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INFLUENCE OF BIOMASS TO GLYCEROL RATIO ON THE LIQUEFACTION OF OAK (*QUERCUS ROBUR*) AND HEMP (*CANNABIS SATIVA*) FOR USE IN FORMALDEHYDE-FREE ADHESIVES

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ABSTRACT

The increasing demand for sustainable materials has accelerated efforts to replace formaldehyde-containing adhesives in wood composites with bio-based alternatives. In this study, the liquefaction of oak wood (*Quercus robur*) and hemp stalks (*Cannabis sativa*) using glycerol as a solvent and sulfuric acid as a catalyst under controlled conditions (150 °C, 120 min) is investigated. Three ratios of biomass to solvent (1:3, 1:4, and 1:5) were analyzed. The oak biomass showed a liquefaction percentage of up to 93.88%, with insoluble residues between 6.12 and 14.45%, and a dry matter content between 50.13 and 54.78%. The hydroxyl number reached a maximum of 841.43 mg KOH/g, indicating a high density of reactive functional groups. Hemp biomass showed a liquefaction percentage of up to 91.64%, insoluble residues of 8.36 to 15.27%, a dry matter content between 57.19 and 63.28%, and a hydroxyl number of up to 829.61 mg KOH/g. Optimum results for both biomass types were achieved at a ratio of 1:5. These results emphasize the potential of liquefied oak and hemp as promising candidates for the development of formaldehyde-free adhesives that promote the use of environmentally friendly materials in the production of wood-based materials.

Keywords: oak, hemp, glycerol, liquefaction, hydroxyl number.

1. INTRODUCTION

The increasing global demand for energy and the environmental concerns associated with fossil fuel consumption have fueled efforts to develop renewable energy sources. Biomass has emerged as a promising alternative due to its renewability, biodegradability, and ability to be converted into fuels, chemicals, and energy carriers (Chowdhury *et al*., 2025). The efficient utilization of biomass requires an understanding of its chemical composition, especially cellulose, hemicellulose, lignin, and minor extractives. Among the thermochemical conversion processes, liquefaction is particularly effective in converting biomass to liquid intermediates using alcohols or phenolic solvents. Process efficiency is influenced by temperature, solvent-to-biomass ratio, catalyst concentration, and reaction time. Lignin is generally easier to liquefy than hemicellulose and cellulose. Liquefied biomass is used in applications such as resin synthesis and the production of composite materials, especially when phenol is used as a solvent (Antonović *et al*., 2014; Feng *et al*., 2018; Zhou *et al*., 2023).

Forest-derived biomass accounts for a significant proportion of the world's biomass resources, making hardwood species such as oak valuable candidates for the development of bio-based materials due to their favorable composition and structural properties (Parikka, 2004). In addition to lignocellulosic raw materials from forestry, agricultural crops such as hemp offer high biomass yields and favorable fiber properties. Hemp is one of the fastest-growing crops and is known for its strong

natural fibers and wide industrial applicability. The chemical composition of hemp fibers includes a high proportion of cellulose, moderate amounts of hemicellulose, and a lower proportion of lignin. Possible uses include textiles, paper, composites, and thermal insulation, with additional potential for the production of biofuel from stalk residues (Ahmed *et al*., 2022).

In this study, the liquefaction behavior of oak and hemp is investigated under identical process conditions (150 °C, 120 min, solvent-to-biomass ratio 1:3, 1:4, and 1:5) to evaluate their suitability for conversion into precursors for bio-composite materials.

2. MATERIALS AND METHODS

2.1. Raw material collection and sampling

Oak and hemp biomass was used for the research. The hemp biomass came from a private producer in the Zagreb region, while the oak biomass was obtained from the company Bjelin Spačva d.o.o., in Vinkovci, Croatia. The chemical analyses were carried out in the laboratories of the University of Zagreb, Faculty of Forestry and Wood Technology, and Faculty of Agriculture, using standardized methods. Before being analyzed, the biomass samples were dried for 48 hours in a Memmert UF 160 laboratory dryer (Memmert GmbH, Germany) at a constant temperature of 60 °C. This drying process ensured moisture equilibrium in the material and allowed a consistent basis for comparison between the samples under standardized conditions.

