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Research Article

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Toward sustainable bioproducts from lignocellulosic biomass: Influence of chemical pretreatments on liquefied walnut shells

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Abstract: The depletion of resources and the generation of significant waste pose considerable environmental challenges. Post-utilization of walnut kernels leaves behind substantial amounts of shells as the unused residue. Walnut shells find application in various production processes, offering an opportunity to mitigate environmental impacts through resource utilization. This study investigates the influence of chemical pretreatment on the properties of liquefied lignocellulosic biomass, specifically focusing on walnut shells as a prominent lignocellulosic material. The results reveal that samples subjected to alcohol pretreatment exhibited the lowest degree of liquefaction (85.00% at 120°C for 45 min), while the highest degree of liquefaction was observed in samples after alkaline pretreatment (90.76% at 90°C for 15 min). Analyzing functional groups in liquefied walnut shell biomass, formed during the addition of polyhydric alcohols, glycols, and organic acids, underscores its potential for diverse bioproducts. Pretreatment significantly increases the hydroxyl (OH) number, irrespective of the type, temperature, and duration of chemical pretreatment. Compared to the untreated sample, alkali pretreatment produces the highest OH number (1288.03 KOH/g), surpassing mean values after acid and alcohol pretreatment. The results highlight the efficacy of chemical pretreatment in tailoring the properties of liquefied walnut shell biomass, addressing the challenges associated with resource depletion and waste accumulation.

Keywords: walnut shell utilization, lignocellulosic biomass, resource efficiency, chemical pretreatment, liquefied biomass

1 Introduction

The escalating global demand for energy and chemicals, coupled with the rapid depletion of fossil fuel reserves, presents an urgent challenge. Traditional fossil fuel-based materials not only contribute to environmental degradation but also are subject to volatile market conditions with diminishing availability. This has led to growing interest in exploring renewable resources, particularly agricultural biomass, as sustainable alternatives. Biomass offers a renewable source of raw materials for creating environmentally friendly fuels, chemicals, and materials, offering a potential solution to the over-reliance on fossil fuels and the environmental concerns they create [1].

Agricultural biomass stands out as a vital source of renewable raw materials, offering substantial production potential. The utilization of biomass as a raw material continues to burgeon across Europe, emphasizing its pivotal role in sustainable resource management [2,3]. A significant proportion of agricultural waste comprises lignocellulosic material, distinguished by its attributes of strength, flammability, biodegradability, and reactivity [4]. The versatility of agricultural biomass extends to its application as a raw material for natural fiber production, presenting an alternative source of materials independent of oil derivatives [5,6].

Despite the potential of lignocellulosic biomass, its industrial application faces several challenges, particularly in the pretreatment and liquefaction processes required for converting it into valuable products like biocomposites [6]. Current methods, such as acid hydrolysis and alkaline pretreatment, often suffer from high costs, inefficiencies, and environmental concerns. This research aims to address

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these limitations by developing novel, more sustainable approaches to biomass pretreatment and liquefaction, contributing to the shift toward greener materials. Global warming and nature conservation have focused attention on testing the properties of natural fibers from biomass. This process resulted in the expansion of the use of natural fibers and the replacement of synthetic fibers in various applications. Many studies have confirmed that the production of biocomposites by adding natural lignocellulosic fibers to synthetic polymer matrices has less harmful impact on the environment than petroleum-based composites [7,8]. Natural fibers can be used as reinforcement in polyurethane resins, which are synthetic polymers that have urethane groups in their structure. One of the methods of obtaining polyols on a natural basis is the liquefaction process of biomass. This method relies on turning the entire biomass into a liquid by reacting the biomass with a suitable solvent and catalyst. The general interest in obtaining polyols from renewable raw materials is caused by the reduction of oil resources and the constant growth of gas and oil prices as well as concern for the environment [7]. Lignocellulosic biomass liquefaction is a process that involves converting complex biomass materials, such as wood, agricultural residues, or dedicated energy crops, into liquid biofuels or valuable chemicals. The liquefaction of lignocellulosic biomass is a promising technology for converting biomass into liquid valuable products through complex chemical and physical reactions, and liquefied biomass represents a possible alternative raw material for polymer synthesis. Polyols obtained by liquefaction of biomass can be used for various materials. With the increase in the level of ecological awareness, biomass and natural fibers in polymer composites are used more and more and represent a sustainable alternative to synthetic fibers [9]. Therefore, as one of the solutions to reduce the impact on the environment, the possibility of replacing polymer materials with biocomposites is increasingly being studied because they are more environmentally friendly compared to traditional polymer materials [8].

Lignocellulosic materials, such as walnut shells, are difficult to degrade due to the crystalline structure of cellulose and the complex structural organization of cellulose, hemicellulose, and lignin, so it is necessary to carry out appropriate pretreatment procedures [10]. By pretreatment, it is possible to improve the decomposition of the raw material, the removal of lignin, and thus enable the partial or complete hydrolysis of hemicellulose and the reduction of the amount of the crystalline fraction of cellulose [11]. In short, lignocellulosic biomass is translated from its natural form, which is inaccessible to cellulases, to a form where enzymatic hydrolysis is possible [4].

Chemical pretreatment of lignocellulosic materials involves the application of chemicals, such as ozone, acids, alkalis, and peroxides, to alter the crystalline structure of cellulose and remove hemicellulose and lignin. This process enhances the contact surface and pores of the lignocellulosic material, leading to partial lignin removal (delignification), reduced lignin polymerization, and partial or complete hydrolysis of hemicellulose [12]. The chemical treatment process of lignocellulosic biomass aims to degrade lignin from the material, with its effectiveness dependent on the lignin proportion [13]. Catalyzed by enzymes, metal salts, acids, or alkalis [14], hydrolysis breaks chemical bonds by inserting water molecules between atoms, transforming large molecules into smaller ones [15,16]. The process involves treatment of lignocellulosic raw material under specific pressure and temperature conditions [14,15,17], hydrolyzing hemicellulose and cellulose into simple compounds [18,19]. Previous studies show hydrolysis as an effective treatment, significantly reducing the lignin content, removing hemicellulose, and disrupting the crystalline structure of cellulose [4,20].

