WOOD2WOOD

A Wood-to-Wood Cascade Upcycling Valorisation Approach

» Deliverable 9.2

Liquefaction process of mixed wood waste

WP No.	9
WP Title	Chemical and Bioremediation Technologies for Wood Waste Upcycling (TRL5)
WP Leader	LERMAB
Due Date:	30/06/2025
Submission Date	30/06/2025
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Status	Draft
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PROJECT INFORMATION

GA Number	101138789
Project Full Title	Wood2Wood Project
Project Acronym	W2W
Funding Scheme	Horizon RIA
Start Date	01/01/2024
Duration	48 months
Coordinator	Dr. Angelos Amditis, Research and Development Director, ICCS
Project Website	In progress

REVISION AND HISTORY CHART

Version	Date	Author	Description of changes
0.1	02/06/2025	PLH, MO, XE, FH, JL	Initial draft
0.2	18/06/2025	PLH, MO, XE, FH, JL	Reviewed version
1.0	30/06/2025	PLH, MO, XE, FH, JL	Final submitted version
2.0			Revised submitted version (if required)

Dissemination Level		
PU	Public	X
RE	Restricted to a group specified by the consortium	
CO	Confidential, only for members of the consortium (including the European Commission Services)	

Legal Disclaimer

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GLOSSARY OF ACRONYMS

Acronym	Extended Definition
BBD	Box-Benkhen Design
CC	Cyclic carbonate
CROP	Cationic Open Ring Polymerization
DMC	Dimethyl Carbonate
DMSO	Dimethyl Sulfoxide
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transformed Infrarred
G	Glycerol
HPSEC	High Performance Size Exclusion Chromatography
NIPU	Non-isocyanate polyurethane
OP	Oxyalkylated Polyol
PEG	Polyethylene glycol
PU	Polyurethane
RSM	Response Surface Methodolgy
Tg	Glass transition temperature
TGA	Thermogravimetric Analysis

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EXECUTIVE SUMMARY

Task 9.3 focuses on the synthesis of bio-polyols and the development of non-isocyanate polyurethanes (NIPUs) using waste wood and derived lignin as feedstock. The main achievements of this task are summarised below:

i. Waste wood from the furniture industry was chemically liquefied using a PEG/glycerol solvent system, and the process was optimised *via* a Box–Behnken design, reaching a yield of 94.5% under optimal conditions (164.85 °C, 90 min, L/S = 7).
ii. Cationic open-ring polymerization (CROP) of organosolv lignin was performed under acidic and basic catalysis. Acidic conditions yielded higher structural modifications, while alkaline catalysis showed limited efficiency.
iii. Structural and physicochemical characterization revealed that polyols from liquefaction (LP) had lower molecular weight, higher functionality (~3), and were liquid at room temperature, making them easier to process than the solid polyols obtained by CROP.
iv. Non-isocyanate polyurethanes (NIPUs) were synthesised *via* a two-step process: cyclic carbonate formation followed by reaction with hexamethylene diamine. Only the LP-derived formulation (L-NIPU) showed successful polymerization.
v. FTIR, DSC, and TGA analyses confirmed the formation of urethane bonds and appropriate thermal performance for L-NIPU, with a T_g around 55 °C and degradation onset at ~150 °C.
vi. CROP-based polyols failed to form proper NIPUs under the tested conditions. Structural and thermal analyses revealed incomplete reaction or pre-cured polymers due to high temperature or limited cyclic carbonate formation.
vii. Overall, liquefied polyols (LP) were validated as the most suitable candidate for NIPU synthesis, offering high reactivity, favourable processability, and properties compatible with adhesive applications in wood panel manufacturing.

1. INTRODUCTION

The increasing global demand for sustainable materials and the urgent need to reduce dependence on fossil-based resources have driven the development of innovative bio-based alternatives. The European Union's Green Deal and the Circular Economy Action Plan highlight the valorization of biomass residues as a key strategy for achieving climate neutrality and resource efficiency. In this context, wood waste—particularly from furniture production and construction—has emerged as an abundant, renewable feedstock for generating value-added bio-based chemicals and materials.

