Preparation and Optimization of Bio-polyols from Sawdust Liquefaction Using Crude Glycerol and Polyethylene Glycol

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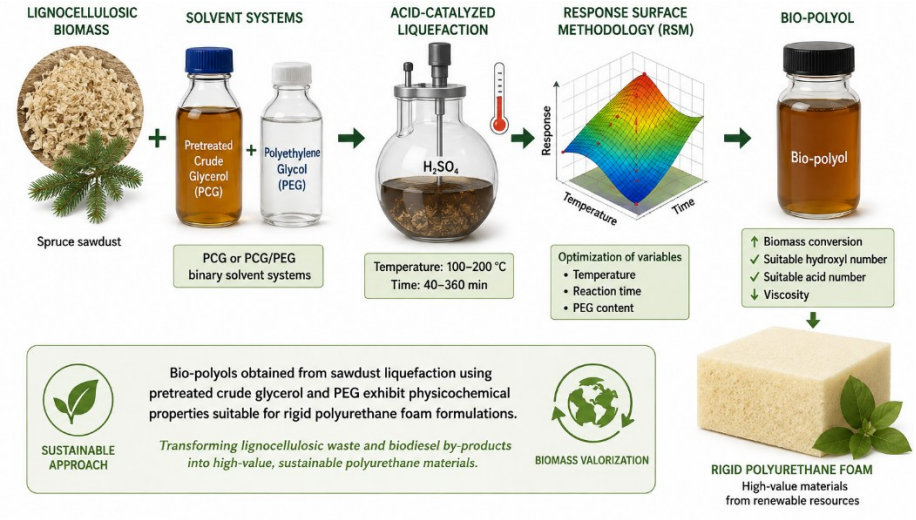
GRAPHICAL ABSTRACT



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Bio-based polyols derived from lignocellulosic biomass have attracted considerable attention as sustainable alternatives to petroleum-based polyols in polyurethane production. In this study, spruce sawdust was liquefied using pretreated crude glycerol (PCG) and pretreated crude glycerol/polyethylene glycol (PCG/PEG) binary solvent systems under acid-catalyzed conditions to produce bio-polyols. The effects of reaction temperature, reaction time, and solvent composition on biomass conversion, hydroxyl number, acid number, and viscosity of the resulting polyols were systematically investigated using response surface methodology (RSM). Liquefaction experiments were conducted at temperatures ranging from 100 to 180 ºC for PCG and 120 to 200 ºC for PCG/PEG mixtures, with reaction times between 40 and 360 min. The results demonstrated that increasing temperature, reaction time, and PEG content significantly enhanced biomass conversion efficiency. Statistical analysis confirmed that temperature and reaction time were the most influential parameters affecting polyol properties and liquefaction performance. The incorporation of PEG improved biomass conversion and reduced viscosity compared with PCG alone. The obtained bio-polyols exhibited physicochemical characteristics within the range generally considered suitable for rigid polyurethane foam polyol formulations, demonstrating the potential of PCG and lignocellulosic waste as sustainable feedstocks for high-value polyurethane materials.

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Keywords: Bio-polyol; Pretreated crude glycerol; Polyethylene glycol; Biomass liquefaction; Sawdust; Polyurethane foam; Response surface methodology

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INTRODUCTION

Polyurethane (PU) materials, which are among the most versatile polymeric products widely used in insulation, construction, automotive, furniture, coating, adhesive, and packaging industries, are prepared through the polyaddition of polyisocyanates and polyols to form urethane linkages. Among these PU products, rigid polyurethane foam, a highly cross-linked polymer with an essentially closed-cell structure, has a wide range of industrial applications due to its excellent thermal insulation performance, good mechanical strength, strong adhesion, good dimensional stability, and ease of processing and manufacturing (Sercer *et al.* 2012). Conventionally, the polyols employed for PU production are derived from petroleum-based resources. However, growing environmental concerns, depletion of fossil resources, increasing crude oil prices, and the global demand

for sustainable materials have accelerated research into renewable alternatives for PU production (Wu *et al.* 2025)

In the context of the present work, the term polyol is defined as a monomeric or oligomeric compound containing a sufficient number of -OH functional groups to perform effectively when combined with diisocyanate reagents during the production of polyurethane products. Specifically, a polyol must have two or more -OH groups. Bio-based polyols have emerged as promising substitutes for petroleum-derived polyols due to their potential to reduce carbon emissions and improve sustainability. To date, vegetable oils and lignocellulosic biomass have been the two primary renewable feedstocks used for bio-polyol production (Li 2011; Mo *et al.* 2024; Jayalath *et al.* 2025; Santos *et al.* 2025). Numerous studies have investigated the conversion of soybean, sunflower, rapeseed, and castor oils into bio-polyols suitable for PU applications (Bernardini *et al.* 2015). Nevertheless, large-scale utilization of edible oils raises concerns regarding competition with food resources, land use, and economic viability (Li and Reeder 2011). Consequently, increasing attention has been directed toward lignocellulosic biomass as a low-cost, abundant, and non-food renewable feedstock for bio-polyol production (Daimary *et al.* 2025). Lignocellulosic biomass, including agricultural residues, forestry waste, and wood-processing by-products, represents an attractive raw material for biorefinery applications. Through thermochemical conversion processes, the complex structure of cellulose, hemicellulose, and lignin can be depolymerized into valuable chemical intermediates and polyol-rich products (Jiang *et al.* 2018; Lozano and Lozano 2018; Serrano *et al.* 2020).

Among the available thermochemical conversion technologies, biomass liquefaction has attracted considerable attention. This process provides an efficient route for producing bio-polyols suitable for the production of flexible polyurethane foams, rigid polyurethane foams, coatings, adhesives, sealants, and elastomers (Demirbas 2010; Kosmela *et al.* 2016; Lange 2018; Bontas *et al.* 2023; Wu *et al.* 2024). Liquefaction is a the either acid- or base-catalyzed process, in which biomass reacts with an excess of polyhydric alcohols, commonly referred to as liquefaction solvents or liquefaction media, at temperatures generally between 150 to 250 °C (Hu 2013; Lange 2018). During liquefaction, the polymeric structure of cellulose, hemicellulose, and lignin is broken into low-molecular-weight hydroxyl-containing fragments that dissolve within the reaction medium (Demirbas 2010). It is important to distinguish between the roles of the liquefaction medium and the final bio-polyol. Polyhydric alcohols such as glycerol, polyethylene glycol (PEG), and ethylene glycol initially serve as reactive liquefaction solvents, promoting solvolysis and stabilizing biomass degradation products. However, unlike conventional solvents that are removed after processing, these polyhydric alcohols remain in the final liquefied product because they themselves contain reactive hydroxyl groups and are fully compatible with polyurethane (PU) synthesis. Consequently, the final bio-polyol consists of a homogeneous mixture of the liquefaction solvents together with newly generated biomass-derived oligomers and monomers, and this entire mixture is directly employed as the polyol component in PU formulations without purification (Hu *et al.* 2012; Kosmela *et al.* 2016; Bontas *et al.* 2023).

