, Prosopis juliflora (PJ) or Velikathan in Tamil is considered to be an aggressive colonizer. The invasion of PJ around the world mainly in tropical and subtropical regions will disrupts the environment by invading farm lands, watercourses, even expelling inhabitants, also these trees will survive in extreme conditions without water, growing even in alkaline soils causes damage to biodiversity. Due to its widespread, worldwide PJ is considered as one of the top 100 most supreme invasion species. The PJ generally a leguminous family, which survives even in nitrogen deficient soil by utilizing the nitrogen gas from the atmosphere through symbiosis, makes it more wild spread tree [8]

The exploitation of biomass using PJ in the production of biopolyol was done by several researchers around the world. The wood of PJ along with polyolefin waste were co-liquefied using bentonite as a catalyst for liquid hydrocarbon production [9]. Similarly, the woody biomass of PJ along with paint waste sludge were liquefied using co-liquefaction method in hydrothermal under varying temperature (340°C-440°C) for the production of liquid hydrocarbon [10]. Likewise, for the production of bio-oil and ferulic acid took place by the wood biomass of PJ using hydrothermal liquefaction method under temperature 200-374°C and pressure (5-20 MPa) [11]. In this work, four methods of liquefaction using the widespread species Prosopis juliflora (PJ) biomass (wood and bark) were employed. The four methods of liquefaction include solvolytic liquefaction, phenol liquefaction yielded a biopolyol, a valuable biobased alternative material instead of the former petroleum-based polyol. The synthesised biopolyol has several applications, mainly in the production polyurethane (PU). In production of polyurethane, it involves in the generation of adhesives, foam, coatings and film making. The implementation of liquefaction of an invasive species into a significant product would be a greater advantage in the introduction of new sustainable biomaterial for greener future.

2. Experimental section

2.1 Materials

The wood and bark biomass of PJ were collected from urban areas in Chennai. Polyethylene glycol (Mw~ 400) and phthalic anhydride were provided by (Sigma, India). Hexane, pyridine, extra pure phenol crystalline \geq 99.5%, phenolphthalein, glycerol anhydrous 99.5% purity and ethanol were purchased from



(Sisco Research Laboratory Pvt. Ltd., Chennai, India). Hydrochloric acid (HCl), sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), dioxane were purchased from (Fisher Scientific Chemicals, Chennai, India).

2.2 Methods

2.2.1 Grinding and Pretreatment of bark and wood of Prosopis juliflora (PJ)

The bark and wood of Prosopis juliflora were cut into small pieces of length 6cm and breadth 2 cm and washed thoroughly using distilled water to remove the dirt. To remove the moisture, the biomass was kept in oven at 70°C for three days. After complete drying the biomass pieces were grinded using fully stainless- steel heavy duty grinder. Then the wood and bark powder were sieved thoroughly using 60 mesh sieves for obtaining fine powder. These fine powders were subjected to Soxhlet extraction to remove the wax and inert impurity present in the biomass by choosing hexane as a solvent. The Soxhlet extraction procedure was carried out for 3 hours and then it was kept in oven for complete removal of solvent at 60°C for 3 hours. This pretreated biomass was further proceeded for liquefaction process [12].

2.2.2 Different methods of liquefaction

Solvolytic liquefaction of wood and bark of PJ

The experiment was carried out by taking the polyhydric alcohols solvent mixture of PEG-400 and glycerol in 80:20 ratio, where the PEG-400 was preheated before to remove the residual moisture. This particular solvent mixture was shown best impeded effect for recondensation and reprecipitation during liquefaction process [13]. Then the biomass (wood/bark) of 3g was taken and added into 250ml RB flask and the solvent mixture were poured into it, both in the ratio of (1:18). To that mixture 3wt% of H₂SO₄, a catalyst was added and the mixture was kept in the oil bath. Initially the reaction temperature was kept at 40°C for 10 minutes and then the temperature was slowly raised to 150°C and proceeded for 2 hours [12].