Among the broad spectrum of plastic materials, polyurethanes (PU) stand out in the industrial sector due to their remarkable versatility. Their adjustable mechanical properties make them suitable for a wide array of applications, including thermoplastics, foams, elastomers, adhesives, coatings, and sealants (Ponnusamy *et al.*, 2019; Haridevan *et al.*, 2021; Quinsaat *et al.*, 2021). PUs are typically synthesized through polyaddition reactions involving hydroxyl-containing components, primarily polyester or polyether polyols, together with diisocyanates and chain extenders. The fundamental chemical reaction occurs between hydroxyl (–OH) and isocyanate (–NCO) functional groups, resulting in the formation of urethane linkages. Consequently, the polymer backbone of PUs consists of repeating urethane units formed through the stepwise reaction of polyols, low molecular weight chain extenders, and diisocyanates (Mahmood *et al.*, 2016).

However, the key chemicals required for PU production are predominantly sourced from the petrochemical industry, contributing to a considerable environmental impact. Addressing this issue remains an ongoing challenge for the chemical sector, especially given the growing pressure from increasingly strict environmental regulations. In response, the PU industry is exploring more sustainable alternatives. One of the most promising strategies is the elimination of isocyanates, the most hazardous component in conventional PU synthesis, through the development of non-isocyanate polyurethanes (NIPUs)—a safer and more environmentally friendly class of materials.

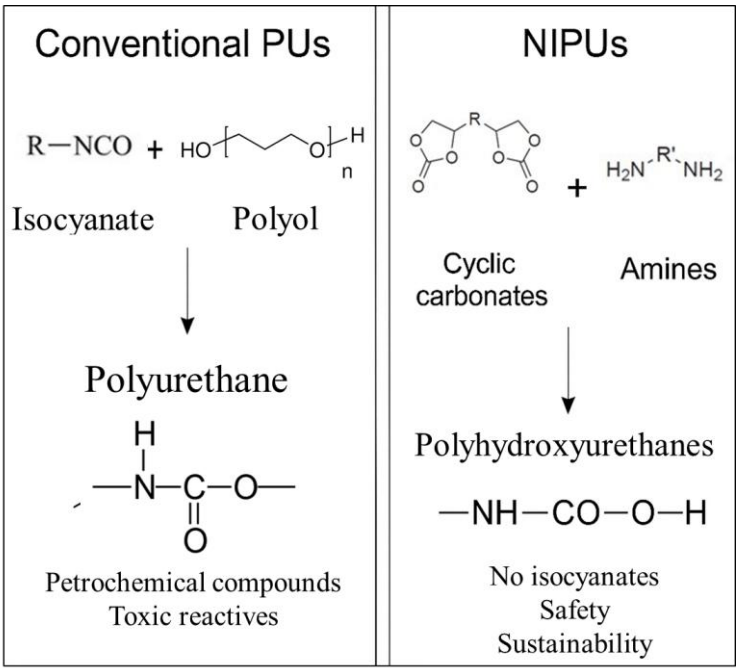

Figure 1. Comparative Synthesis Pathways for Polyurethanes: Traditional and Non-IsocyanateThe second course of action involves replacing petroleum-based polyols, isocyanates, and chain

extenders with bio-based counterparts. Over the past decades, the feasibility of obtaining these components from biomass has been extensively studied. Notable bio-based raw materials include vegetable oils (Fridrihsone *et al.*, 2020), fatty acids (Paraskar and Kulkarni, 2020), fatty acid methyl esters (FAME) (Mohd Norhisham *et al.*, 2017), crude glycerol (Cui, Liu and Li, 2017) and various compounds derived from lignocellulosic biomass, such as, lignin (Li, Luo and Hu, 2015).