Despite its effectiveness, conventional biomass liquefaction requires relatively large quantities of petroleum-derived solvents, which significantly increase production costs and reduce the overall sustainability of the process (Lee *et al.* 2000). Therefore, the replacement of conventional solvents with low-cost renewable alternatives has become an important research objective. Crude glycerol (CG), a major by-product of biodiesel production, has attracted considerable interest as a liquefaction solvent because of its low

market value, high availability, and elevated hydroxyl functionality (Hu *et al.* 2012; Xu *et al.* 2013). Approximately 10 wt% of biodiesel production is generated as crude glycerol (CG), creating a substantial surplus that requires value-added utilization pathways (Hu and Li 2014). Previous studies have demonstrated that crude glycerol can effectively liquefy lignocellulosic biomass and produce bio-polyols suitable for PU production (Hu *et al.* 2012; Kosmela *et al.* 2016). Furthermore, residual impurities such as fatty acids, soaps, glycerides, and methyl esters may influence the structure of the resulting bio-polyols and, consequently, the properties of polyurethane materials (Hu and Li 2014).

However, compared with conventional glycerol/PEG solvent systems, CG generally exhibits lower biomass conversion efficiency and produces bio-polyols with relatively high viscosity, which may limit processing performance and final PU properties (Xu *et al.* 2013). Polyethylene glycol (PEG) is widely used as a liquefaction co-solvent because of its excellent solvating ability and its capability to reduce polyol viscosity while improving biomass conversion efficiency (Jo *et al.* 2015). The incorporation of PEG into CG-based liquefaction systems may therefore provide an effective strategy to enhance liquefaction performance and improve the physicochemical properties of the resulting bio-polyols.

One of the major challenges of using crude glycerol (CG) as a liquefaction solvent is its varying composition, which is caused by differences in feedstocks, processes, and post-treatments at biodiesel plants. The varying compositions of crude glycerol could cause problems in the consistency of the properties of the produced polyols and PU products. (Hu and Li 2014). Although several studies have investigated the liquefaction of lignocellulosic biomass using crude glycerol (CG), most of the reported investigations employed CG derived from biodiesel produced using a single vegetable oil feedstock (Hu *et al.* 2012; Xu *et al.* 2013). In contrast, the crude glycerol used in the present study originated from an industrial biodiesel process utilizing a mixture of waste vegetable oils, representing a more realistic industrial by-product with a more complex chemical composition.

Spruce sawdust is an abundant lignocellulosic residue generated by wood-processing industries and is often underutilized despite its high carbohydrate and lignin content. Valorization of this waste stream through liquefaction offers an environmentally sustainable route for producing value-added polymer precursors. Therefore, this study provides additional insight into the utilization of industrially relevant crude glycerol for the production of bio-polyols from Spruce sawdust, which were systematically optimized using Response Surface Methodology (RSM). In separate work, the authors have evaluated the suitability of bio-polyols, regarding their suitability in production of rigid PU foams (Rastegarfar *et al.* 2018).

EXPERIMENTAL

Materials

Spruce (*Picea abies* (L.) H. Karst.) sawdust was used as the lignocellulosic feedstock. It was collected from a local carpentry workshop located in Noor, Iran. Crude glycerol (CG) was obtained from the biodiesel production unit of the Faculty of Agriculture, Tarbiat Modares University, Tehran, Iran. The CG was generated during biodiesel production from mixed waste vegetable oils. The chemical composition of CG was determined according to the procedure of Hu *et al* (2012). The composition is summarized in Table 1.

Table 1. Chemical Composition of CG

Material	Value (wt%)
Glycerol	26.6±0.1
Methyl ester	29.1±1
Fatty acid	4±0.1
Glycerides	6±0.1
Water	3.6±0.1
Methanol	7.9±0.1
Soap	18.5±0.1

Polyethylene glycol (PEG 400), sulfuric acid (98 wt%), phthalic anhydride, dioxane, pyridine, sodium hydroxide, hydrochloric acid, and ethanol of analytical grade were purchased from Merck (Germany) and used without further purification.

Methods

Preparation of biomass feedstock

The collected sawdust was passed through a 60-mesh sieve and was dried in a laboratory oven at 105 °C for 24 h before being used for liquefaction tests (Wang and Tuohedi 2020).

Pretreatment of crude glycerol

Prior to liquefaction, the biodiesel-derived crude glycerol was subjected to pretreatment according to the method reported by Hu and Li (2014). Briefly, concentrated hydrochloric acid was added to adjust the pH of CG to approximately 1.0. Under acidic conditions, soap impurities were converted into free fatty acids and inorganic salts. Subsequently, residual methanol and water were removed in a rotary evaporator operated at 70 °C under reduced pressure. The CG was then centrifuged at 10,000 rpm for 10 min, resulting in phase separation into three layers: an upper organic phase containing fatty acids and glycerides, a middle glycerol-rich phase, and a lower salt-rich phase. The upper and middle phases were collected and used as liquefaction solvents.

Fig. 1. Experimental liquefaction

Liquefaction procedure

Liquefaction experiments were conducted in a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet (Fig. 1). Initially, 100 g of liquefaction solvent and 3 g of sulfuric acid catalyst were introduced into the reactor and heated to the desired reaction temperature. After thermal equilibrium was achieved, 10 g of oven-dried sawdust was gradually added to the reaction mixture under continuous stirring. The liquefaction reaction was performed under a nitrogen atmosphere to minimize oxidative degradation. Reaction temperatures and times were varied according to the experimental design. At the end of each experiment, the reactor was rapidly cooled in cold water to terminate the reaction.

The liquefied product was filtered to separate the insoluble residue from the liquid fraction. The liquid fraction was designated as bio-polyol and used for subsequent characterization, whereas the insoluble residue was used solely for determining the biomass conversion ratio, and was not further investigated.

Solvent formulations

Four solvent systems consisting of PCG and PEG 400 were investigated. The solvent compositions are presented in Table 2.

Table 2. Weight Ratio of PCG to PEG

Polyol	PCG (g)	PEG (g)
Type 1	100	0
Type 2	90	10
Type 3	85	15
Type 4	80	20

Experimental design and optimization

Response surface methodology (RSM) was employed to evaluate the effects of liquefaction temperature and reaction time on bio-polyol properties and biomass conversion efficiency. A central composite design (CCD) generated using Design-Expert software was used for experimental planning and model development. These two variables were selected because they are the primary process parameters governing biomass liquefaction according to previous studies, whereas the biomass-to-solvent ratio and catalyst loading were maintained constant based on optimized conditions obtained in other studies. Biomass conversion, hydroxyl number, acid number, and viscosity were selected as response variables because they are the principal physicochemical properties used to evaluate bio-polyols intended for polyurethane applications.

Quadratic polynomial models were developed to describe the relationships between process variables and response parameters. Analysis of variance (ANOVA) was performed to evaluate the significance of model terms and the adequacy of the developed models. Model quality was assessed using coefficients of determination (R^2), adjusted R^2 values, and lack-of-fit analysis. Five replicate experiments at the center point were conducted to estimate experimental error and evaluate model reproducibility. Unless otherwise stated, all analytical measurements were performed in triplicate and the reported values represent the mean of three determinations.