Inorganic acids, predominantly sulfuric or hydrochloric acid, are commonly used, with hydrolysis with dilute sulfuric acid being a successful method that accelerates subsequent cellulose hydrolysis [21]. However, the costs associated with dilute acid pretreatment are higher due to the need for corrosion-resistant and high-pressure reactor materials [22,23]. There are two main pretreatment types: continuous with low acid concentration at high temperatures and discontinuous with concentrated acid at low temperatures, resulting in cellulose hydrolysis and hemicellulose conversion to monosaccharides [24]. Acid procedures, particularly with diluted sulfuric acid, are commonly used but are more expensive due to equipment corrosion resistance requirements. After acid pretreatment, pH neutralization and salt extraction are necessary, further increasing costs [25].

Alkaline pretreatment stands as a widely adopted technique for the solubilization of lignin, achieved by diminishing the degree of polymerization and disrupting the bonds between lignin and other polymers using different bases [26]. The reagents employed for alkali pretreatment encompass sodium hydroxide, potassium hydroxide, ammonium hydroxide, and aqueous ammonia, among others [21,27]. Being effective, especially for hardwood and agricultural residues, it enhances lignocellulosic raw material porosity, enabling lignin removal and hemicellulose modification [18,28].

Organic solvent pretreatment involves the utilization of organic or aqueous organic solvent mixtures, sometimes in conjunction with inorganic acid catalysts, for delignification. Several organic solvent combinations, including triethylene glycol, methanol, ethanol, ethylene glycol, tetrahydrofurfuryl alcohol, and acetone, have been applied at defined temperatures and pressures, often in the presence of specific catalysts. This organosolv pretreatment method aims to achieve high-quality lignin extraction, producing a value-added product [21].

2 Materials and methods

In this study, walnut shell biomass from the domestic cultivar Šejnovo (Sisak-Moslavina County, Croatia) served as the primary research material. Following the separation of walnut shells from the kernels, the shells underwent natural air-drying. Subsequently, the air-dried samples were milled to various particle sizes using a Fritsch–Pulverisette 19 knife-mill. Sieving was conducted using a laboratory electromagnetic sieve shaker Cisa RP–08 (shaking time: $t = 15 \pm 1$ min) following TAPPI T 264 cm-97 standards. After crushing and sieving the walnut shell samples, particles between 600 µm and 1.25 mm were selected, since the uniformity module showed that medium particles predominate in samples that have been pulverized and sieved several times. Initial chemical analysis was made on the selected sample (initial – “raw sample”), and the chopped walnut shells (600 µm–1.25 mm) were subjected to chemical pretreatment.

2.1 Chemical pretreatment

After the initial analysis of the walnut shell, the lignocellulosic biomass was subjected to chemical pretreatment. Hydrolysis was carried out in a laboratory autoclave (WR2 reactor, Indianapolis, USA) in three ways:

- acid pretreatment (dilute H_2SO_4 5%),
- alkali pretreatment (dilute KOH 5%),
- alcohol pretreatment (ethanol)

under the following conditions:

- time (t1 – 15′, t2 – 30′, and t3 – 45′),
- temperature (T1 – 80°C, T2 – 90°C, T3 – 100°C, T4 – 110°C, and T5 – 120°C), and
- 4 bar pressure.

The indicated temperatures are lower than those in previous studies, and they were chosen for reasons of energy saving; therefore, the duration of the pretreatment is longer than in previous literature values.

2.2 Liquefied biomass preparation

Liquefied biomass was prepared following a methodology (Figure 1) outlined by Antonović et al. [29].

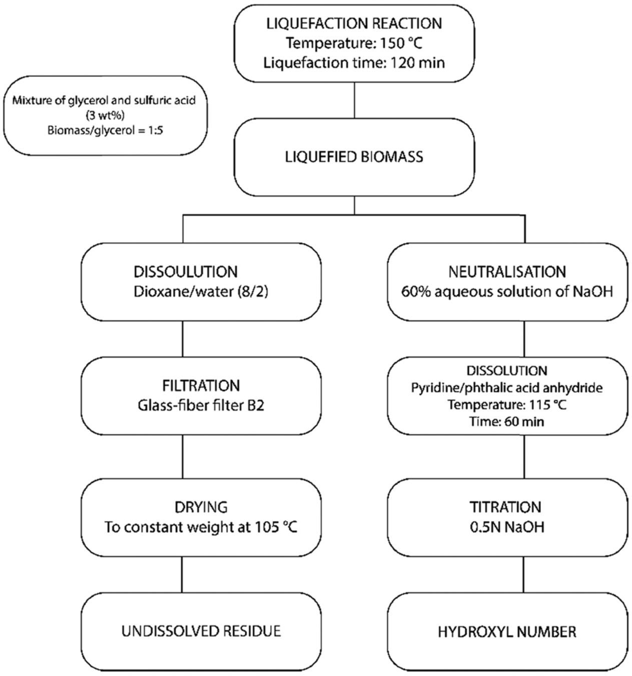

Figure 1: Liquefaction procedure and analytical methods for liquefied biomass characterization [30].

Smaller samples, obtained without prior chemical treatment, underwent liquefaction using a mixture of glycerol and sulfuric acid (H_2SO_4) as an acid catalyst (biomass/glycerol = 1:5, sulfuric acid at a concentration of 3 wt%) for 120 min at 150°C. The evaluation of polymer properties for the liquefied biomass involved determining the percentage of undissolved residue (UR), wood liquefaction degree (LD), and hydroxyl number (OH number). These parameters were crucial for identifying optimal liquefaction conditions.

