Research Article

Idalina Domingos*, José Ferreira, Luísa P. Cruz-Lopes, Bruno Esteves

Liquefaction and chemical composition of walnut shells

Abstract: The cultivation of walnut (*Juglans regia* L.) for the exploitation of the fruit has been increasingly recognized worldwide; therefore, it is important to valorize a large amount of biomass from walnut shells (WS), where liquefaction may play an important role. This work intends to contribute to an improved understanding of the best uses for this material. The assays were made with a binary mixture of ethylene glycol and glycerol (1:1 v/v) as solvents, catalyzed by sulfuric acid. The tested parameters were as follows: particle size >0.420–0.177 mm, temperature 140–200°C, and reaction time between 15 and 60 min. The initial dried material, the liquefied material, and the resulting solid residue were analyzed by FTIR-ATR for polyol characterization. The results showed that WS are mostly composed of lignin with 35.0% and polysaccharides, 30.0% cellulose and 24.9% hemicelluloses. High-lignin content indicated that WS might be used as a bio-fuel or adhesives. Extractives represent 10.2% with almost half (4.6%) of polar extractives. The best conditions to attain the optimal liquefaction yield were 160°C, 30 min, and 0.420–0.250 mm particle size, for the tested parameters. FTIR spectrum of the liquefied material is very different from the original material, and solid residue spectra seem to indicate that there is higher liquefaction of polysaccharides when compared with lignin since there is a higher absorption at 1,600 cm^{-1} and lower absorption at 1,040 cm^{-1} and that liquefied compounds are probably in smaller molecules.

Keywords: walnut shells, chemical composition, polyalcohol liquefaction, biomass

* **Corresponding author: Idalina Domingos,** CERNAS-IPV Research Centre, Polytechnic Institute of Viseu, Campus Politécnico, Repeses, 3504-510 Viseu, Portugal, e-mail: ijd@estgv.ipv.pt
José Ferreira, Luísa P. Cruz-Lopes, Bruno Esteves: CERNAS-IPV Research Centre, Polytechnic Institute of Viseu, Campus Politécnico, Repeses, 3504-510 Viseu, Portugal

1 Introduction

The worldwide population growth in recent years, combined with improvements in living conditions, has led to higher consumption of agriculture products, producing a higher agro-industrial wastes. To minimize the effects on the environment, namely the depletion of natural resources, the last decade has been marked by an increasing interest in reusing or recycling these wastes, for instance, through the valorization of fruit shells and other agricultural wastes [1].

The growth of walnut trees (*Juglans regia* L.) for fruit production has shown an increasing trend in Portugal in the last few years, registering about 4,750 tons, while the world production was about 4 million tons of walnuts; China is the largest producer, with 2.5 million tons followed by USA, Chile, and Iran [2]. This increasing trend is, in turn, essentially associated with the walnuts' organoleptic characteristics, which, as a component of the human diet, have been highly recognized in recent years, as well as the knowledge of the effects they can have on consumer's health. Under this perspective, the great diversity of uses of their products contributes to the increasing cultivation, since in addition to human food, it is also used in the pharmaceutical industry, in the manufacture of dyes, liquors, and even in the processed wood industry [3].

Walnuts are considered one of the healthiest fruits, and their production has been increasing worldwide. In the walnut processing industry, to extract the edible part (kernels), large amounts of by-products are produced that are not properly valued. These materials, such as husk and shells, are the major parts of the fruits (greater than 60%) and are often underutilized, resulting in waste that can still have a high value [4]. Producing high value-added products from these by-products, instead of burning them, can increase the profitability of walnut processers and lead to several environmental and socioeconomic benefits. Consequently, these materials could be used for the production of fuel or high-value-added chemicals by, for instance, pyrolysis [1,4].

Consequently, it becomes very useful to value the biomass of walnut shells (WS). One of the most used processes is thermochemical conversion, which can be subdivided into gasification, pyrolysis, and liquefaction. Gasification is a process occurring at very high temperatures (until 1,000°C) resulting mostly in CO and H_2 gases. The main difference against pyrolysis is that this later one is made in an environment without oxygen. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid, which can be successfully used for the production of heat, power, and chemicals. Biomass liquefaction can be carried out by two different processes. The first one is similar to pyrolysis but conducted at pressures of about 5–10 MPa and lower temperatures [5]. The second process is called solvolysis where the biomass is dissolved in reactive organic solvents, such as phenol, polyhydric alcohols, ethylene carbonate, among others. Moderate temperatures are applied (100–250°C) and can be used with or without a catalyst [6]. This process has attracted considerable attention because it is not necessary to impose high pressures or drying processes, being carried out at moderate temperatures.