Phenol liquefaction of wood and bark of PJ

This procedure was undergone by taking biomass (wood/bark) powder of 3g and added to a 250ml RB flask. Then the solvent phenol 24g was added into it. The biomass and solvent were added in the ratio of 1:8. Finally to that mixture 3 wt% of catalyst H_2SO_4 was added. The complete mixture was allowed to stir at 40°C for 10 minutes initially in oil bath. Then the temperature was gradually increased to 150°C for 2 hours, where this particular temperature is reported as a perfect liquefaction temperature[14, 15].

Hydrothermal liquefaction of wood and bark of PJ

In the hydrothermal liquefaction process, the both biomass (wood/bark) powder were taken for about 3g, along with that 5wt% catalyst (i.e) NaOH and 50ml of distilled water was added into a Teflon-lined stainless autoclave. To supress the char produced in the hydrothermal reaction mostly base catalyst was preferred, instead of acid catalyst [16]. The autoclave was tightly sealed, and maintained at 180°C for 2 hours. After complete cooling, the hydrothermal based liquified product was obtained.

Microwave liquefaction of wood and bark of PJ

Microwave assisted liquefaction was carried out in lab made microwave reactor. Initially, 3g of biomass (wood/bark) was taken in an 100ml RB flask, into that solvent mixture of PEG-400 and glycerol (1:1)



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ratio were added. Then 5wt% of H_2SO_4 was added, the mixture was allowed to react for first 2min at 500W and finally, it was further reacted for the second time for 5 min at 300W [17].

2.3 Unliquified residual wood and bark calculation

The remaining unliquified residues from both bark and wood of Prosopis juliflora were filtered using Whatman filter paper and the residues were washed thoroughly with acetone and kept in oven at 110°C for 24 hours. After achieving the constant weight, the residues were weighed. The unliquified residues were calculated from the following equation (1) [18].

Percentage of residue (R%) = (Weight of residue \div Weight of biomass) \times 100 (1)

2.4 pH calculation

After the unliquified residual calculation, the extracted biopolyols were neutralised using the 0.1M acid (H_2SO_4) and 0.1M base (NaOH). The neutralisation process was done until the pH reaches the value 7. After neutralisation the precipitated salt was filtered using filter paper and the supernatant was collected, where excess solvent was removed using rotary evaporator at 70°C to obtain pure liquefied biopolyol.

2.5 Hydroxyl number (-OH) and Acid number calculation (-COOH)

The hydroxyl number were determined using ASTM standard D4274-05. Initially phthalation reagent was prepared by dissolving 10g of phthalic anhydride in 70ml of pyridine. Taking 25ml of phthalation reagent and 0.5 g of liquified biopolyol in a 250 ml RB, which was allowed to heated at 115°C for 1hour. After complete cooling, 1% of phenolphthalein solution was added and the mixture was titrated against 0.1M NaOH. The same procedure was repeated without the addition of liquified biopolyol sample, considered it as blank. The following equation (2) is used to calculate the hydroxyl number of the sample.

$$Hydroxyl number = [(B - A) \times M \times 56.1] \div W + AN$$
(2)

(A & C- Volume of the 0.1M NaOH were consumed during the titration of the sample, B- Volume of the 0.1M NaOH were consumed during the titration of the blank, M- Molarity of the NaOH, W- Weight of the sample used, AN- Acid number)

For calculating the acid number, 0.5g of biopolyol sample was weighed in 250ml beaker and dissolved in dioxane/water solvent mixture in the ratio of (4:1). Then 0.5ml of phenolphthalein indicator solution with 1% ethanol was added into to the mixture. This mixture was titrated against 0.1M NaOH solution until the equivalence point is reached. The equation (3) is used to calculate acid number. [19].