2.3 LD and UR

After the liquefaction process, the UR in the liquefied biomass was assessed using a dioxane/water mixture, recognized as a universal diluent for liquefied biomasses. Specifically, 1 g of liquefied biomass was mixed with a dioxane/water solution in an 8/2 ratio and agitated on a magnetic stirrer for 60 min. Subsequently, the mixture underwent filtration through a glass-fiber filter B2 under vacuum conditions. The residue was subjected to repetitive rinsing with the same diluent until a colorless filtrate was obtained, and the UR was then dried in an oven at 105 ± 2°C until a constant weight was achieved. The percentage of UR was determined using the following equation according to Antonović et al. [29]:

$$\mathrm{UR} = \frac{\text{weight of UR (g)}}{\text{weight of liquefied wood (g)}} \times 100(\%).$$

LD percentage was calculated according to the following equation:

$$\mathrm{LD} = 100 - \mathrm{UR}(\%).$$

2.4 OH number

A weight of 1.5–2.5 g of liquefied biomass was precisely weighed into two 250 mL Erlenmeyer flasks, and the process was initiated with the addition of 10 mL of a reagent mixture containing pyridine and phthalic acid anhydride. A third flask, serving as the blank solution, received only the reagent. Each flask, equipped with a condenser and a magnetic stirrer serving as a heater and an oil bath, maintained a constant temperature at 115°C, ensuring the condensation of the reagent. The mixture in the flask was heated for precisely 1 h from the point of the first drop condensation. Following that, 50 mL of pyridine was introduced into the cooled mixture, and titration was carried out using a 0.5 M sodium hydroxide solution in the presence of phenolphthalein until reaching the equivalent point (ensuring the absence of bright red staining for at least 30 s). The OH number for the liquefied biomass sample, expressed as mg KOH/g, was determined (following the approach of Antonović et al [29]) using the following equation:

$$\text{OH number} = \frac{(B - A) \times c_{\mathrm{NaOH}} \times 56.1}{m} (\text{mg KOH/g}),$$

where A is the volume of the NaOH solution used for sample titration (ml); B is the volume of the NaOH solution used for blank solution titration; C_{NaOH} is the normality of the NaOH solution (M); m is the weight of the liquefied biomass sample.

The titration, following the ASTM D4274-05 standard, was continued until the solution turned pink. However, in the titration of the liquefied walnut shell biomass sample, a very dark red color appeared instead of the expected pink color, as in the case of the blank, so the method was modified.

The dark color was likely a result of the fact that the addition of the sample to the esterification reagent already produced a dark brown hue, stemming from the natural color of the liquefied walnut shell biomass. Since it is difficult to recognize the moment of neutralization or the equivalent point based on the color change, the method was modified in this part. To address this, the pH was continuously measured during titration to accurately identify the equivalent point and determine the precise consumption of sodium hydroxide.

The dry matter content of different particle sizes was determined by drying a sample in an oven, at two temperatures (102 and 150°C), until a constant weight was obtained.

2.5 Statistical analysis

Statistical analysis was performed using the TIBCO STATISTICA 13.3.0 software package (StatSoft TIBCO Software Inc.). Data presentation includes mean values accompanied by standard deviation. A random block design incorporating a time variable (15, 30, and 45 min) and five temperature regimes (80, 90, 100, 110, and 120°C) was employed. The statistical analysis involved calculating mean values and standard deviations for observed samples across five different temperatures and three distinct time intervals for each temperature regime. Analysis of variance (ANOVA) was conducted, followed by Tukey's post hoc HSD. Additionally, principal component analysis (PCA), also known as Karhunen–Loève expansion and Karhunen–Loève transformation in the literature, was employed as a method of multivariate statistics.

3 Results

The properties of the liquefied walnut shell biomass were initially investigated before pretreatment to establish a baseline for comparison with the LD and UR, and the dry matter and OH number of the liquefied biomass were examined after pretreatment with acid, alkali, and alcohol depending on the following parameters: time (15, 30, and 45 min) and temperature (80, 90, 100, 110, and 120°C).

3.1 LD and UR

The LD of walnut shell biomass before chemical pretreatment was 90.58%, dry matter was 56.1%, and the OH number of the untreated sample was 385.67 mg KOH/g. Univariate ANOVA of data on the LD of all analyzed samples depending on the temperature, time, and type of pretreatment is shown in Table 1.

The influences of the linear coefficients of temperature and time on the product (interaction) of time and temperature are not statistically significant in any of the LD models. Similarly, the impact of error is also not statistically significant in one model of liquefaction.

Table 1: Univariate analysis of the change in the LD and undissolved walnut shells with respect to the pretreatment type (solvent, temperature, and duration of the process)

	DF	Acid pretreatment		Alkali pretreatment		Alcohol pretreatment	
		SS					
		LD (%)	UR (%)	LD (%)	UR (%)	LD (%)	UR (%)
Temperature	4	$47.37^{n.s.}$	$47.37^{n.s.}$	$39.01^{n.s.}$	$43.87^{n.s.}$	$84.90^{n.s.}$	$85.38^{n.s.}$
Time	2	$4.91^{n.s.}$	$4.91^{n.s.}$	$15.40^{n.s.}$	$18.81^{n.s.}$	$2.72^{n.s.}$	$2.64^{n.s.}$
Temp. × Time	8	$23.07^{n.s.}$	$23.07^{n.s.}$	$40.69^{n.s.}$	$49.78^{n.s.}$	$15.28^{n.s.}$	$15.60^{n.s.}$
Error	30	$8.72^{n.s.}$	$8.72^{n.s.}$	$6.15^{n.s.}$	$3.92^{n.s.}$	$4.28^{n.s.}$	$4.33^{n.s.}$

LD – liquefaction degree; UR – undissolved residue; n.s. – not significant; DF – degree of freedom; SS – sum of squares; Error – model error; P – probability of acceptance of the null hypothesis.