The chemical composition of WS is not much different from other lignocellulosic materials being mostly lignin, cellulose, and hemicelluloses, the main components. Through hydrolytic processes (catalyzed by acid or bases), it is possible to decompose the cell walls of biomass into their components, such as xylose, mannose, galactose, and arabinose [7]. In accordance to De Bhowmick et al. [8], other high value-added products can be obtained, such as biogas, bio-oil, or other bio-based chemicals that have numerous industrial applications [8,9].

Nowadays, biomass liquefaction at low temperatures and pressures is widely used by researchers to obtain large molecules, which have been stated earlier by several authors; they can be polymerized later on to produce some value-added products such as adhesive plastics or other polymers [10–14]. Polyhydric alcohols such as glycerol, ethylene glycol, and polyethylene glycol (PEG) are widely used in biomass liquefaction as mentioned earlier [11,15,16]. The molecules obtained from the liquefaction of biomass depends not only on the solvent used but also on the catalyst used, which can be acidic, basic, or cyclic carbonates [17,18] stated that using a co-solvent mixture in the liquefaction process is advantageous, namely a binary solvent mixture (PEG 400/glycerol) since, in accordance to these authors, it increases the speed of the liquefaction process and restrains re-condensation of the liquefied components.

Polyols obtained through the liquefaction of different agro-wastes have been widely used in the production of polyurethane foams, for example, cork [12,19], sugar bagasse [20], chestnut shells [7], coffee grains [21], soy wool [22], wood [23], wheat straw [24], cork rich barks such as *Pseudotsuga Menziesii* and *Quercus cerris* [25], and Eucalypt branches [26].

The aim of this study is the valorization of WS through liquefaction with polyhydric alcohols obtained from renewable sources, such as ethylene glycol that can be produced from bioethanol and glycerol, which is a by-product of biodiesel production. To find the potential applications for these by-products, it is important to determine their chemical compositions.

2 Materials and methods

2.1 Material

WS used in this study are the wastes produced by a local company in the Viseu region based in Portugal. The samples were milled in a Retsch SMI mill (Haan, Germany) and sieved in a Retsch AS200 (Haan, Germany) for 20 min at a speed of 50 rpm. Four fractions, which are >40 mesh (>0.420 mm), 40–60 mesh (0.420–0.250 mm), 60–80 mesh (0.250–0.177 mm) and <80 mesh (<0.177 mm), were obtained and dried at 105°C for at least 24 h as reported earlier [7].

2.2 Chemical composition

WS were characterized by the ash content, extractives (in dichloromethane, ethanol, and hot water), cellulose, lignin, and hemicelluloses. The average chemical composition of the two samples was determined, and a fraction of 0.420–0.250 mm was used.

The extractive content was determined by the Soxhlet extraction of 3 g from each sample and 200 mL of solvent. The extraction was sequential starting with the less polar solvent, dichloromethane (DCM), followed by solvents with increased polarity, ethanol, and hot water, according to Tappi T 204 "Solvent Extractives of Wood and Pulp" [27]. The extraction time was 6 h for DCM and 16 h for ethanol and water. The extractive content is determined in relation to the dry mass.

Insoluble lignin was determined by the Klason method TAPPI T 222 om-02 [28] with some changes, which

are as follows: 3 mL of 72% iced sulfuric acid was added to 350 mg of each sample placed in a beaker and after that transferred to a thermal bath at 30°C for 1 h, mixing with a glass rod every 10 min. Afterward, 84 mL of distilled water was added, and the mixture was placed in 100 mL thermal glass bottles inside an autoclave with water at the bottom. The samples were kept in the autoclave for 1 h at a temperature of 120°C, and after this time, the samples were removed and cooled in an ice bath. In the end, the samples were filtered with No 4 (5–15 μm) crucibles, dried, and weighed. Insoluble lignin was determined in the percentage of dry wood.

Holocellulose was obtained by the acid chlorite method. This process can last for 8 h to remove almost all lignin. The hemicellulose content was determined by the difference between holocellulose and α-cellulose. The holocellulose and α-cellulose content were determined for extractive-free samples by TAPPI 429 cm-10 [29] as described in Domingos et al. [30]. The percentage of holocellulose and α-cellulose was determined in relation to the dry mass of wood.