Acid number (AN) =
$$[(C - A) \times M \times 56.1] \div W$$
 (3)

2.6 Characterisation of Biomass (wood & bark) and Liquefied biopolyol

2.6.1 FTIR Analysis

The functional group identification in both wood and bark biomass, also the liquefied polyol was carried out using FTIR spectrometer with ATR mode (TENSOR 27, Bruker, Billerica, MA, USA) in the range of 500-4000cm⁻¹.



2.6.2 NMR Analysis

The proton (¹H) and carbon (¹³C) of the liquefied biopolyol obtained from the wood and bark of PJ were analysed using Nuclear Magnetic Resonance (NMR) Bruker AVANCE 400 MHz spectrometer. For analysis 0.5mg sample of liquefied biopolyol was dissolved in NMR solvent (DMSO-D₆).

2.6.3 Thermogravimetric Analysis

The TGA analysis of both biomass and liquefied polyol were carried out, to study its thermal properties. The thermal analysis was carried out using SetaramTM 92-16.18 TG analyser using alumina crucible with the temperature range of 30-800°C at a scan rate of 10°C/minute under nitrogen atmosphere where 5mg sample weight was taken for analysis.

2.6.4 Differential Scanning Calorimetry Analysis

The phase transition properties of biomass and liquefied biopolyol were analysed using Setaram setline DSC instrument where 5mg sample was taken in pan and analysed for 10°C/minute under nitrogen atmosphere in the temperature range of 30-300°C.

3. Result and Discussion

3.1 Yield and unreacted residue comparison of wood and bark of PJ.

The four different liquefaction method were carried out for the wood and bark of PJ by using different solvent and reaction conditions. The yield of liquified biopolyols from the wood and bark of PJ was determined. The unreacted residue obtained after the completion of the four different liquefaction process was also calculated by above mentioned residue calculation method. Table 1 provides the data for the yield and unreacted residue of wood and bark.

The data in the Table 1 shows the liquefaction yield and unliquefied yield of both wood and bark. The highest liquefaction yield was obtained from phenol liquefaction of both wood and bark. The phenol used as a solvent here has a greater effect on the liquefaction of lignocellulosic biomass particularly the lignin and hemicellulose which results in the greater yield of the biopolyol. The solvent phenol not only act as a good solvent but also as a reagent in producing liquefied product with combination of phenol.

Liquefaction method	Liquefied biopolyol yield (%)		Unliquefied residue yield (%)	
	Wood	Bark	Wood	Bark
Solvolytic	97.20	98.4	2.8	1.6
Hydrothermal	25.60	30	74.4	70
Phenol	98.23	98.7	1.77	1.3
Microwave	73.97	82.3	26.03	17.7

Table 1: Yield and unreacted residue comparison of wood and bark of PJ



The lowest liquefaction yield was observed in the hydrothermal method. The obtained liquefied product in hydrothermal method was \leq 30 % of both wood and bark biomass. It also resulted in more unliquefied residue yield. In the solvolytic method, the yield of liquefied product was high where polyhydric alcohol was used as a solvent. Similarly, in microwave method the yield was good in both the bark and wood biomass of PJ.

3.2 pH measurement

After the unliquified residual calculation, the extracted biopolyols were neutralised using the 0.1M acid (H_2SO_4) and 0.1M base (NaOH). The neutralisation process was done until the pH reaches the value 7. After neutralisation the precipitated salt was filtered using filter paper and the supernatant was collected, where excess solvent was removed using rotary evaporator at 70°C to obtain pure liquefied biopolyol. The initial pH was measured for all the eight types of biopolyols obtained from four different methods. The pH value for all the samples were represented in the Figure 1(a) and 1(b).





3.3 Hydroxyl and acid number for wood and bark of PJ

The hydroxyl number (OH) and acid number (-COOH) was determined using ASTM standard D4274-05 and ASTM D 4662-08 methods. Each method was carried out for three times to obtain an average value. The obtained values were represented in graphical representation in below Figure 2(a) and 2(b).