The LD and UR of walnut shell biomass after pretreatment depending on the type, duration, and temperature of pretreatment are shown in Table 2.

The statistical analysis determined the mean values and standard deviation of the observed samples of the LD and the UR at five different temperatures and three different times for each temperature regime after pretreatment with acid, alkali, and alcohol. Different mean values in the same column with a different letter in the exponent represent a statistical difference ($p \leq 0.05$) according to Tukey's post hoc test. It was found that the LD in the T4 treatment (alkali, 90°C, and 15 min) had the highest mean value (90.76%), while the lowest average value was 84.76% for the T7 treatment (alkali, 100°C, and 15 min).

Figure 2 graphically presents the data from Table 2, illustrating the relationships between pretreatment type, temperature, and duration.

By applying PCA, the parameters that have a significant influence on the distribution of samples based on the obtained data were analyzed using the first principal component, which explains 44.88% of all interactions in the observed data set. Figure 2 shows the PCA and the grouping of the samples in the direction of the vectors (variables) in relation to the type, temperature, and time duration of pretreatment (Figure 3).

As shown on the upper right side of the PCA diagram, the highest value of LD was observed for treatment T8 after acid pretreatment, treatment T4 after alkaline pretreatment, and treatment T1 after alcohol pretreatment.

Table 2: LD after pretreatment

			Acid pretreatment		Alkali pretreatment		Alcohol pretreatment	
No.	Temp (°C)	Time (min)	LD (%)	UR (%)	LD (%)	UR (%)	LD (%)	UR (%)
T1	80	15	87.74 ± 0.72^{bcde}	12.26 ± 0.72^{cdef}	86.74 ± 0.19^{b}	13.26 ± 0.19^{g}	90.15 ± 0.41^{e}	9.85 ± 0.41^{ab}
T2		30	87.17 ± 0.38^{b}	12.83 ± 0.38^{f}	89.42 ± 0.14^{defgh}	10.58 ± 0.14^{bcd}	88.03 ± 0.28^{cd}	11.97 ± 0.28^{cd}
T3		45	85.32 ± 0.36^{a}	14.68 ± 0.36^{g}	89.34 ± 0.52^{defg}	10.66 ± 0.52^{bcd}	90.03 ± 0.35^{e}	9.97 ± 0.35^{ab}
T4	90	15	88.38 ± 0.26^{bcdef}	11.62 ± 0.26^{bcdef}	90.76 ± 0.13^{h}	9.24 ± 0.13^{a}	89.27 ± 0.61^{e}	10.73 ± 0.61^{ab}
T5		30	89.80 ± 0.69^{fg}	10.20 ± 0.69^{ab}	90.26 ± 0.39^{gh}	9.74 ± 0.39^{ab}	90.10 ± 0.09^{e}	9.83 ± 0.10^{a}
T6		45	89.80 ± 0.54^{fg}	10.2 ± 0.54^{ab}	89.43 ± 0.33^{defgh}	10.57 ± 0.33^{bcd}	89.68 ± 0.29^{e}	10.32 ± 0.29^{ab}
T7	100	15	89.07 ± 0.14^{cdefg}	10.93 ± 0.14^{abcde}	84.76 ± 1.11^{a}	15.91 ± 0.34^{h}	89.64 ± 0.55^{e}	10.36 ± 0.55^{ab}
T8		30	90.58 ± 1.23^{g}	9.42 ± 1.23^{a}	89.34 ± 0.38^{defg}	10.66 ± 0.38^{bcd}	89.44 ± 0.16^{e}	10.56 ± 0.16^{ab}
T9		45	88.99 ± 0.5^{cdefg}	11.01 ± 0.5^{abcde}	88.88 ± 0.28^{cdef}	11.12 ± 0.28^{cde}	89.54 ± 0.67^{e}	10.46 ± 0.67^{ab}
T10	110	15	88.38 ± 0.04^{bcdef}	11.62 ± 0.04^{bcdef}	88.35 ± 0.3^{cde}	11.65 ± 0.3^{def}	89.78 ± 0.05^{e}	10.22 ± 0.05^{ab}
T11		30	87.50 ± 0.53^{bc}	12.5 ± 0.53^{ef}	88.17 ± 0.36^{cd}	11.83 ± 0.36^{ef}	89.85 ± 0.18^{e}	10.12 ± 0.24^{ab}
T12		45	87.59 ± 0.4^{bcd}	12.41 ± 0.4^{def}	87.67 ± 0.46^{bc}	12.33 ± 0.46^{fg}	89.02 ± 0.45^{de}	10.98 ± 0.45^{bc}
T13	120	15	87.19 ± 0.31^{b}	12.81 ± 0.31^{f}	89.28 ± 0.63^{defg}	10.72 ± 0.63^{bcd}	87.18 ± 0.12^{bc}	12.82 ± 0.12^{de}
T14		30	89.27 ± 0.52^{efg}	10.73 ± 0.52^{abc}	89.53 ± 0.33^{efgh}	10.47 ± 0.33^{bc}	86.17 ± 0.45^{b}	13.83 ± 0.45^{e}
T15		45	89.15 ± 0.37^{defg}	10.85 ± 0.37^{abcd}	89.86 ± 0.29^{fgh}	10.14 ± 0.29^{abc}	85.00 ± 0.26^{a}	15.00 ± 0.26^{f}

T1–T15 denotes interaction of samples shown in Figure 2 (PCA) in relation to the changes in the variables studied; LD – liquefaction degree; UR – undissolved residue. The values with different letters in the column indicate a statistically significant difference ($p \leq 0{,}05$) according to Tukey's HSD test.