2.2. Methods

2.2.1. Preparation of samples for analysis

After the drying process, the biomass was first ground using an SM400 laboratory mill (Retsch GmbH, Germany) equipped with a 6.0 mm round-hole sieve, in accordance with the HRN EN ISO 14780:2017 standard. The material was then further processed using an SR300 hammer mill (Retsch GmbH, Germany) with a 1.0 mm trapezoidal perforated sieve, which also complies with the same standard. The samples were then sieved using a Retsch AS 200 BASIC vibrating sieve shaker (Retsch GmbH, Germany), in accordance with the HRN EN ISO 17827-2:2016 standard. Various mesh sizes were used, in accordance with the ISO 3310-1:2016 specification, in order to achieve the desired particle size distribution. After the grinding and sieving process, particles with a size of 0.50 to 1.00 mm were selected for further analysis, as this size range has been shown in previous studies to be optimal for isolating the desired chemical components. To ensure the reproducibility of the results, each sample was analyzed at least three times.

2.2.2. Lignocellulosic composition

The analysis of the lignocellulosic composition, in particular the extractives, cellulose, lignin, and hemicellulose, was carried out according to standardized methods and previous studies (Antonović *et al*., 2019; Jovičić *et al*., 2022; Matin *et al*., 2024). The structural analysis included the determination of the extract content (TAPPI T 204) using a Soxhlet R108S BEHRotest extractor (Behr Labour-Technik GmbH, Germany), with a solvent mixture of methanol (CH_3OH) and benzene (C_6H_6) in a volume ratio of 1:1. The cellulose content was determined by treating the sample with a mixture of nitric acid (HNO_3) and ethanol (C_2H_5OH) in a volume ratio of 1:4 and then boiling in a Hydro H9V Lauda water bath (Lauda GmbH, Germany). The lignin content was analyzed according to the TAPPI T 222 standard, using 72% sulfuric acid (H_2SO_4) and heating on an IKA C-MAG HS 7 magnetic stirrer (IKA®-Werke GmbH & Co. KG, Germany). The hemicellulose (HC) content was calculated using the following equation:

$$HC = 100 - (ash\% + extractives\% + cellulose\% + lignin\%) \quad [1]$$

2.2.3. Liquefaction of the biomass samples

The liquefaction process was performed according to previous research (Jovičić *et al*., 2022). Glycerol ($C_3H_8O_3$), a type of polyhydric alcohol, was used as the liquefying agent, while 3% sulfuric acid (prepared from 98% H_2SO_4) served as the acid catalyst. Liquefaction was carried out in a 500 mL round-bottom flask equipped with a condenser and heated using a magnetic stirrer controlled by a thermostatically controlled hot plate. The process began with the addition of 50 g glycerol and 1.5 g sulfuric acid to the flask. The mixture was stirred and heated until it reached a temperature of 150 °C. Once the target temperature was reached, a measured amount of the biomass sample was added to the flask. The amount of biomass varied depending on the chosen mass ratio between the sample and the solvent mixture (1:3, 1:4, or 1:5). Liquefaction was then carried out for 120 minutes at 150 °C, with the temperature of the solvent being continuously monitored throughout the process.

2.2.4. Analysis of the liquefied biomass samples

The analysis of liquefied biomass samples in this study was performed according to methods established in previous studies by Antonović et al. (2019) and Matin et al. (2024). These studies provided a comprehensive framework for evaluating the key properties of liquefied lignocellulosic materials that are critical for assessing the efficiency of the liquefaction process and the potential application of the resulting polyols. By applying and adapting these validated methods, this study ensured consistency with the existing literature while allowing comparison of results for different biomass types and process conditions.

2.2.4.1. Insoluble residue

The insoluble residue (IR) refers to the portion of the biomass that does not dissolve during the liquefaction process and remains as a solid. To determine this proportion, the liquefied samples were treated with a solvent mixture of 1,4-dioxane and water in a volume ratio of 8:2. The liquefied mixture was stirred thoroughly on a magnetic stirrer for 60 minutes and then filtered through a B2 glass fiber filter. The filtrate was repeatedly washed with the same solvent mixture until a colorless solution was obtained, ensuring complete removal of the soluble components. The remaining dioxane-insoluble fraction was then dried in a laboratory oven at 105 °C until a constant weight was reached. The mass of the dried insoluble residue was recorded and expressed as a percentage of the original mass of the liquefied sample. The percentage of insoluble residue was calculated using the following equation:

$$IR = [m(fp+ds) - m(fp)] / m(s) \times 100\ (\%) \quad [2]$$

Where:
m(fp + ds) - the mass of the filter paper together with the dried sample (g),
m(fp) - the mass of the filter paper (g),
m(s) – the mass of the sample (g).