Figure 2(a) and 2(b) - Hydroxyl and acid number for wood and bark of PJ

The Figure 2(a) and 2(b) represents the hydroxyl value and acid for both wood and bark in all the four liquefaction methods including solvolytic method (SL), hydrothermal method (HL), phenol method (PL), microwave method (ML). In Figure 2(a) the hydroxyl value obtained for all the method were above \geq 265, compared to all method the highest amount of hydroxyl number was measured in phenol liquefaction method whereas the lowest yield was produced from microwave liquefaction method. Similarly, the Figure 2(b) represent the acid value present in all the four liquified product. Here, the phenol liquefication possessed more acid value than the other liquefied product. Also, the lowest acid value is obtained from microwave liquefaction method. Final results shows that both the hydroxyl and acid numbers are high in phenol liquefaction method and low in microwave method. The liquefied bark contains more hydroxyl and acid number than in the liquefied wood products.

3.4 Solubility analysis of biopolyols

The eight types of biopolyol sample from wood and bark of PJ were undergone solubility analysis using different types of solvents. 0.1 ml of biopolyol samples were dissolved in 3ml of solvent for identifying its solubility nature. The solubility analysis was represented in Table 2 and Figure 3.

Solvent	Solubility	
Deionised water	Completely soluble	
Acetone	Mostly soluble	
Ethanol	Mostly soluble	
Methanol	Mostly soluble	
Tetrahydrofuran (THF)	Partially soluble	
Dichloromethane (DCM)	Partially soluble	
Dimethyl sulfoxide (DMSO)	Completely soluble	
Toluene	Insoluble	
Dimethyl formamide (DMF)	Completely soluble	
Hexane	Insoluble	

Table 2: Solubility analysis of biopolyols



Totally 10 solvents were used for analysing the solubility of the biopolyol samples. The solvents DI water, DMSO, DMF, possessed complete solubility. Whereas solvents like toluene, hexane were not dissolved the biopolyols. In acetone, ethanol, methanol, the biopolyol samples were mostly soluble. Also, in THF and DCM the biopolyols were undergone partial solubilization [20].

Figure 3 - Solubility analysis of biopolyols



3.5 IR Data Analysis





The identification of functional group was processed using Fourier Transform Infrared spectroscopy. The FTIR analysis of wood and bark of PJ was shown in Figure 4(a) and 4(b). The significant hydroxyl group (-OH) or phenols present in both wood and bark biomass showed a peak around 3300-3400 cm⁻¹. The C-H stretching of both the biomass vibration are present around 2920-2925 cm⁻¹. Finally, the C-O stretching and C=C aromatic stretching were found in the region around 1600-1800 cm⁻¹ due to the presence of lignin in the biomass samples, because lignin shows significant peaks around these regions [21,22].





Figure 4(c) and 4(d) – FTIR analysis of biopolyol from wood and bark.

Here the liquefied biopolyols were obtained from four different method using two different biomasses (wood & bark) of PJ. The four different liquefaction methods samples of wood and bark such as solvolytic (SLW, SLB); hydrothermal (HLW, HLB); phenol (PLW, PLB); microwave (MLW, MLB) were analysed for functional group identification using FTIR were represented in the above Figure 4(c) and 4(d). Initially the -OH stretching vibration are present in all eight samples shows that it possesses a greater number of hydroxyl group (OH) may be due to the lignin in the liquefied biopolyol, phenolated carbohydrates, usage of PEG-400 and glycerol in liquefaction process or maybe due to the free phenol. The two -CH stretching vibrations for all samples were found around the region of 2835-2853 cm⁻¹ and 2916-2923 cm¹ due to the stretching vibrations produced from methyl and methylene groups. The sharp significant peaks of lignin which has been present in the both wood and bark of PJ around the range of 1600 cm⁻¹ was not found in the liquefied samples due to the lignin degradation into smaller molecular weight compounds during liquefaction process. The presence of high sugar content (C-O stretching vibration of carbohydrates) in the liquefied samples were found in the region of 1100 cm⁻¹ which was not found in the biomass samples [23,24].