Table 3. Treatment Levels for Liquefaction by PCG and PCG/PEG

PCG		PCG/PEG	
Temperature (ºC)	Time (min)	Temperature (ºC)	Time (min)
100	200	120	200
120	120	140	120
120	280	140	280
140	40	160	40
140	360	160	360
140	200	160	200
140	200	160	200
140	200	160	200
140	200	160	200
140	200	160	200
160	120	180	120
160	280	180	280
180	200	200	200

The treatment levels were determined using the RSM within Design Expert software for two important process variables: In the temperature range of 100 to 180 °C for the liquefaction of sawdust with PCG, and in the temperature range of 120 to 200 °C for the liquefaction of sawdust with PCG and PEG, over a duration of 40 to 360 min (Table 3). In this way, a variable amount of PEG was added to the PCG in different weight percentages, as shown in Table 2, and considered as the liquefaction solvent. The liquefaction of sawdust with PCG encountered problems and was stopped after 180 °C. Likewise, there were problems when using the solvent mixture after 200 °C. Consequently, treatments for temperatures above 180 and 200 °C, respectively, were not tested or investigated for these cases.

Characterization of Bio-Polyols

Determination of acid number

The acid number was determined according to ASTM D4662-08 (2008). Approximately 2 g of bio-polyol was dissolved in 50 mL of ethanol and titrated with standardized 0.1 N sodium hydroxide solution until the endpoint was reached.

Determination of hydroxyl number

The hydroxyl number was measured according to ASTM D4274-05 (2005). An esterification reagent was prepared by dissolving 150 g of phthalic anhydride in a mixture of 900 mL dioxane and 100 mL pyridine. Subsequently, 10 mL of reagent was added to 1.0 g of bio-polyol and heated at 100 °C for 20 min. After cooling to room temperature, the excess reagent was titrated using standardized 0.5 N sodium hydroxide solution.

Viscosity measurement

The viscosity of bio-polyols was determined according to ASTM D4878-08 (2008), using a Brookfield DV-II rotational viscometer operated at 25 °C.

Biomass Conversion Ratio

The suspension was vacuum-filtered, and the residue was dried at 105 °C for 24 h. The biomass conversion ratio represents the fraction of biomass converted into solvent-soluble products during liquefaction. After dissolving a known amount of bio-polyol in a

water/dioxane (1:4, v/v) mixture, the insoluble residue was separated by vacuum filtration, dried at 105 °C for 24 h to constant weight, and weighed. The biomass conversion ratio was calculated according to Eq. (1),

$$BSR = 100-((W_1-W_2)/W_3*W_4*100)/W_5 \quad (1)$$

where BSR is the biomass conversion ratio (%), W_1 is the dry weight of the filter paper and sawdust residue (g), W_2 is the net weight of the filter paper without the sawdust residue (g), W_3 is the weight of polyols weighed for the calculation of production yield (g), W_4 is the total weight of polyols obtained from the liquefaction process (g), and W_5 is the weight of sawdust used in the liquefaction process (g).

RESULTS AND DISCUSSION

Effect of Liquefaction Conditions on Acid Number

The acid number is an important parameter for evaluating the quality of bio-polyols. Excessive acidity may interfere with isocyanate reactions during foam synthesis. Therefore, controlling the acid number is essential for obtaining bio-polyols with suitable reactivity and processability for polyurethane production. Figure 2 illustrates the effects of reaction temperature and reaction time on the acid number of bio-polyols produced from spruce sawdust liquefaction using PCG and PCG/PEG solvent systems.

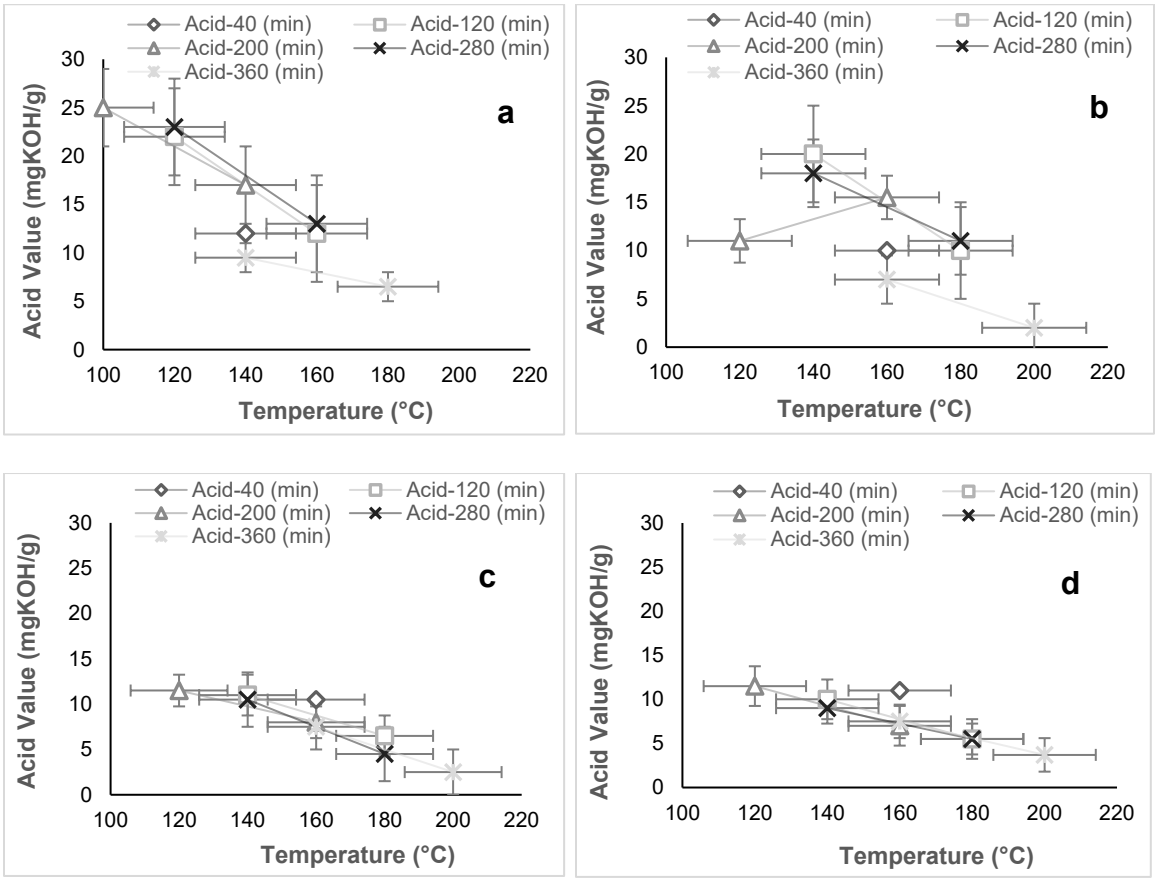

Fig. 2. The effect of processing temperature and time on the acid value of polyols. a: PCG, b: PCG/PEG (90/10), c: PCG/PEG (85/15), d: PCG/PEG (80/20)