2.3 Polyalcohol liquefaction

Liquefaction was performed in a double shirt reactor (600 mL, Parr 5100 Low Pressure Reactor) heated with an oil jacket (Parr Instruments Co., Moline, IL). The liquefaction runs were made in duplicate. The reactor charge was 10 g of dried WS powder (0.420–0.250 mm) introduced in the reactor. The mixture was homogenized before starting, and the reactor's stirrer was set at 70 rpm. A mixture of glycerol and ethylene glycol 1:1 was used as a solvent, and sulfuric acid (3% based on solvent mass) was used as a catalyzer. These polyalcohols were chosen because of their low costs and relatively small environmental impact. The liquefaction temperature is measured in the oil present in the reactor jacket, and the liquefaction time started when the oil reached the working temperatures: 140 160, 180, and 200°C. The reaction time ranged between 15 and 60 min. The reactor was cooled down in ice to stop the reaction. Liquefied samples were dissolved in 100 mL of methanol and filtered in a Buchner funnel over a paper filter. To remove the excess solvent, the residue was washed with approximately 200 mL of water. The liquefied material was evaporated in a rotary evaporator, at reduced pressure, to remove methanol and water and placed in an oven at 105°C to remove any water remaining after evaporation and cooled in a desiccator. Liquefaction yield was determined in accordance with equation (1):

$$\text{Liquefaction yield (\%)} = \frac{\text{Initial dry mass (g)} - \text{Solid dry residue (g)}}{\text{Initial dry mass (g)}} \times 100. \quad (1)$$

2.4 Infrared spectroscopy analysis

The initial dried material, the liquefied material, and the resulting solid residue were analyzed by FTIR-ATR. In a Perkin Elmer UATR Spectrum Two spectrometer with 72 scans min^{-1} with a resolution of 4.0 cm^{-1} over the 4,000 to 400 cm^{-1} range. The samples were dried for 1 week in an oven at 102 ± 2°C, to assure that water was completely removed. After performing the background by measuring the absorbance without any sample or FTIR arm over the 2 mm^2 crystal, the sample was placed over the crystal, so that the entire surface is covered. Solid samples were pressed against the crystal while a droplet was placed over the crystal for liquid samples. An average of three spectra was used. ATR and baseline corrections were made for all spectra.

3 Results and discussion

3.1 Chemical composition

Table 1 presents the WS chemical composition, which is important to understand the potential value-added products that can be produced from WS' chemical conversion.

The WS' chemical composition is characterized by a moderate content of polar extractives, a low mineral content, and a high lignification. Ashes represent only 1.3% of the sample.

The mean chemical composition (in % of the oven-dry sample) showed that WS have a high amount of lignin that is around 35%, holocellulose was 55.2%,

Table 1: Chemical composition of walnut shells (% dry material)

Parameters		Content (%)
Ashes		1.32 ± 0.06
Extractives	Dichloromethane	2.94 ± 0.41
	Ethanol	2.71 ± 0.08
	Hot water	4.56 ± 0.50
Klason Lignin		34.98 ± 0.14
α-Cellulose		30.36 ± 0.68
Hemicelluloses		24.85 ± 0.53

which represents a little more than half of the chemical compounds, 30.4% from α-cellulose and 24.9% from hemi-celluloses. Regarding extractives (10.2%), the highest amount belongs to water extractives 4.6%, followed by dichloromethane 2.9% and ethanol 2.7%.

The extractives are non-structural organic compounds that can be removed from the samples without changing their structure. Usually, the extraction of solvents should be done along the same sequential order, which is gener-ally in ascending order of polarity, so that the results obtained for each of the solvents can be compared. If the extraction is made in a different order, different results are expected. The values found here are in the range reported by other researchers, despite a large variation of values found for a specific walnut shell. The content of extractives in organic solvents is low, and the present results obtained in dichloromethane/ethanol, 5.6%, do not differ too much from the reported values, 4.5%, obtained by Queirós et al. [31] with the walnuts grown in Portugal. The results obtained in this study in organic solvents are also similar to the results obtained by Pirayesh et al. [32] in ethanol/benzene, 3.2%, and Yang and Qui [33] in the same type of solvents, 5.2%, for the walnuts grown in Iran and China, respectively. For hot water extractives, the present value 4.6% do not differ substantially from the reported values by Queirós et al. [31], 5.4%, and lower than the reported values obtained by Pirayesh et al. [32], 10.2%.

The high amount of Klason lignin obtained in this study for WS, 35%, is similar to that reported by Yang and Qiu [33] and Queirós et al. [31] with 37.1 and 29.5%, respectively. However, Pirayesh et al. [32] obtained 49.1% and Demirbas [34] obtained 52.3%, which are higher than the content obtained here. Nevertheless, the big differ-ences in lignin content might be due to the extraction procedures done before lignin determination because if tannins are not removed, they can resist the acid treat-ment and be accounted as lignin.