3.6 NMR Analysis

3.6.1 ¹H NMR spectrum

Figure 5(a), 5(b), 5(c), 5(d), 5(e), 5(f), 5(g), 5(h) represents ¹H NMR spectrum of liquefied biopolyol from both wood and bark under solvolytic, phenol, hydrothermal, microwave.



The ¹H NMR spectrum of each biopolyol from liquefied wood and bark of PJ using four different liquefaction methods was represented in Figure 5(a), 5(b), 5(c), 5(d), 5(e), 5(f), 5(g), 5(h). The common peaks found around the region of 0.5-2.0ppm in all the biopolyols due to the methyl and methylene group. These peaks were generated due to the degradation of tannin or another extractive group like lignin or terpenoids where not due to any sugar degradation product. The chemical shift around 2.0-3.0ppm, some protons peaks were found which attributes to levulinate methylene ester. The peak around 2.5ppm was due to the NMR solvent DMSO-D₆. The chemical shift around 3.0-4.0ppm was due to the solvent PEG-400, the shift around 3.5ppm was due to the methylene group, the carbon having proton in the α position to the hydroxyl group and the hydroxyl proton around 3.6-3.7ppm. The aromatic region was found around the region of 6-8ppm. The peak found around 8.5ppm was a significant aldehyde proton peak of formic ester [25,26].



3.6.2 ¹³C NMR spectrum

Figure 6(a), 6(b), 6(c), 6(d), 6(e), 6(f), 6(g), 6(h) represents ¹³CNMR spectrum of liquefied biopolyol from both wood and bark under solvolytic, phenol, hydrothermal, microwave.



The protons of biopolyols were identified using ¹H NMR spectrum, then for identifying carbon present in the biopolyols ¹³C NMR was used for each biopolyol sample that was represented in Figure 6(a), 6(b), 6(c), 6(d), 6(e), 6(f), 6(g), 6(h). The primary and the secondary carbon atoms of solvent PEG-400 were found around in the region 60.7 and 70.2ppm, these regions were present only in biopolyol which undergone liquefaction using PEG-400 as a solvent. The cellulose particles peaks were found around the region of 72.2-72.4ppm. In phenol liquefaction, the C-OH group present in phenol of free phenol in biopolyol of both wood and bark were found in the region of 153.8ppm. The shift around 110-130 attributes to the guaiacyl units in liquefied biopolyol. The shift took place around 73-80 was due to the - CH-OH and -CH₂OH present in the polysaccharides [26,27].



3.7 Thermogravimetric Analysis

Figure 7(a) and 7(b) – TGA analysis of biomass of PJ



The thermal properties of wood and bark powder of PJ was represented in Figure 7(a) and 7(b). The initial weight loss around 100°C, indicates the presence of water molecule present in both wood and bark. The further degradation of both biomasses occurs in three step process. The first step degradation mainly occurs in all the wood and bark was due to the hemicellulose which usually breaking down around the temperature 180-350°C. The cellulose is the one which breaks down around 275-350°C in the second step degradation process. The last step degradation around 250-500°C is due to the lignin present in both the biomass. The degradation of hemicellulose and cellulose took place before 400°C, in that both the moieties undergo cleavage where the volatile CO and CH₄ results in the formation of C-O and C-C bonds [28,29].

Figure 7(c) and 7(d) – TGA analysis of wood and bark biopolyol



The Liquefied wood and bark biopolyols thermal properties were shown in Figure 7(c) and 7(d). In the liquefied biopolyol from wood and bark of PJ shows an initial weight loss around 35°C -125°C, was due to the water evaporation. The larger biopolymers like hemicellulose, cellulose and lignin of the liquefied biopolyol degrades around the temperature of 280°C -330°C, 350°C, and 450°C. The initial degradation



results in releasing volatile compounds carbon monoxide, carbon dioxide, methane which was due to the cleavage of side chains. Above the temperature 400°C-450°C, final decomposition took place by forming char residues [30].