For all solvent formulations, increasing reaction temperature generally resulted in a reduction in acid number. In the PCG system, the acid number decreased from approximately 25 mg KOH/g at 100 °C to 5.6 mg KOH/g at 180 °C. Similar behavior was observed for the PCG/PEG systems. After 200 min of liquefaction, the acid number decreased from 22 to 7 mg KOH/g for the PCG/PEG (90/10) system, from 11.5 to 2.5 mg KOH/g for PCG/PEG (85/15), and from 11.5 to 3.7 mg KOH/g for PCG/PEG (80/20) as the temperature increased from 120 to 200 °C. The reduction in acid number with increasing temperature can be attributed to enhanced esterification and condensation reactions occurring between fatty acids, glycerol, PEG molecules, and biomass degradation products. Elevated temperatures accelerate these reactions, promoting the consumption of acidic species and reducing the concentration of free carboxylic groups in the resulting bio-polyols (Hu and Li 2014; Chang *et al.* 2021). The incorporation of PEG significantly influenced acid number behavior. Compared with PCG alone, PCG/PEG mixtures exhibited lower acid values under identical reaction conditions. PEG molecules provide additional hydroxyl functionalities that can react with acidic intermediates generated during biomass depolymerization, thereby reducing the concentration of free acidic compounds in the liquefied product (Jo *et al.* 2015). Reaction time also affected the acid number of the resulting polyols.

In general, prolonged liquefaction led to lower acid values because esterification and secondary condensation reactions continued throughout the reaction period. For example, at a constant temperature of 160 °C, the acid number decreased from 17 to 15 mg KOH/g for the PCG/PEG (90/10) system, from 10.5 to 7.5 mg KOH/g for PCG/PEG (85/15), and from 9 to 7 mg KOH/g for PCG/PEG (80/20) when reaction time increased from 40 to 360 min. The observed trends indicate that both temperature and reaction time contributed significantly to the reduction of acidity in bio-polyols.

Increasing the reaction severity beyond the optimum conditions did not further improve polyol quality. At temperatures above approximately 180 °C for the PCG system, extensive secondary condensation and repolymerization reactions became dominant because of the relatively high impurity content of crude glycerol. As a result, liquefaction became unstable and further experiments at higher temperatures were not conducted. In contrast, the addition of PEG reduced the viscosity of the reaction medium and improved process stability, allowing the reaction temperature to be increased to 200 °C.

Table 4. ANOVA Results Related to the Regression Equations in Design Expert for the Acid Number of Polyols

Liquefaction Solvent (wt%)	Equation	Sum of Squares	Mean Square	F Value	P-Value Prob > F	Lack of Fit	Standard Error	R^2	Adj. R2
PCG	Y=17.58-3.34A–0.66B +0.28AB+1.55A^2+0.24B^2	238.08	118.54	222	<0.0001	4.73	0.73	0.9780	0.9736
PCG/PEG, 90/10	Y=15.35-3.92A–0.25B +0.75AB+2.22A^2+0.84B^2	184.83	92.42	185.11	<0.0001	1.29	1.04	0.9445	0.9334
PCG/PEG, 85/15	Y=8.37-2.69A–0.66B +0.37AB+0.22A^2+0.10B^2	53.39	10.68	164.34	<0.0001	4.41	0.41	0.9817	0.9664
PCG/PEG, 80/20	Y=7.33-2.13A-0.43B+ 0.13AB+0.14A^2+0.17B^2	58.00	11.60	432.92	<0.0001	0.56	0.16	0.9968	0.9945

Y: Response (Acid number), A: Temperature, B: Time

The statistical analysis presented in Table 4 confirms the significance of the developed response surface models. For all solvent systems, the regression models exhibited high coefficients of determination ($R^2 > 0.94$), indicating excellent agreement between experimental and predicted values. The regression equation after the analysis of variances (ANOVA) gave the level of acid number as a function of the reaction time and temperature. The empirical relationship between acid number (Y) and the two test variables in coded units obtained by the application of RSM is given by equations in table 4, where Y is acid value (mg KOH/g), A and B are reaction temperature (°C) and time (min). The model F-value and P-values ($P < 0.0001$) further demonstrate that reaction temperature, reaction time, and their interaction significantly affected the acid number of the produced bio-polyols.

Among all formulations, the PCG/PEG (80/20) system produced the most desirable bio-polyol, exhibiting an acid number of 3.7 mg KOH/g under optimized liquefaction conditions. Such low acidity is advantageous for polyurethane synthesis because it minimizes side reactions with isocyanates and improves process controllability during foam production.

Effect of Liquefaction Conditions on Hydroxyl Number

The hydroxyl number is one of the most important characteristics of bio-polyols because it directly determines their reactivity toward isocyanates and influences the crosslinking density and mechanical performance of the resulting polyurethane materials. Therefore, understanding the effects of liquefaction parameters on hydroxyl functionality is essential for optimizing bio-polyol production. Figure 3 illustrates the effects of reaction temperature and reaction time on the hydroxyl number of bio-polyols produced from spruce sawdust liquefaction using PCG and PCG/PEG solvent systems.

For all solvent formulations, the hydroxyl number exhibited a decreasing trend with increasing reaction temperature and reaction time. For the PCG system, increasing the temperature from 100 to 180 °C at a reaction time of 200 min reduced the hydroxyl number from approximately 340 to 315 mg KOH/g. Similar behavior was observed for the binary solvent systems. The hydroxyl number decreased from 350 to 295 mg KOH/g for PCG/PEG (90/10), from 282 to 259 mg KOH/g for PCG/PEG (85/15), and from 285 to 262 mg KOH/g for PCG/PEG (80/20) as the reaction temperature increased.

The observed decrease in hydroxyl number can be attributed to the progressive consumption of hydroxyl-containing compounds during liquefaction. At elevated temperatures, depolymerized biomass fragments undergo secondary reactions such as esterification, etherification, dehydration, and condensation. These reactions consume free hydroxyl groups and consequently reduce the hydroxyl number of the resulting bio-polyols. Similar trends have been reported for lignocellulosic biomass liquefaction in polyhydric alcohol media, where increasing reaction severity promoted biomass conversion while simultaneously reducing hydroxyl functionality (Jo *et al.* 2015; Kosmela *et al.* 2016; Chang *et al.* 2021; Wu *et al.* 2024)

Reaction time showed a comparable effect. At 140 °C, increasing the liquefaction time from 40 to 360 min reduced the hydroxyl number of PCG-based polyols from approximately 360 to 335 mg KOH/g. Likewise, at 160 °C, the hydroxyl number decreased from 320 to 295 mg KOH/g for PCG/PEG (90/10), from 275 to 260 mg KOH/g for PCG/PEG (85/15), and from 269 to 261 mg KOH/g for PCG/PEG (80/20) as the reaction time increased from 40 to 360 min.