2.2.4.2. Liquefaction percentage

The liquefaction (LP) indicates the proportion of biomass that has been successfully converted into a liquid state during the liquefaction process. To determine the LP, 1 g of the liquefied biomass sample is weighed into a dry beaker. Subsequently, 100 mL of distilled water and a magnetic stirrer are added. The beaker is then placed on a magnetic stirrer with several positions and stirred for 30 minutes. During this time, the mass of a filter paper is measured. After stirring, the mixture is filtered through the weighed filter paper, which is placed in a glass funnel over an Erlenmeyer flask. The undissolved part of the sample remains on the filter paper, while the dissolved fraction passes into the flask. The filter paper with the solid residue is then dried at 80 °C ± 2 °C for 24 hours until a constant weight is achieved. The liquefaction percentage is calculated using the following equation:

$$LP = 100 - \text{Insoluble residue (IR) (\%)} \quad [3]$$

2.2.4.3. Dry matter

The dry matter content (DM) of liquefied wood indicates the amount of solid substances that remain in the liquid product after the thermochemical liquefaction of wood biomass. To determine the dry matter content, an empty watch glass was first weighed. Then, 1 g of the liquefied sample was placed on the watch glass. The samples were dried in a dryer at 150 ± 2 °C for 24 hours, cooled in a desiccator, and weighed again together with the watch glass. The percentage of dry matter was calculated using the following equation:

$$DM = [m(wg+ds) - m(wg) / m(s)] \times 100\ (\%) \quad [4]$$

Where:
m(wg+ds) - mass of the watch glass plus dried sample (g),
m(wg) - mass of the empty watch glass (g),
m(s) - mass of the original sample (g).

2.2.4.4. Hydroxyl (OH) number

The hydroxyl number (OH) indicates the amount of potassium hydroxide (KOH), in milligrams, that is required to neutralize the hydroxyl groups in one gram of a sample. It serves as a quantitative measure of the content of hydroxyl groups (OH) in chemical compounds and is given in mg KOH/g. This parameter is a key indicator of the hydroxyl group concentration in polyols and plays a crucial role in the formation of urethane bonds, which have a direct impact on the physical and mechanical properties of the resulting polyurethane products. A higher hydroxyl number corresponds to a larger number of reactive hydroxyl groups, which leads to stronger cross-linking and, consequently, to a stiffer and more durable end material. Therefore, monitoring and controlling the hydroxyl number is essential in polyol production.

The OH number was determined according to the methods described in previous studies. A sample weighing between 0.51 and 0.56 g was placed in a beaker, to which 25 mL of an esterification reagent was added. The beaker was then heated in a water bath for 5 to 10 minutes until the sample separated from the bottom. The beaker was then kept in a water bath at 98 ± 2 °C for 15 minutes, with the water level adjusted so that the part of the beaker containing the sample was submerged.

After heating, the samples were removed from the water bath and allowed to cool. Then, 50 mL of pyridine and 10 mL of hot distilled water were added to each beaker. A magnetic stirrer was introduced, and the beaker was placed on a magnetic stirrer for thorough mixing. A pH meter was introduced into the mixture to monitor the titration process. Instead of flasks, beakers with lids were used to accommodate the pH meter during the titration. Finally, the samples were titrated to the equivalence point using a previously standardized 0.5 M potassium hydroxide (KOH) solution.

The hydroxyl number (OH) of the liquefied biomass sample, expressed in mg KOH/g, was calculated using the following equation:

$$OH = [(B-A) \times N \times 56.1 / m] \times 100\ (\%) \quad [5]$$

Where:
B - consumption of KOH (mL),
A - consumption of KOH for the blank test (mL),
N - normality of the solution,
m - mass of the sample (g).

3. RESULTS AND DISCUSSION

In this study, the effect of different biomass-solvent ratios on key liquefaction properties was investigated, including liquefaction percentage, isolable residue, dry matter, and hydroxyl value (OH). The results of the lignocellulosic composition are shown in Table 1.

Table 1. *Lignocellulose composition of the oak and hemp biomass samples (%).*

Sample	Cellulose	Lignin	Hemicellulose	Extractives
Oak	48.91	25.78	22.01	3.64
Hemp	47.13	21.89	17.10	4.89

Table 2. shows the degree of liquefaction, the isolable residue, the dry matter, and the hydroxyl value (OH) of the liquefied biomass samples of oak and hemp.

Table 2. *Percentage of LP, IR, DM, and OH number (mg KOH/g) in the liquefied samples of oak and hemp.*

Sample	Ratio	LP	IR	DM	OH
Oak	1/3	85.55	14.45	54.78	639.12
	1/4	89.11	10.89	52.91	742.23
	1/5	93.88	6.12	50.13	841.43
Hemp	1/3	84.73	15.27	63.28	561.68
	1/4	87.45	12.55	58.99	782.38
	1/5	91.64	8.36	57.19	829.61

Since the hydroxyl number (OH number) is the most critical parameter in liquefaction and provides essential information about the reactivity and binding potential of the liquefied biomass in subsequent syntheses, it is considered more important than other liquefaction properties such as the liquefaction percentage and the dry matter content.