Task 9.3 focuses on the valorization of industrial wood residues through the synthesis of bio-polyols *via* two approaches: liquefaction of waste wood and cationic open-ring polymerization (CROP) of lignin obtained from the waste wood. These bio-polyols are then employed in the formulation of NIPUs *via* a two-step process involving cyclic carbonate intermediates. The work includes the optimization of the liquefaction process, the structural and thermal characterization of the resulting polyols, and the evaluation of their reactivity and performance in NIPU synthesis. Through this approach, Task 9.3 contributes to the broader objective of replacing fossil-based polyurethanes with bio-based, non-toxic alternatives derived from waste biomass.

2. EXPERIMENTAL METHODS

In this chapter, the process carried out for the elaboration of bio-polyols by using the waste wood coming from furniture industry and lignin is depicted. Furthermore, the subsequent steps followed in the preparation of non-isocyanate polyurethanes are described.

2.1. SYNTHESIS OF POLYOL VIA LIQUEFACTION

2.1.1. Liquefaction reaction, purification and neutralization

The process for the synthesis of the bio-polyols had a previous work carried out within our research group by Da Silva et al. 2019 as starting point (da Silva, Egüés and Labidi, 2019). For the liquefaction, a glass round bottom-three neck flask with a volume of 1L was used as reactor, provided with a mechanical paddle blade stirrer, a thermocouple and a reflux condenser. Concerning the raw materials and reagents, the wood waste and a mixture Polyethylene Glycol/Glycerol PEG/G (60/40 w/w) were fed into the reactor with the corresponding ratio of solid to liquid. Then, sulphuric acid 4.5% w/w with respect to the solvent was added as catalyst. The reaction was run at the selected conditions of temperature and time until completion. Once the liquefaction was finished, acetone was added to the raw bio-polyols obtained and filtered with cellulose filters (12µm) under vacuum, to remove the insoluble solid residue. Finally, the remaining bio-polyols were purified by means of rotatory evaporator to recover the acetone added previously and they were neutralized to pH 6-7.

2.1.2. Optimization process for the liquefaction reaction

The previously described process of liquefaction was optimized using a Box-Behnken experimental design combined with a response surface methodology, to elucidate the more convenient conditions for the production of the bio-polyols.

A response surface methodology (RSM) was used to determine the effect of the independent variables: Temperature (°C), Time (min) and Liquid to solid ratio (v/w) on the yield (%) of bio-polyols. A three block Box-Benkhen Design (BBD), was selected for the experimental design and optimisation which consisted in some experiments with three runs of the central point to evaluate the pure error.

The experimental variables considered in this study (**Table 1**), include the fixed variables, the independent variables, as well as the dependent ones including the corresponding variation ranges of each variable.

Table 1: Experimental variables involved in the study.

Variable	Definition	Units
Fixed	Catalyst	%wt.
	PEG/Glycerol	v/v
Independents	Temperature	°C
	Time	min
	L/S*	v/w
Dependents	Yield	%wt.
	Molecular weight	g/mol

*Liquid to solid ratio (L/S)

2.2. SYNTHESIS OF POLYOL VIA CATIONIC OPEN RING POLYMERIZATION

2.2.1. Reaction of cationic open ring polymerization

This type of reaction was performed as an alternative to the liquefaction process previously presented, since it allows the utilization of milder conditions of temperature and pressure and it usually results in a more homogeneous polymer. Two catalytic approaches were tested: alkaline (catalyst 1) and acidic (catalyst 2). Reactions were carried out between 25–40 °C to avoid boiling of butylene oxide (Tb = 65 °C).. The procedure of the reaction was based on previous works from the literature (Lee, Park and Lee, 2017; Perez-arce *et al.*, 2021; Wu *et al.*, 2021; Lorenzo *et al.*, 2025). The different reactions previously described and the oxyalkylated polyols obtained are presented next in **Table 2**.

Table 2: Formulations of polyols obtain by means of open ring polymerization.