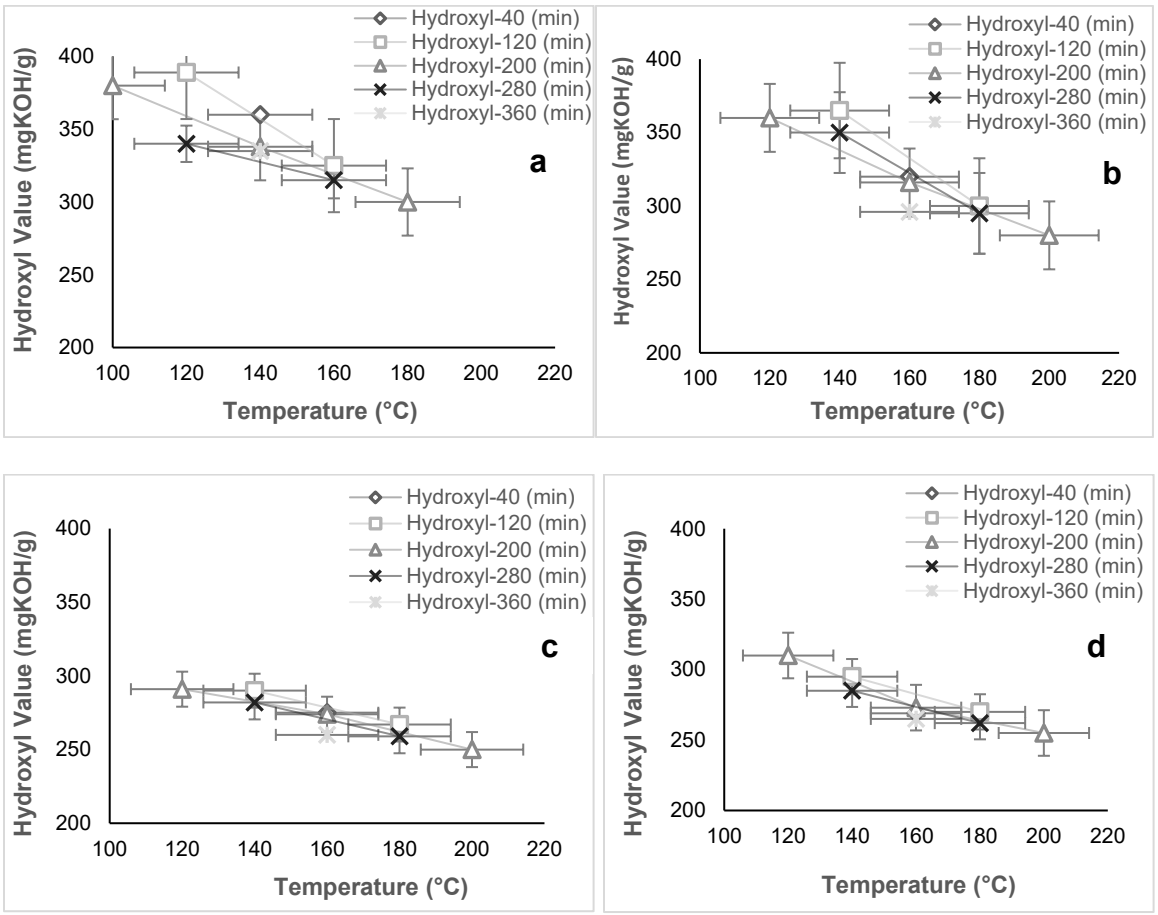

Fig. 3. The effect of process temperature and time on the hydroxyl number of polyols, a: PCG, b: PCG/PEG (90/10), c: PCG/PEG (85/15), d: PCG/PEG (80/20)

Although longer reaction times and higher temperatures reduced the hydroxyl number, they also enhanced biomass conversion. This inverse relationship is commonly observed during biomass liquefaction and reflects the balance between depolymerization and secondary condensation reactions. Initially, lignocellulosic macromolecules are cleaved into smaller fragments rich in hydroxyl functionalities. As the reaction progresses, some of these hydroxyl groups participate in secondary reactions, resulting in lower hydroxyl numbers despite higher liquefaction yields (Jo *et al.* 2015; Chang *et al.* 2021).

The incorporation of PEG significantly influenced the characteristics of the resulting bio-polyols. PEG acts not only as a liquefaction solvent but also as a reactive participant in solvolysis reactions, improving the accessibility of biomass components and promoting more efficient depolymerization. Consequently, PCG/PEG systems exhibited improved liquefaction performance while maintaining hydroxyl numbers within the range typically required for PU foam production. According to previous studies, hydroxyl numbers between 200 and 350 mg KOH/g are generally suitable for rigid and semi-rigid polyurethane applications (Hu *et al.* 2012; Hu and Li 2014). The hydroxyl numbers obtained in the present study therefore indicate that all synthesized bio-polyols possessed sufficient reactivity for polyurethane synthesis.

The statistical analysis presented in Table 4 confirmed the adequacy of the developed response surface models. All regression models were highly significant ($P < 0.0001$), indicating that reaction temperature and reaction time strongly affected hydroxyl

number development. Although the PCG/PEG (90/10) formulation exhibited a slightly lower coefficient of determination (R^2) than the other solvent systems, the model remained statistically significant and adequately described the experimental behavior. This deviation may be attributed to the transitional nature of the solvent composition, where the competing effects of CG-derived components and PEG on hydroxyl-group formation and consumption occurred simultaneously, resulting in greater experimental variability. Nevertheless, the obtained coefficient of determination remained within an acceptable range for process optimization studies and did not affect the predictive capability of the model.

Table 5. ANOVA Results Related to the Regression Equations in Design Expert for the Hydroxyl Number of Polyols

Liquefaction Solvent (wt%)	Equation	Sum of Squares	Mean Square	F Value	P-Value Prob > F	Lack of Fit	Standard Error	R2	Adj. R2
PCG	Y=535.52-43.75A-12.08B+8.75AB+19.22A^2-4.84B^2	6537.08	2172.08	62.73	<0.0001	4.39	5.89	0.9544	0.9391
PCG/PEG, 90/10	Y=316.54-23.33A–5.83B-7.55AB-21.72A^2-3.34B^2	6941.67	3470.83	25.16	<0.0001	7.30	11.75	0.8342	0.8011
PCG/PEG, 85/15	Y=275.69-10.67A–3.83B+2.50AB-1.08A^2-1.83B^2	1626.39	325.29	22.42	<0.0001	2.51	3.81	0.9412	0.8992
PCG/PEG, 80/20	Y= 273.84-13.48A–1.67B+1.45AB+2.24A^2-2.12B^2	2527.97	505.60	106.47	<0.0001	1.15	2.16	0.9870	0.9778

Y: Response (Hydroxyl number), A: Temperature, B: Time

Among the investigated formulations, the PCG/PEG (80/20) solvent system produced bio-polyols with a hydroxyl number of approximately 255 mg KOH/g under optimum liquefaction conditions. This value falls within the range generally reported for rigid polyurethane polyols (Bontas *et al.* 2023). Overall, the results demonstrate that hydroxyl number is strongly influenced by reaction severity. While increasing temperature and reaction time improve biomass liquefaction efficiency, excessive reaction severity promotes hydroxyl-group consumption through secondary reactions. Therefore, optimization of liquefaction conditions is necessary to achieve high biomass conversion while preserving sufficient hydroxyl functionality for polyurethane applications.