Lignocellulosic composition analysis revealed that oak biomass contains slightly more cellulose (48.91%) and lignin (25.78%) compared to hemp (47.13% and 21.89%, respectively). This indicates that oak has a stiffer structure, which could make it more resistant to chemical degradation during liquefaction. The hemicellulose content was also higher in oak (22.01%) than in hemp (17.10%), indicating a potentially higher reactivity of oak in the early stages of liquefaction, as hemicellulose is more easily degraded than cellulose. On the other hand, hemp showed a higher content of extractives (4.89%) than oak (3.64%). These non-structural compounds can influence the liquefaction process by increasing the reactivity or influencing the composition of the final product.

The lignocellulosic composition of oak wood does not deviate from the literature data, in which Antonović *et al*. (2019) report 47.23% cellulose and 21.82% lignin, Donata *et al*. (2010) 46.3 to 48.1% cellulose, 26.5 to 27.1% lignin, and 3.8 to 4.2% extractives, and Matin *et al*. (2025) 49.11% cellulose, 29.43% lignin, 14.95% hemicellulose, and 7.74% extractives.

According to Marrot *et al*. (2022), the chemical composition of hemp comprises 46.1% cellulose, 22.81% lignin, 24.12% hemicellulose, and 4.14% extractives. Similarly, Danielewicz and Surma-Ślusarska (2010) reported a cellulose content of 36.3 to 46.9%, a lignin content of 18.2 to 27.1%, a hemicellulose content of 21.9 to 34.3%, and an extractives content of about 1.2%. These values show that the results obtained in this study are generally consistent with the values reported in the literature.

The liquefaction results showed that the biomass-to-solvent ratio had a significant effect on all analyzed parameters: liquefaction percentage (LP), insoluble residue (IR), dry matter content (DM), and hydroxyl number (OH), for both oak and hemp samples. As expected, increasing the amount of solvent (i.e., changing from a 1:3 to a 1:5 biomass to solvent ratio) resulted in a higher degree of liquefaction.

For oak, the degree of liquefaction increased from 85.55 (1:3 ratio) to 93.88% (1:5), while for hemp it increased in the same range from 84.73 to 91.64%. Accordingly, the amount of insoluble residue decreased the more biomass was converted into the liquid phase, with a decrease from 14.45 to 6.12% for oak and from 15.27 to 8.36% for hemp. The dry matter content showed a decreasing trend with higher solvent contents. Oak showed a decrease from 54.78 to 50.13%, while hemp showed a stronger decrease from 63.28 to 57.19%. This trend indicates a dilution effect, as a larger volume of solvent

reduces the concentration of solids in the liquefied mixture. The hydroxyl number, which is a key indicator of the reactivity of the liquefied product, increased significantly with higher solvent levels. For oak, the OH number increased from 639.12 (1:3) to 841.43 mg KOH/g (1:5), and for hemp, from 561.68 to 829.61 mg KOH/g. This increase is related to the more efficient degradation of biomass components and the release of hydroxyl-rich compounds under higher solvent volumes, making the resulting polyols more suitable for further polyurethane synthesis.

Overall, the oak samples showed a slightly higher liquefaction efficiency and higher OH values compared to hemp under the same conditions, suggesting a greater potential for polyol production. However, the hemp-based liquefied products showed a higher dry matter content at each ratio, which may be advantageous in applications where solid yield is a priority. Comparing the results obtained with previous studies (Antonović *et al*., 2019; Đurović *et al*., 2024; Matin *et al*., 2025), it can be concluded that both oak and hemp biomass have sufficiently favorable liquefaction properties for further application.

CONCLUSIONS

This study showed that the ratio of biomass to glycerol significantly affects the liquefaction efficiency of oak (*Quercus robur*) and hemp (*Cannabis sativa*) and has an impact on key parameters such as liquefaction percentage, insoluble residue, dry matter, and hydroxyl number. Increasing the solvent ratio improved the liquefaction efficiency, with the 1:5 ratio giving the best results for both biomasses. Oak showed slightly better overall performance, but hemp also proved to be a promising alternative for bio-based applications. The hydroxyl number was confirmed as the most important indicator of suitability for further use in formaldehyde-free adhesives. These results underpin the potential of oak and hemp as sustainable raw materials for environmentally friendly adhesive systems and provide a basis for future research to optimize liquefaction conditions and expand the development of bio-based adhesives.

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