Reaction catalyst	Temperature [°C]	Time [h]	Polyol formulation
Catalyst 1	T1	24	OP_1
	T2		OP_2
Catalyst 2	T1	24	OP_3
	T2		OP_4

2.2.2. Characterization of bio-polyols

The chemical structure of the polyols was elucidated by means of Fourier Transformed Infrared Spectroscopy analysis (FTIR). In addition to that, the molecular weight of the polyols was also determined by high-performance size exclusion chromatography (HPSEC). The determination of hydroxyl groups (–OH) and the acid number of the polyols was carried out in accordance with ASTM E1899-23 and ASTM D974, respectively, following the methodology described below. In both cases, the quantification of the functional groups—hydroxyl (–OH) and acidic—was performed by

potentiometric titration using an automatic titrator (888 Titrando, Metrohm) operated *via* Tiamo 2.5 software.

2.3. PRODUCTION OF NON-ISOCYANATE POLYURETHANES (NIPU)

2.3.1. Reaction for the synthesis of non-isocyanate polyurethanes (NIPU)

The production of non-isocyanate polyurethanes (NIPUs) involved a two-step process: synthesis of cyclic carbonate (CC) intermediates, followed by polyurethane formation. In the first step, bio-polyols, dimethyl carbonate (DMC), and potassium carbonate (K_2CO_3) were reacted in a 1:5:0.5 molar ratio at 75 °C for 24 h. The resulting dark, viscous CC was used in the next stage.

In the second step, CC was reacted with hexamethylene diamine (HMDA) at a 1:1 molar ratio at 160 °C for 1 h, yielding a dark, sticky NIPU material.

In **Table 3**, the different formulations of the products synthesized is shown.

Table 3. Formulations cyclic carbonates and non-isocyanate polyurethane product synthesized

Raw materials [polyol]	Intermediates [cyclic carbonates]	NIPU formulation
LP (liquefaction polyol)	LCC	L-NIPU
OP_1	CC_1	$NIPU_1$
OP_2	CC_2	$NIPU_2$
OP_3	CC_3	$NIPU_3$
OP_4	CC_4	$NIPU_4$

2.3.2. Characterization of non-isocyanate polyurethane (NIPU)

The different formulations of non-isocyanate polyurethanes (NIPU) were analysed concerning their structure and thermal properties. The chemical structure of the NIPUs, was analysed by Fourier Transform Infrared Spectroscopy analysis (FTIR). The thermal performances of the NIPUs, were assessed by thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC).

3. RESULTS AND DISCUSSION

3.1. OPTIMIZATION OF SYNTHESIS OF POLYOL VIA LIQUEFACTION

As previously mentioned in section 2.1.2, a response surface methodology (RSM) combined with a Box–Behnken experimental design was employed to optimise the reaction conditions for the production of bio-polyols with tailored properties. This statistical approach allows for the evaluation of the individual and interactive effects of multiple variables on the response, thereby facilitating the identification of optimal operational parameters.

The experimental design was created using Statgraphics software, which generated a matrix of experiments aimed at efficiently exploring the design space. The experimental conditions tested, along with the corresponding laboratory measurements obtained for the dependent variables,

namely the polyol yield and molecular weight. The yield values ranged from 24.89% (exp. 5) to 96.03 % (exp. 10). Otherwise, the molecular weight of the obtained polyols varied from 440 g/mol (Exp. 6) to 1233 g/mol (Exp. 12).

An optimisation process was undertaken to determine the optimal conditions for maximising polyol yield. The conditions identified, as presented in **Table 4**, correspond to a theoretical yield of 100%. The reaction parameters were systematically varied to determine the specific values of the independent variables that lead to the highest polyol production. The optimized reaction settings are summarised in **Table 4,** which includes both the normalised and non-normalised values of the independent variables. These conditions correspond to a theoretical yield of 100%.