Effect of Liquefaction Conditions on Polyol Viscosity

Viscosity is a critical parameter affecting the processing behavior of bio-polyols and their subsequent application in PU foam production. Polyols with excessively high viscosity may hinder mixing efficiency, reduce reaction homogeneity, and negatively affect foam morphology. Therefore, controlling viscosity during biomass liquefaction is essential for obtaining bio-polyols with suitable processing characteristics. Figure 4 illustrates the effects of reaction temperature and reaction time on the viscosity of bio-polyols produced from spruce sawdust liquefaction using PCG and PCG/PEG solvent systems. In general, viscosity increased with increasing reaction temperature for all solvent formulations.

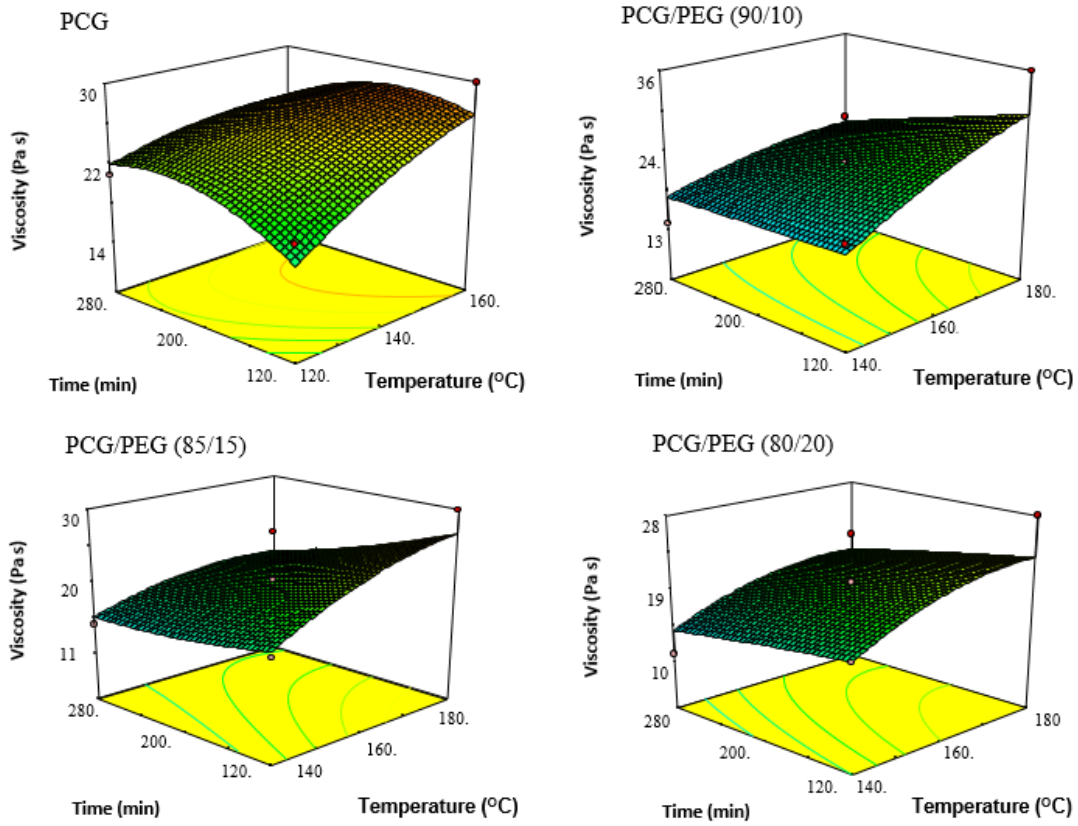

Fig. 4. The effect of process temperature and time on the viscosity of polyols

For PCG-based liquefaction, the viscosity increased from approximately 4 Pa·s at 100 °C to 13 Pa·s at 180 °C. Similar trends were observed for the binary solvent systems. The viscosity of the PCG/PEG (90/10) polyol increased from approximately 10 to 24 Pa·s, whereas values ranging from 10 to 19 Pa·s and from 7 to 15 Pa·s were observed for the PCG/PEG (85/15) and PCG/PEG (80/20) formulations, respectively.

The increase in viscosity with reaction temperature can be attributed to the formation of higher-molecular-weight compounds through condensation, etherification, and repolymerization reactions. At elevated temperatures, depolymerized biomass fragments may undergo secondary reactions, producing larger molecular structures that increase the resistance to flow. Simultaneously, evaporation of volatile compounds and partial solvent loss may further contribute to viscosity development (Hu *et al.* 2012; Hu and Li 2014).

Reaction time also significantly affected viscosity. During the early stages of liquefaction, biomass depolymerization predominates, generating smaller molecular fragments. However, prolonged reaction times favor condensation reactions among these intermediates, leading to gradual increases in molecular weight and viscosity. Similar behavior has been reported in previous studies on lignocellulosic biomass liquefaction (Xu *et al.* 2013; Chang *et al.* 2021). The incorporation of PEG significantly improved the rheological behavior of the resulting bio-polyols. Compared with crude glycerol alone, PEG-containing systems exhibited lower viscosities under equivalent liquefaction conditions. This behavior can be attributed to the flexible molecular structure and lower

intermolecular interaction strength of PEG, which improves molecular mobility and reduces resistance to flow (Xu *et al.* 2013; Jo *et al.* 2015).

The RSM presented in Table 6 demonstrated excellent agreement with experimental data, with coefficients of determination exceeding 0.95 for all solvent systems. The low P-values ($P < 0.0001$) confirmed that both reaction temperature and reaction time significantly influenced viscosity development during liquefaction.

Table 6. ANOVA Results Related to the Regression Equations in Design Expert for Viscosity of Polyols

Liquefaction Solvent (wt%)	Equation	Sum of Squares	Mean Square	F Value	P-Value Prob > F	Lack of Fit	Standard Error	R2	Adj. R2
PCG	Y=30.31+1.17A–1.33B-2.50AB+1.96A^2-0.54B^2	58.48	11.69	14.02	<0.0001	5.66	0.91	0.9092	0.8443
PCG/PEG, 90/10	Y=26.54-1.20A–3.03B-2.08AB-1.20A^2+0.86B^2	59.02	11.83	43.16	<0.0001	4.30	0.52	0.9687	0.9462
PCG/PEG, 85/15	Y=28.16-1.90A–2.53B-1.40AB-0.97A^2+0.71B^2	113.74	22.75	50.42	<0.0003	4.01	0.67	0.9807	0.9614
PCG/PEG, 80/20	Y=27.05-1.84A–2.67B-1.50AB-1.09A^2+0.66B^2	185.31	37.06	59.47	<0.0001	1.22	0.79	0.9770	0.9606

Y: Response (Viscosity), *A*: Temperature, *B*: Time

Effect of Liquefaction Conditions on Biomass Conversion Ratio

Biomass conversion ratio is one of the most important indicators of liquefaction efficiency because it reflects the extent to which lignocellulosic components are transformed into soluble products. Higher conversion ratios indicate more effective depolymerization and improved utilization of biomass feedstocks. The effects of reaction temperature and reaction time on biomass conversion are presented in Fig. 5.