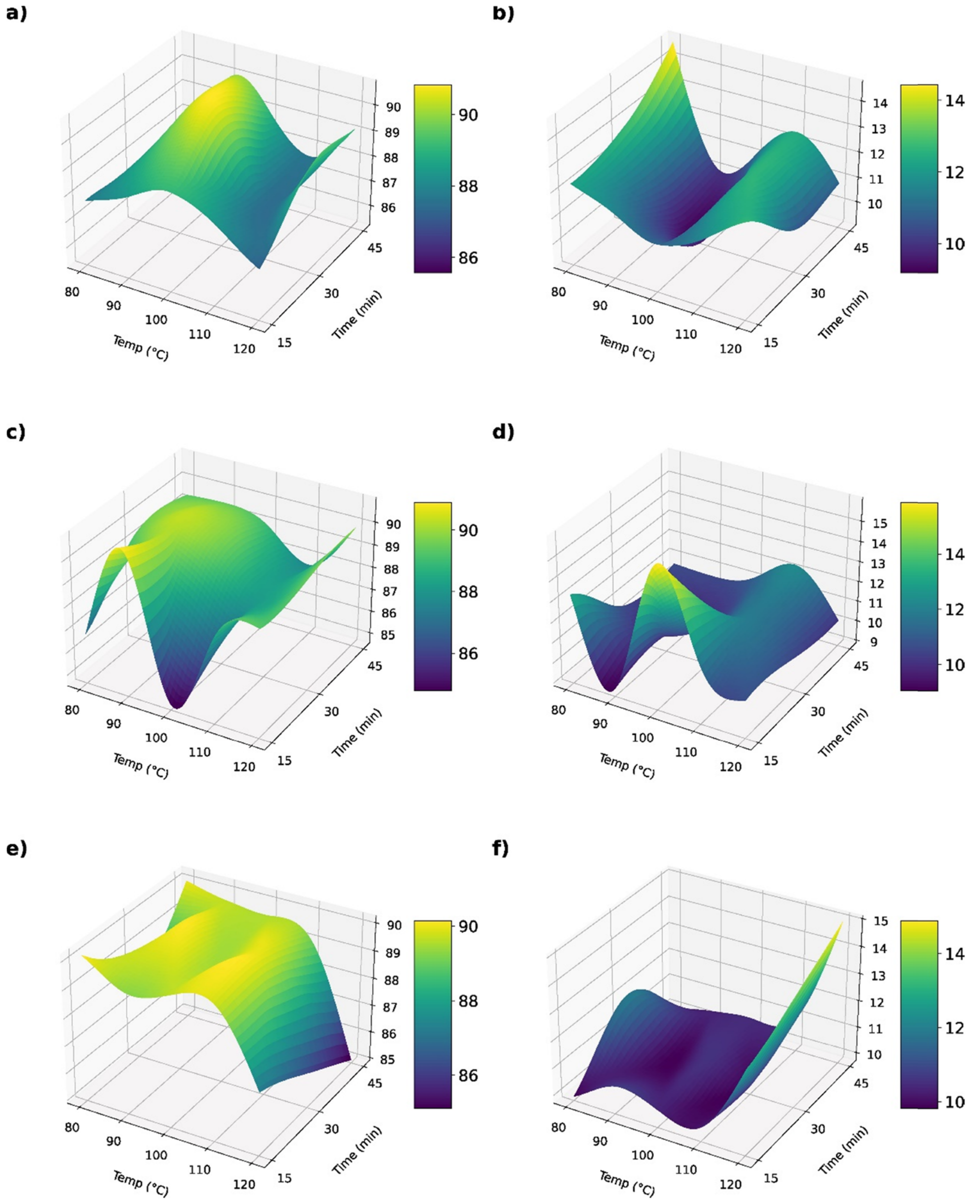

Figure 2: LD and UR of walnut shell biomass after pretreatment. (a) LD after acid pretreatment. (b) UR after acid pretreatment. (c) LD after alkali pretreatment. (d) UR after alkali pretreatment. (e) LD after alcohol pretreatment. (f) UR after alcohol pretreatment.

3.2 Dry matter content

Univariate ANOVA of data on the dry matter of all analyzed samples depending on the temperature, time, and type of pretreatment is shown in Table 3.

The influences of the linear coefficients of temperature and time and the product (interaction) of time and temperature are not statistically significant in the models of dry matter content in samples treated with acid and alcohol. The influence of the linear coefficient of time in the model of dry matter content, in samples treated with alkali, proved to be the most influential, statistically significant at the $p \leq 0.05$ level, while the effects of the linear coefficient of temperature and the product (interaction) of time and temperature were not statistically significant. The influence of error is not statistically significant in any model of dry matter content.

The dry matter content depending on the type of pretreatment, duration, and temperature of pretreatment is shown in Table 4. Different mean values in the same column with different letters in the exponent represent a statistical difference ($p \leq 0.05$) according to Tukey's post hoc test.

Statistical analysis determined the mean values and standard deviation of the dry matter content of the

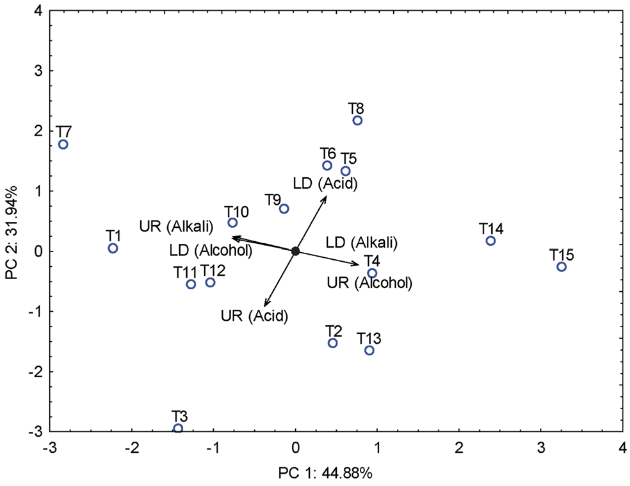

Figure 3: PCA of the LD and UR.

observed samples at five different temperatures and three different times for each temperature regime after pretreatment with acid, alkali, and alcohol. It was found that the dry matter content in the T1 treatment (80°C, 15 min) had the lowest mean value (51.81%) in the samples treated with alcohol, while the highest mean value was 61.06% for the T15 treatment (120°C, 45 min) for samples also treated with alcohol.