Table 4: Not normalised and normalised values of the independent variables for the optimal point.

Independent variables	Normalized values	Not-normalized values
Temperature (°C)	0.99	164.85
Time (min)	1	90
L/S (v/w)	1	7

To verify the model, a triplicate of each experiment was performed under the optimal reaction conditions, resulting in a reaction yield of 94.05 ± 1.41 %. These experimental results were compared with the theoretical yield (100 %). As a result of this comparison, it was established that the experimental results were in good concordance with the data predicted by the software, and therefore, the Box-Behnken design was validated. Once the model was validated and its reliability confirmed, a preliminary scale-up of the process was conducted to assess the reproducibility and robustness of the identified optimal conditions.

3.2. CHARACTERIZATION OF POLYOLS FORMULATIONS

In this section all the results from the characterization of the bio-polyols formulations produced, both from wood waste and lignin derived ones, are presented.

3.2.1. Structural characterization

The different biopolyol formulations synthesized were analyzed first regarding their molecular weights. Polyols produced via oxyalkylation show significantly higher molecular weights (2338–2588 g·mol^{-1}) compared to those from liquefaction (760 g·mol^{-1}). Acid-catalyzed oxyalkylation yields slightly higher molecular weights and polydispersity indices than basic conditions. It is noteworthy that the molecular weight of the polyol produced by liquefaction is lower than expected for this type of polyols (Hu, Luo and Li, 2014), The lower molecular weight and polydispersity of liquefied polyols are attributed to raw material origin and a high lignin/solvent ratio, leading to unreacted solvent presence. Despite this, the lower polydispersity may benefit the reproducibility of the resulting non-isocyanate polyurethanes (NIPUs). I,

3.2.2. Physical-chemical characterization

The different bio-polyols synthesized were also characterized regarding their major physico-chemical parameters. Regarding the hydroxyl groups in the optimized polyol obtained through liquefaction of the raw material, it is worth noting that the hydroxyl index (I_{OH}) value obtained is very similar to those reported by other authors when liquefying lignin or non-delignified raw materials. Similarly, the acid number obtained is within the typical range for polyols produced

using this type of process and lignocellulosic feedstock (Hu, Luo and Li, 2014; Hernández-Ramos *et al.*, 2023).

On the other hand, the hydroxyl indexof the polyols obtained through lignin oxyalkylation showed divergent values between those synthesized under basic conditions and those produced under acidic conditions. In this regard, the former exhibited very similar I_{OH} and acid number (An) values regardless of the temperature used. In contrast, polyols synthesized under acidic conditions showed a tendency for the hydroxyl index (IOH) to increase with temperature.

3.3. CHARACTERIZATION OF NIPU FORMULATIONS

In this section, the results obtained from the analyses of the different non-isocyanate polyurethane formulations, are presented.

3.3.1. Structural characterization

The process for the production of non-isocyanate polyurethanes (NIPU) was monitored *via* FTIR analysis in two stages, namely synthesis of cyclic carbonate from biopolyols and synthesis of NIPUs from cyclic carbonates. Thus, through comparison of the FTIR spectra from each of the formulations it was possible to assess if the reaction achieved the final aim or not.

Based on these findings, it could be observed that the formation of cyclic carbonates as intermediate step for the synthesis of NIPU was more efficient in general with polyols obtained from liquefaction than with those of oxyalkylation since the former exhibited higher reactivity compared to the rest of the polyol, as indicated by their I_{OH} values and functionality . Concerning these last type, formulations OP3 and OP4 (acid catalysis) displayed greater structural changes compared to OP1 and OP2, as shown by the spectra of the corresponding cyclic carbonates.