For all solvent systems, biomass conversion increased with increasing reaction temperature and reaction time. For PCG liquefaction, increasing the reaction temperature from 100 to 180 °C enhanced biomass conversion from approximately 14% to 47%. Similarly, conversion increased substantially in the binary solvent systems. At a reaction time of 200 min, biomass conversion increased from 16% to 54% for PCG/PEG (90/10), from 29% to 66% for PCG/PEG (85/15), and from 37% to 80% for PCG/PEG (80/20) as the temperature increased from 120 to 200 °C.

The positive effect of temperature can be attributed to accelerated solvolysis and depolymerization reactions. Elevated temperatures increase solvent penetration into the biomass matrix and promote cleavage of ether and glycosidic linkages present in lignin, cellulose, and hemicellulose (Shi *et al.* 2016; Wu *et al.* 2024). Consequently, larger proportions of biomass are converted into soluble compounds (Kumar *et al.* 2014; Wu *et al.* 2024). Reaction time exhibited a similarly positive influence on biomass conversion. At constant temperatures, conversion ratios continuously increased with increasing reaction time due to prolonged exposure of biomass particles to the liquefaction medium. Extended reaction times promote further degradation of residual solid fractions and improve overall efficiency of liquefaction (Zhang *et al.* 2012a).

The addition of PEG significantly enhanced biomass conversion compared with PCG alone. PEG possesses excellent solvating properties and improves the accessibility of biomass components to the liquefaction medium. Furthermore, PEG participates in

solvolysis reactions and stabilizes intermediate degradation products, thereby suppressing recondensation reactions and increasing conversion efficiency (Jo *et al.* 2015).

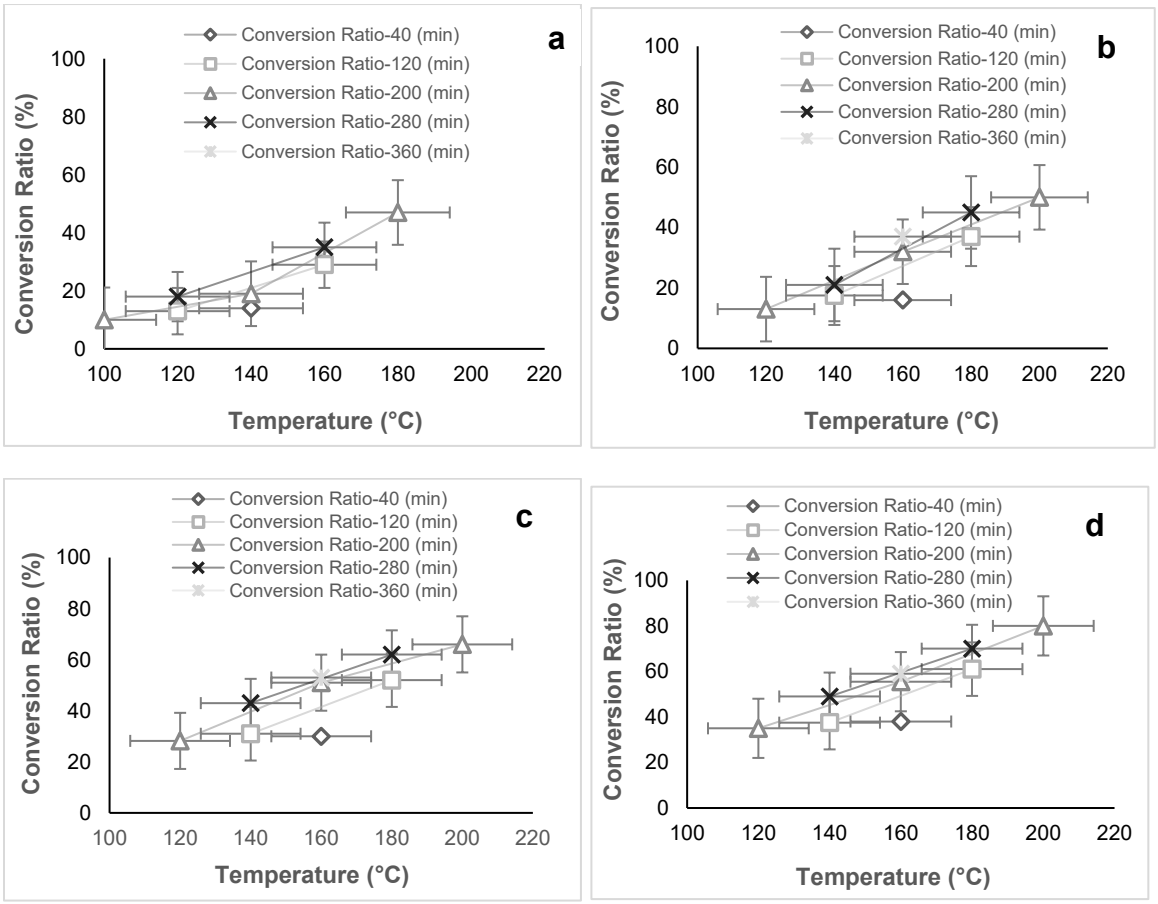

Fig. 5. The effect of process temperature and time on biomass conversion ratio, a: PCG, b: PCG/PEG (90/10), c: PCG/PEG (85/15), d: PCG/PEG (80/20)

Statistical analysis confirmed the significance of temperature, reaction time, and their interaction effects on biomass conversion. The RSM exhibited excellent predictive capability, with coefficients of determination ranging from 0.97 to 0.99 (Table 7).

Table 7. ANOVA Results Related to the Regression Equations in Design Expert for Conversion Ratio of Biomass

Liquefaction Solvent (wt%)	Equation	Sum of Squares	Mean Square	F Value	P-Value Prob > F	Lack of Fit	Standard Error	R2	Adj. R2
PCG	Y=33.72-0.75A+5.58B-3.25AB-6.14A^2-1.14B^2	1185.48	237.09	99.78	<0.0001	5.31	1.54	0.9862	0.9763
PCG/PEG, 90/10	Y=31.48+9.72A+4.55B+1.35AB-0.033A^2-1.28B^2	1429.02	285.83	87.16	<0.0001	2.55	1.80	0.9843	0.9731
PCG/PEG, 85/15	Y=30.31+1.17A–1.33B-2.50AB+1.96A^2-0.54B^2	1672.74	334.75	76.42	<0.0003	2.01	0.67	0.9996	0.9982
PCG/PEG, 80/20	Y=55.44+11.25A+5.34B-0.73AB+0.53A^2-1.79B^2	1962.31	392.06	33.47	<0.0001	0.68	0.34	0.9996	0.9993

Y: Response (Conversion ratio), A: Temperature, B: Time

These results demonstrate that the developed models accurately described the relationship between liquefaction conditions and conversion efficiency. Among all investigated solvent systems, PCG/PEG (80/20) exhibited the highest conversion efficiency, achieving approximately 80% biomass conversion under optimized liquefaction conditions. This result confirms the beneficial role of PEG in promoting biomass liquefaction and improving bio-polyol production.