Figure 4 shows the PCA and the grouping of the samples in the direction of the vectors in relation to the type of pretreatment for the dry matter content.

Parameters that have a significant influence on the distribution of samples based on the obtained data were analyzed in the first main component, which explains 55.97% of all interactions in the observed data set.

Table 3: Univariate analysis of the change in dry matter of liquified walnut shells with respect to the pretreatment type

		Acid pretreatment	**Alkali pretreatment**	**Alcohol pretreatment**
			SS	
	DF	**DM (%)**	**DM (%)**	**DM (%)**
Temperature	4	40.81$^{\text{n.s.}}$	68.13$^{\text{n.s.}}$	181.09$^{\text{n.s.}}$
Time	2	4.30$^{\text{n.s.}}$	8.60*	30.25$^{\text{n.s.}}$
Temp. × Time	8	39.48$^{\text{n.s.}}$	71.87$^{\text{n.s.}}$	34.49$^{\text{n.s.}}$
Error	30	25.46$^{\text{n.s.}}$	25.67$^{\text{n.s.}}$	12.53$^{\text{n.s.}}$

DM – Dry matter; DF – number of degrees of freedom of variability source; SS – sum of square values; Error – model error; P – probability of acceptance of the null hypothesis; statistical significance: $*p < 0.05$; n.s. – not statistically significant.

Table 4: Dry matter content after pretreatment

			Acid pretreatment	**Alkali pretreatment**	**Alcohol pretreatment**
Treatment	**Temp (°C)**	**Time (min)**	**DM (%)**	**DM (%)**	**DM (%)**
T1	80	15	55.71 ± 0.75^{abcde}	57.48 ± 0.59^{de}	51.81 ± 0.42^{a}
T2		30	56.50 ± 0.75^{bcde}	54.99 ± 0.08^{abcd}	55.98 ± 1.50^{de}
T3		45	58.08 ± 0.37^{e}	54.82 ± 2.09^{abcd}	54.18 ± 0.27^{bcd}
T4	90	15	55.11 ± 0.97^{abcd}	52.31 ± 1.24^{a}	52.82 ± 0.29^{abc}
T5		30	53.59 ± 1.37^{a}	55.04 ± 0.37^{abcd}	53.69 ± 0.44^{abc}
T6		45	53.97 ± 0.43^{abc}	55.65 ± 1.06^{bcd}	53.61 ± 0.32^{abc}
T7	100	15	54.52 ± 1.10^{abcd}	58.87 ± 0.44^{e}	52.46 ± 0.25^{ab}
T8		30	53.84 ± 1.07^{ab}	54.23 ± 0.32^{abc}	54.51 ± 0.04^{cd}
T9		45	55.07 ± 0.84^{abcd}	54.61 ± 1.68^{abc}	53.86 ± 1.09^{bc}
T10	110	15	55.44 ± 0.23^{abcde}	55.94 ± 0.27^{cd}	52.78 ± 0.75^{abc}
T11		30	56.64 ± 0.40^{cde}	54.55 ± 0.97^{abc}	54.44 ± 0.67^{cd}
T12		45	54.82 ± 0.29^{abcd}	56.87 ± 0.44^{cde}	53.64 ± 0.41^{abc}
T13	120	15	56.83 ± 1.26^{de}	52.50 ± 0.30^{a}	57.56 ± 0.89^{e}
T14		30	53.27 ± 0.70^{a}	52.94 ± 0.91^{ab}	57.30 ± 0.26^{e}
T15		45	53.49 ± 1.75^{a}	52.76 ± 0.30^{a}	61.06 ± 0.31^{f}

T1–T15 denote interactions of single samples in Figure 3 (PCA) in relation to the changes in the variables studied; DM – dry matter; the values with different letters in the column indicate a statistically significant difference ($p \le 0{,}05$) according to Tukey's HSD test.

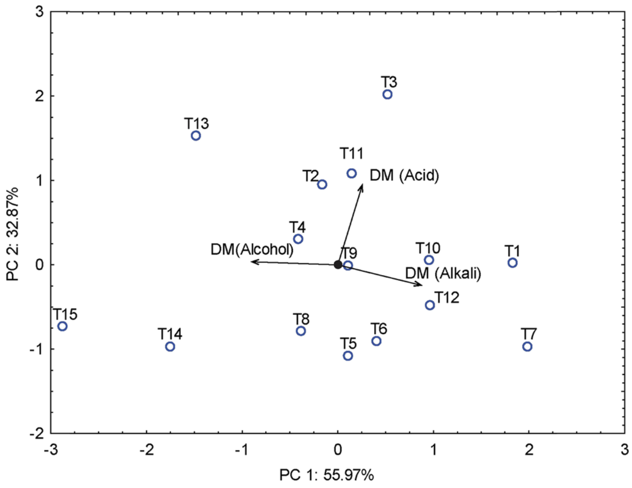

Figure 4: PCA for dry matter.

On the left side of the PCA diagram, treatment T15 has the highest value of the dry matter content after pretreatment with alcohol (52.46%), while treatment T7 has the highest value after pretreatment with alkali (58.87%), and treatment T3 showed the highest dry matter content after acid pretreatment (58.08%).

3.3 OH number

Univariate ANOVA of data on the OH number of all analyzed samples depending on the temperature, time, and type of pretreatment is shown in Table 5.