3.8 DSC analysis



Figure 8(a) and 8(b) – DSC analysis of biomass of PJ

The DSC analysis for both wood and bark powder of PJ were represented in Figure 8(a) and 8(b). The DSC analysis shows the phase transition like glass transition, melting point and crystallinity of the material. The sharp endothermic peak observed in both the graph of wood and bark powder around the temperature 96°C ad 104°C. These peaks maybe attributes to the moisture present in the sample [31,32].



Figure 8(c) and 8(d) – DSC analysis of biomass of PJ

The liquefied wood and bark DSC analysis were shown in Figure 8(c) and 8(d). In both the wood and bark biopolyol all figure represents the endothermic peak. This endothermic generally attributes to the glass transition temperature (T_g). The biopolyols from liquefied wood and bark of. four methods were given as follows, solvolytic wood (61°C), solvolytic bark (63°C), hydrothermal wood (78°C), hydrothermal bark



(76°C), phenol wood (106°C), phenol bark (101°C), microwave wood (75°C), microwave bark (81°C) [33].

4. Application of biopolyol in polyurethane (PU)

Due to their abundance, low cost and environmentally friendly nature, the liquified polyol has paved a greater substitute for the petroleum-based polyol used for the production of polyurethanes. Utilizing this liquified biopolyol in the polyurethane production results in the greater advantage to human beings and the environment. The polyurethane (PU) materials like rigid and flexible foams, films, coatings, adhesives produced from the liquefied biopolyol considered to be a sustainable material for the greener future [34,35]. The liquefied biopolyol obtained from the soyabean straw using glycerol as a solvent resulted in the production of an efficient polyurethane foam material [36]. Another lignocellulosic biomass, lemon bagasse which was liquefied using crude glycerol used for the production of PU foam having good dimensional stability [37]. Similarly, grape pomace was liquefied by solvothermal method and the liquefied biopolyol was used in the production of rigid PU foam [38].

PU adhesives of biopolyol used for bonding wood, metal, glass and so on. The bio polyurethane adhesives synthesised using the biopolyol obtained from three types of biomass sewage sludge, hemp stalk hurds and sugar beet pulp. The produced adhesives exhibited a high tensile strength of (5.77-11.03 MPa) [39]. The liquefication of wood sawdust using polyhydric alcohol and the obtained liquefied biopolyol provides a highest shear strength of $4.82 \pm 1.01 \text{ N/mm}^2$ and $4.80 \pm 0.49 \text{ N/mm}^2$ for adhesives [40]. The liquefied biopolyol obtained from corn straw and starch by co-liquefication used for the production of biocontent degradable polyurethane coated-fertilizer [41]. The liquefied biopolyol obtained from Acacia mangium reacted with pMDI to produce biobased polyurethane film [42]. The application of biopolyol is not only in the field of polyurethane and also in other several fields. The emerging biopolyol trend will override the former petroleum-based polyol in polyurethane production.

5. Conclusion

In an era, where the sustainability and waste valorisation are fundamental, this study presents a robust approach to converting the Prosopis juliflora, a prolific colonizing species into a high valuable bio-based polyol. Employing four distinct methods of liquefaction such as solvolytic, hydrothermal, phenol and microwave assisted where the wood and bark biomass of PJ were depolymerized into valuable chemical feedstock material. Structural and functional analysis of polyol were analysed using FTIR, NMR, TGA, DSC and other factors like identification of acid and hydroxyl number, pH measurement, solubility checking. This approach provides an ecologically friendly means to replace the former petroleum-based polyol in industrial formulations. It also positioned itself towards greener, by benefitting in ecological restoration and material innovation.



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