Secondly, the final reaction for the elaboration of the non-isocyanate polyurethanes (NIPU) was assessed by FTIR. It was seen a broad band related to hydroxyl groups again in the range 3600-3100 cm^{-1}. In addition to this, in L-NIPU a signal embedded in this band was detected at 3300 cm^{-1} related to N-H bond stretching vibrations (Janvier, Ducrot and Allais, 2017). Next, the signal observed in the previous spectra of CCL, related to carbonyl group of cyclic carbonates was considerably reduced, owing to the reaction with the amine for the formation of polyurethanes. Nevertheless, the peaks confirming the formation of the polyurethanes were those detected at 1695 cm^{-1}, 1535 cm^{-1} and 1370 cm^{-1}, which corresponded to the carbonyl groups, amide moieties (N-H) and C-N linkages of polyurethanes correspondingly (Parcheta-Szwindowska, Rohde and Datta, 2022). Based on the signals obtained from the spectra of the different NIPU formulations, the previously commented signals were mostly found in the spectra of the NIPU formulation coming from the polyols obtained by liquefaction (L-NIPU). This observation suggests that the NIPU synthesis process was largely carried out using polyols derived from the liquefaction process (LP). Polyols obtained from cation open ring polymerization (OP1, OP2, OP3, OP4), though, either did not bring to completion the synthesis of polyurethanes or, due to the high temperature of the last stage, cured the polymer completely.

3.3.2. Thermal characterization

Besides, the structural characterization, non-isocyanate polyurethanes (NIPU) were also analysed concerning their thermal performance. With this aim, DSC analysis and TGA were performed.

On the one hand, the DSC analysis was carried out to elucidate the main thermal events and parameters. L-NIPU exhibited two main thermal events, namely endothermic and exothermic. The first one (90-125ºC) may be related to a process of evaporation either of some remaining unreacted reagents or solvent from the stages of synthesis or water present in the formulation due to the condensation reactions between the amine and the cyclic carbonates (Carré, Bonnet and Avérous, 2014). Once these compounds are evaporated, it was seen a second signal associated with a process of reticulation (curing) of the non-isocyanate polyurethane (NIPU). This event was detected at the range 160-180ºC approximately and it was related to deamination condensation of the hexamethylene diamine and formation of urethane bonds (Lee, Park and Wu, 2024). Moreover, this signal displayed two peaks that might be related to curing of both the reacted amine and the free one. The reticulation temperature range for this formulation was consistent with what has been published in other works from the literature(Saražin *et al.*, 2022; Wu *et al.*, 2025). In addition to that, in the second heating cycle, based on the inflexion point of the curve the glass transition temperature was studied. Even though it was challenging to detect this parameter, based on the software from the analysis it was found an inflexion point around 55 °C. In general, the T_g of the NIPUs is appearing at lower temperatures, however it has been reported that the utilization of biomass as raw material in the synthesis process can result in higher values for this property (Gholami *et al.*, 2021).

The NIPU formulations obtained with the polyols from cationic open ring polymerization, exhibit significantly different tendencies. For the cases of NIPU 1 and NIPU 2, very similar curves were obtained, with an endothermic signal in the range 110-150 °C and T_g at 50 °C approximately. NIPU 3, showed the most different results since no peaks were found within the range of temperatures in two heating process. In NIPU 4, a considerable endothermic event was found, but in this case, the range of temperatures was higher than for the cases of NIPU 1 and NIPU 2 (175-210 °C). Accordingly, in this formulation the mentioned event would be corresponding to the evaporation of unreacted and remaining hexamethylene diamine (T_{evap}=200 °C).

Likewise, in all the formulations no exothermic events were detected. This means that no reticulation was occurring during either of the heating cycles and therefore there was no formation of new urethane bonds. As mentioned previously, this could be associated to various reasons. On the one side, it was possible that since no clear cyclic carbonate formation was detected in the FTIR spectra, the final reaction with the amines was not taking place. On the other side, it could be that owing to the high temperature used during the reaction with the hexamethylene diamine, the NIPUs formed were already cured after synthesis reaction and therefore no reticulation events are seen in the DSC analysis.