The influences of the linear coefficients of temperature and time and the product (interaction) of time and temperature are not statistically significant in any model regarding the OH number content.

The OH number was determined for all samples of liquefied walnut shell biomass after hydrolysis with acid, alkali, and alcohol, depending on the temperature and duration of pretreatment. The mean values with standard deviation are shown in Table 6.

Statistical analysis revealed that the OH number in the T7 treatment (100°C, 15 min) had the lowest value (922.03) in the samples after alkali hydrolysis, while the highest value observed was 1288.03 for the T5 treatment (90°C, 30 min) for samples treated with alkali.

4 Discussion

Biomass liquefaction technology breaks down high-molecular-weight components in biomass into low-molecular-weight gases, liquids, and solid residues [31]. This study examined the liquefaction properties of walnut shell biomass following various chemical pretreatments. The initial LD of untreated walnut shell biomass was 90.58%, with a dry matter content of 56.10% and an OH number of 385.67 mg KOH/g.

4.1 Effect of pretreatment on dry matter content

The dry matter content decreased following pretreatment. Specifically, alcohol pretreatment resulted in the lowest dry matter content compared to acid and alkali pretreatments. This suggests that alcohol pretreatment is more effective in reducing the dry matter content of walnut shells. The reduction in dry matter content across pretreatment methods indicates successful removal of certain biomass components, which is critical for subsequent processing [31].

4.2 Impact of pretreatment on LD

The LD of the untreated walnut shell biomass was 90.58%. The pretreatment processes did not significantly increase the LD, with alkali pretreatment at 90°C for 15 min, yielding the highest degree of 90.76%. In contrast, alcohol pretreatment consistently resulted in the lowest LDs compared to acid and alkali pretreatments.

Table 5: Univariate analysis of the change in the OH number of liquified walnut shells with respect to the pretreatment type

		Acid pretreatment	**Alkali pretreatment**	**Alcohol pretreatment**
			SS	
	DF	**OH number (mg KOH/g)**	**OH number (mg KOH/g)**	**OH number (mg KOH/g)**
Temperature	4	186,572.88$^{\text{n.s.}}$	115,541.33$^{\text{n.s.}}$	204,769.29$^{\text{n.s.}}$
Time	2	7,498.43$^{\text{n.s.}}$	76,375.67$^{\text{n.s.}}$	6,183.08$^{\text{n.s.}}$
Temp. × Time	8	125,759.90$^{\text{n.s.}}$	175,593.60$^{\text{n.s.}}$	40,739.04$^{\text{n.s.}}$
Error	30	1.71$^{\text{n.s.}}$	1.43$^{\text{n.s.}}$	1.95$^{\text{n.s.}}$

Statistical significance: *$p < 0.05$; n.s. – not statistically significant; DF – number of degrees of freedom of the variability source; SS – sum of square values; Error – model error; P – the probability of acceptance of the null hypothesis.

This finding is consistent with the research of Domingos et al., who examined the influence of temperature, time, and biomass particle size on the LD of walnut shells [32]. They observed that over 70% of walnut shell biomass liquefied within the first 15 to 30 min, achieving a high liquefaction yield of 85% at 200°C. However, their results were lower than those obtained in this study. Domingos et al. also found that smaller granulation particles achieved higher liquefaction yields. Specifically, the LD increased slightly from 75 to 82% for particles of size from 0.420 to 0.250 mm. For even smaller particles (40–60, 60–80, and <80), the differences were not significant, with yields showing a tendency to increase up to 82% for 0.420–0.250 mm particle size and 80% for <0.177 mm particle size [32].

In their study, Domingos et al. used a solvent mixture of glycerol and ethylene glycol (1:1 ratio), catalyzed by sulfuric acid at 3% of the total mass, with a walnut shell/solvent ratio of 1:10. In contrast, this study employed glycerol as the liquefaction reagent and used sulfuric acid as the acidic catalyst (also at 3% of the total mass), but with a walnut shell/solvent ratio of 1:5 [32]. The highest LD observed by Domingos et al. was 85% at 200°C for 30 min, which is significantly lower than the degrees achieved in this study, where larger particles (0.63–1.25 mm) were analyzed.

4.3 Comparison with forest biomass

When compared to forest biomass, walnut shell biomass showed slightly lower LDs than hardwood species, which ranged from 88.47% for beech to 91.98% for common oak [29]. However, walnut shell biomass had higher LDs than softwood species, which ranged from 91.98% for common oak to 94.94% for spruce [29,33]. For example, Esteves et al. reported a LD of 80% for pine bark, and Yona et al. found LDs of 61–85% for cork oak, depending on the catalyst used [33,34]. The LD for Douglas fir bark, investigated by Esteves et al., was lower than the values observed for walnut shells in this study, with a maximum of 70% [35].

4.4 OH number analysis

The OH number, which reflects the concentration of OH groups, increased significantly following pretreatment. The untreated walnut shell sample had an OH number of 385.67 mg KOH/g. Pretreatment methods, particularly alkaline hydrolysis, led to a notable increase in the OH number. This enhancement is significant as the OH number is crucial for the application of liquefied biomass in various bioproducts. Antonović et al. reported higher OH numbers for hardwood, such as beech (798 mg KOH/g), compared to softwood, with spruce having the lowest OH number (544 mg KOH/g) [29]. Although the untreated walnut shells had a lower OH number compared to forest biomass, pretreatment markedly increased the OH number in all treated samples.