Mechanistic Interpretation of Temperature and Time Effects

The observed changes in polyol properties can be explained by the complex reaction pathways occurring during lignocellulosic biomass liquefaction. Biomass liquefaction involves a combination of solvolysis, depolymerization, hydrolysis, dehydration, hydrogenolysis, and condensation reactions that occur simultaneously and whose relative contributions vary with reaction severity (Kumar *et al.* 2014). Temperature is a key parameter governing these reactions. Increasing temperature accelerates the cleavage of ether bonds in lignin and glycosidic bonds in cellulose and hemicellulose, leading to enhanced biomass conversion. Consequently, larger quantities of soluble intermediates and polyol precursors are generated. However, excessive temperatures may also promote secondary condensation and repolymerization reactions, which consume hydroxyl groups and increase molecular weight, thereby affecting hydroxyl number and viscosity (Shi *et al.* 2016; Chang *et al.* 2021).

Reaction time exerts a similar influence. During the initial stages of liquefaction, hemicellulose, lignin, and amorphous cellulose are rapidly degraded due to their relatively accessible structures. In contrast, crystalline cellulose is more resistant to solvent penetration and degrades more slowly (Zhang *et al.* 2012a; Zhang *et al.* 2012b). As liquefaction proceeds, additional biomass components become solubilized, increasing biomass conversion. However, prolonged reaction times may eventually favor condensation reactions among degradation products, reducing hydroxyl functionality and increasing viscosity.

The behavior observed in PCG-based liquefaction differs slightly from that of conventional polyhydric alcohol systems due to the presence of impurities such as fatty acids, soaps, glycerides, and residual methyl esters. These compounds participate in esterification and transesterification reactions, influencing acid number, hydroxyl number, and viscosity development during liquefaction (Hu *et al.* 2012; Hu and Li 2014). The incorporation of PEG modifies the reaction environment and enhances solvent effectiveness. PEG improves biomass swelling, increases solvent penetration, and facilitates depolymerization reactions. Furthermore, PEG contributes to the formation of more homogeneous polyol structures and suppresses excessive condensation reactions, resulting in improved liquefaction efficiency and more favorable physicochemical properties (Jo *et al.* 2015; Xu *et al.* 2013). The results indicate that bio-polyol quality depends on achieving an appropriate balance between depolymerization and condensation reactions. Considering all measured physicochemical properties together, including hydroxyl number, acid number, viscosity, and biomass conversion, the optimized PCG/PEG formulation (80/20) exhibited characteristics comparable to those reported for bio-polyols used in rigid polyurethane formulations, which was reported on our previous research (Rastegarfar *et al.* 2018).

The highest biomass conversion obtained in the present study was approximately 80%, which is somewhat lower than the values reported for liquefaction systems employing purified glycerol or conventional glycerol/PEG solvent mixtures. This difference is

primarily attributed to the use of industrial crude glycerol derived from mixed waste vegetable oils. Compared with purified glycerol, this crude glycerol contained relatively high concentrations of impurities, which reduced the effective glycerol content available for biomass liquefaction and consequently limited the overall conversion efficiency.

In addition, temperatures higher than 180 °C for the PCG system and 200 °C for the PCG/PEG systems were not investigated because preliminary experiments showed that severe condensation and rapid viscosity increase occurred under these conditions, leading to process instability and preventing further liquefaction. Although increasing the PEG content beyond 20 wt% could potentially improve biomass conversion by reducing viscosity and enhancing solvent mobility, the present study intentionally limited PEG addition to 20 wt% in order to evaluate whether satisfactory liquefaction efficiency could be achieved while minimizing the consumption of additional chemical solvent. Approximately 20% of the biomass remained as an insoluble residue under the optimum conditions. This residue most likely consisted of highly condensed lignin fragments together with crystalline cellulose, which are known to be more resistant to liquefaction under the investigated conditions (Zhang *et al.* 2012a; Shi *et al.* 2016). Because the primary objective of this work was the optimization of bio-polyol production, the chemical characterization of the residual solids was beyond the scope of the present study.

Future Work

Future research should focus on improving the biomass conversion efficiency while preserving desirable hydroxyl functionality through further optimization of liquefaction conditions and solvent composition. In addition, the influence of different industrial crude glycerol sources and their compositional variability on liquefaction behavior and bio-polyol quality should be systematically investigated. Further characterization of bio-polyols and valorization of the insoluble liquefaction residue could also contribute to improving the overall resource efficiency and sustainability of the process. Finally, scale-up studies, process optimization, and techno-economic and life-cycle assessments are recommended to evaluate the industrial feasibility of producing bio-polyols from lignocellulosic biomass and crude glycerol within a circular bioeconomy framework

CONCLUSIONS

1. Spruce sawdust was successfully liquefied using industrial crude glycerol (CG) derived from mixed waste vegetable oils and crude glycerol/polyethylene glycol solvent systems under acid-catalyzed conditions to produce bio-polyols.

2. The bio-polyol product was a blend of biomass-derived fragments and the incorporated polyol-based solvents (PCG, PEG) that actively participated in the liquefaction process.

3. Reaction temperature and reaction time significantly affected biomass conversion, hydroxyl number, acid number, and viscosity, confirming that these variables are the principal processing parameters governing bio-polyol quality.

4. Increasing reaction severity enhanced biomass conversion but simultaneously promoted secondary condensation reactions, resulting in decreased hydroxyl number and increased viscosity. Therefore, optimization was necessary to achieve an appropriate balance among these properties.

5. The incorporation of poly(ethylene glycol) (PEG) improved solvent performance by increasing biomass conversion while reducing viscosity and maintaining hydroxyl numbers within the desirable range for rigid polyurethane formulations.

6. Among the investigated formulations, the CG/PEG (80/20) solvent system exhibited the best overall performance. Under optimized conditions (200 °C and 200 min), biomass conversion reached approximately 80%, while the bio-polyol exhibited an acid number of 3.7 mg KOH/g, a hydroxyl number of 255 mg KOH/g, and a viscosity of 15 Pa·s.

7. The obtained bio-polyols exhibited characteristics suitable for potential polyurethane foam production and demonstrated an effective pathway for the valorization of lignocellulosic residues and biodiesel-derived crude glycerol.

8. This study demonstrates a practical route for the simultaneous valorization of spruce sawdust and industrial crude glycerol derived from mixed waste vegetable oils, contributing to the sustainable utilization of renewable resources and biodiesel by-products within a circular bioeconomy framework.

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