Thereby, concerning the NIPU formulation based on polyols obtained *via* liquefaction (L-NIPU), three main stages of degradation were detected. The first one (150-190 °C) it could be related to some free HMDA, whose boiling point is around 190 °C. The second step (200-270 °C), was related to the initial decomposition of the samples, owing to low molecular weight substances and more unstable bonds e.g. ether (Xu *et al.*, 2020). The third stage was the most important one, it was depicted in the range 290-425 °C, and it was corresponding mostly to the degradation of the urethane groups (Chen *et al.*, 2022).

Regarding the NIPU formulations based on polyols obtain through cationic open ring polymerization (NIPU1-4), the thermograms showed discrepancies between each other and also

compared to L-NIPU. In this study, again similar tendencies were found in the formulations obtain under the same type of catalysis. Thus, NIPU 1 and NIPU 2 showed two main stages of degradation in the range 100-200 °C and at 300 °C. The first one would be most certainly related to the evaporation of solvent and unreacted compound from the synthesis, as described in the DSC analysis. The second one could be related the degradation of polymer of similar structure to polyurethanes, since it appeared in the same range but at a rather lower temperature compared to L-NIPU.

On the contrary, formulations NIPU 3 and NIPU 4, did not exhibited a clear pattern regarding their stages of degradation. In these cases, though, it was observed that the stage of maximal degradation was at a much lower temperature around 200 °C (especially for NIPU 4). This would probably mean that not cyclic carbonates were obtained in the intermediate stage, and thereby during the reaction with the amine the major part remained unreacted. Consequently, this degradation step would be associated with the evaporation of the HMDA as it was described in the DSC analysis.

4. CONCLUSIONS

Taking into consideration the previously presented results, several outcomes can be outlined and they are listed in this section.

First, it was confirmed that it was possible to obtain bio-polyols both from the wood waste coming from the industry and from the lignins extracted from the previously mentioned raw material. On the one hand, the first type of bio-polyols could be synthesized by means of a liquefaction treatment. This process was optimized to achieve the maximum efficiency and best properties of the obtained material, resulting in optimum conditions at 170 °C, 90 minutes and S:L ratio 1:7. In addition to that, it was determined during the optimization that these conditions had a prominent effect over the yield of the process. Nevertheless, other parameters of the polyols such as the molecular weight or their hydroxyl value, were not significantly influenced by the process conditions. This was attributed to the fact that the starting raw material displayed a considerable heterogeneous nature. On the other hand, the synthesis *via* cationic open ring polymerization (CROP) was also performed by using lignin as raw material. In this case, the conditions did influence the bio-polyols thus obtained. It was observed that the process carried out with alkaline catalysis was not very efficient in modifying the structure of the pristine lignins used a raw material. The reaction with acid catalysis though, achieved a higher degree of modification of the structure of the starting lignins.

The characterization of the different bio-polyols synthesized, provided useful information and it depicted the first differences regarding their properties. It was confirmed that the bio-polyols obtained through liquefaction exhibited better properties compared to those obtained by CROP. Thereby the first type presented better reactivity and a lower molecular weight, which are very convenient properties for their utilization in the synthesis of polyurethanes afterwards.

Concerning the elaboration of the non-isocyanate polyurethanes (NIPU), it was corroborated that the favourable parameters of the bio-polyols obtained by means of liquefaction resulted in a successful synthesis of the aimed polyurethanes. Additionally, these obtained polymers showed adequate thermal parameters (as shown by DSC and TGA analysis) for their utilization as adhesives

afterwards in the manufacturing of wood panels. On the contrary, the NIPU synthesis based on bio-polyols obtained by CROP, was not successful as it could not be confirmed the formation of urethane bonds, as based on the structural and thermal analysis. This would be associated with the fact that the bio-polyols obtained through CROP at milder conditions, presented a lower level of reactivity and a structure with a higher level of grafting. Therefore, more study should be done in this respect so that it would be possible to successfully synthesized NIPU formulations based on this type of bio-polyols.

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