The bio-polyols derived from liquefied biomass, which include derivatives of carbohydrates, esters, ethers, glycols, and acids, exhibit a wide range of OH numbers

Table 6: OH number of liquefied biomass after pretreatment

	Temperature (°C)	Time (min)	OH number after acid pretreatment (mg KOH/g)	OH number after alkali pretreatment (mg KOH/g)	OH number after alcohol pretreatment (mg KOH/g)
T1	80	15	1104.80 ± 0.2^{e}	1059.97 ± 0.15^{b}	1178.90 ± 0.26^{h}
T2		30	1071.13 ± 0.32^{b}	1222.10 ± 0.36^{k}	1069.93 ± 0.31^{d}
T3		45	928.13 ± 0.15^{a}	1205.13 ± 0.32^{i}	1204.03 ± 0.06^{l}
T4	90	15	1101.13 ± 0.32^{d}	1277.13 ± 0.15^{n}	1204.27 ± 0.25^{l}
T5		30	1192.07 ± 0.21^{h}	1288.03 ± 0.06^{o}	1217.03 ± 0.25^{n}
T6		45	1249.27 ± 0.25^{n}	1201.07 ± 0.06^{g}	1193.10 ± 0.1^{j}
T7	100	15	1203.07 ± 0.12^{i}	922.03 ± 0.15^{a}	1181.33 ± 0.31^{i}
T8		30	1242.07 ± 0.31^{m}	1260.37 ± 0.4^{m}	1159.07 ± 0.12^{f}
T9		45	1235.17 ± 0.15^{l}	1182.27 ± 0.23^{f}	1095.23 ± 0.25^{e}
T10	110	15	1212.83 ± 0.38^{j}	1151.07 ± 0.12^{e}	1202.43 ± 0.45^{k}
T11		30	1139.33 ± 0.31^{f}	1125.17 ± 0.15^{d}	1210.10 ± 0.17^{m}
T12		45	1150.17 ± 0.15^{g}	1119.13 ± 0.15^{c}	1167.43 ± 0.38^{g}
T13	120	15	1084.07 ± 0.12^{c}	1210.13 ± 0.15^{j}	1025.30 ± 0.26^{c}
T14		30	1219.07 ± 0.21^{k}	1227.07 ± 0.06^{l}	1008.10 ± 0.17^{a}
T15		45	1213.20 ± 0.17^{j}	1204.37 ± 0.32^{h}	1012.13 ± 0.15^{b}

The values with different letters in the column indicate a statistically significant difference ($p \leq 0,05$) according to Tukey's HSD test.

from 77.8 to 800 mg KOH/g [28,36–40]. These bio-polyols are promising for the production of resinous materials such as polyurethane foams, adhesives, and epoxy resins. The high OH numbers observed in this study suggest that the liquefied biomass could be effectively used to produce materials with desirable thermal and mechanical properties, as evidenced by high thermal stability and performance of films prepared from liquefied polyol/starch/glycerol [41].

When evaluating the OH numbers across different pretreatment methods, it is evident that alkaline hydrolysis consistently yields the highest OH numbers compared to those of acid and alcohol pretreatments. The untreated walnut shell biomass had an average OH number of 385.67 mg KOH/g. Pretreatment significantly elevated the OH number across all methods, underscoring the effectiveness of these processes in enhancing the biomass potential for various applications.

Comparative analysis of LDs among various hardwood species reveals that softwood generally exhibits a lower content of UR and a higher LD than hardwood. However, hardwood demonstrates substantially higher OH numbers. Antonović et al. reported the highest OH number in beech biomass (798 mg KOH/g) and the lowest in spruce (544 mg KOH/g) [29]. In contrast, the untreated walnut shell sample in this study had a lower OH number compared to that of forest biomass. Nevertheless, pretreatment markedly increased the OH number, with all treated samples showing a significant rise regardless of the pretreatment type, temperature, or duration.

4.5 Implications for bio-polyols

The liquefaction process yields bio-polyol, a product rich in OH groups, derived from the degradation of cellulose, hemicellulose, and lignin [35,42]. These bio-polyols, which include derivatives such as carbohydrates, esters, ethers, glycols, and acids, exhibit a wide range of OH numbers from 77.8 to 800 mg KOH/g [28,36–40]. This diversity highlights the potential of bio-polyols as valuable resources for the production of resinous materials. They are suitable for applications in polyurethane foams [42,43], polyurethane adhesives [39], urea-urethane elastomers [40], and epoxy resins [28]. Furthermore, polymer composites incorporating polyethylene and liquefied biomass demonstrate exceptional thermal stability [41]. Films composed of liquefied polyol/starch/glycerol also exhibit superior thermal, dynamic, and mechanical properties [36].

In summary, these findings underscore the critical role of pretreatment in optimizing the functional properties of biomass-derived polyols, thus enhancing their potential for diverse industrial and environmental applications. This study provides insights into the effects of chemical pretreatment on the LD and OH number of walnut shell biomass. While pretreatments did not significantly enhance the LD beyond the untreated biomass, they notably increased the OH number, especially with alkaline hydrolysis. These findings underscore the potential of using pretreatment methods to improve the quality and application of bio-polyols derived from biomass.

5 Conclusions

This study underscores the environmental challenges associated with unsustainable resource depletion and substantial waste generation. The utilization of walnut shells, often discarded as unused residue post-kernel extraction, emerges as a promising solution to these issues. The growing interest in liquefied biomass for environmentally friendly applications underscores the potential of walnut shells due to their favorable properties. With lower hygroscopic and higher hydrophobic components compared to forest biomass, walnut shell fillers offer significant commercial advantages in the production of polymer-based composite materials, particularly for outdoor products requiring high resistance. Moreover, walnut shells prove to be a versatile and valuable biomass resource employed in various production processes. The investigation into the OH number further reveals the positive impact of pretreatment, especially through alkaline hydrolysis, resulting in a substantial increase in the OH number. The exceptionally high OH number values observed in walnut shell biomass after pretreatment, irrespective of the solvent, temperature regime, or duration, position it as a promising candidate for diverse polymerization applications. This, coupled with favorable percentages of UR and LD, underscores the potential of walnut shell biomass in contributing to sustainable and versatile solutions in the realm of materials science and production.

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