As regards the cellulose content obtained, 30.4%, it was slightly higher than the value obtained by Demirbas [34], 25.6%, or Pirayesh et al. [32], 25.4%.

The amount of hemicelluloses, 24.9%, obtained in this study is in the same range as reported by Yang and Qiu [33], 29.3%, Pirayesh et al. [32], 21.2%, and Demirbas [34], 22.1%.

These results show that there are different chemical compositions for the WS, which might be due to dif-ferent growing parameters, such as planting soils, spacing between walnut trees, sun exposure, and fruit maturation. The chemical composition is an important condition for selecting the best conversion pathway. The high content of lignin in WS will be of interest for biofuels production or adhesives, while the hemicelluloses can be a source of xylo-oligosaccharides and other sugars [31].

3.2 Liquefaction

In this study, the process of liquefying WS was carried out in the presence of a mixture of solvents (glycerol and ethylene glycol 1:1) and a WS/solvent ratio of 1:10. The effect of temperature, particle size, and liquefaction reac-tion time on biomass was also investigated.

Figure 1 presents the liquefaction yield (%) variation with the different fractions. In these tests, a temperature of 160°C, a time of 60 min, and the WS/solvent ratio of 1:10 were used.

As can be seen in Figure 1, WS' particle size does not impact considerably the liquefaction efficiency. Liquefac-tion yield increased slightly from particles bigger than 0.420 to 0.250 mm from 75 to 82%. For smaller particles (40–60, 60–80, and <80), the differences are not substan-tial, showing similar liquefaction yields; however, it shows a decreasing tendency between 82% for 0.420–0.250 mm
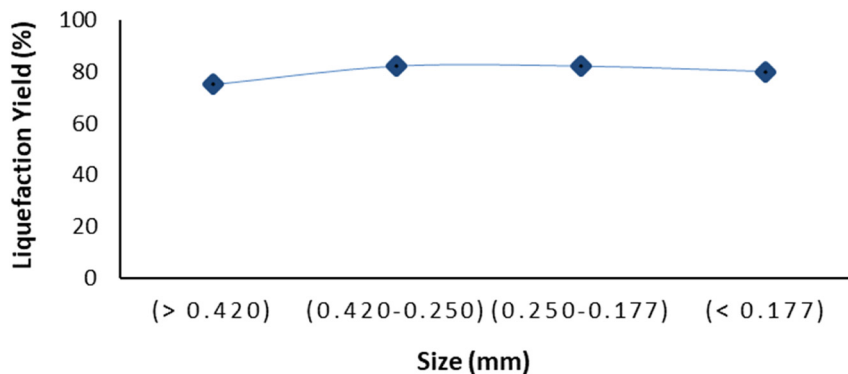

Figure 1: Liquefaction yield (%) with fraction for walnut shells.

and 80% for <0.177 mm. Zhang et al. [35] obtained a decrease in liquefaction yield for smaller rice straw particles. These authors stated that this finding is contrary to a universally agreed standpoint that smaller particle size will provide greater contact area and then bring a higher reactivity. The lower conversion ratio for lower particle sizes might be due to the different chemical compositions of these particle sizes as shown by Sen et al. [36] for *Q. cerris* bark, a heterogeneous material. Esteves et al. [12] presented similar results for cork liquefaction before, which has been attributed to the higher amount of suberin in larger particles, compared to smaller ones.

Figure 2 presents the liquefaction yield variation for reaction temperatures from 140 to 200°C. In these tests, the particle size used was <0.177 mm, a time of 60 min and the WS/solvent ratio of 1:10.

Liquefaction yield increased with the reaction temperature reaching a maximum value of 93% at 160°C, decreasing afterward. Figure 2 showed that the conversion ratio increased with an increase in temperature until 160°C but decreased later on, which can be due to some condensation reactions between liquefied materials. Jin et al. [37] stated that rising temperature would promote the decomposition of biomass but could also lead to re-condensation of liquefaction intermediates. Re-polymerization produces an insoluble material that increases the residue fraction, decreasing the conversion ratio. Therefore, the liquefaction effect is improved as the reaction temperature increases from 140 to 160°C but when re-polymerization produces insoluble material at higher temperatures 160 to 200°C, the conversion ratio decreases. With respect to this, the experiment indicates that the optimal temperature for this material/solvent is 160°C, reaching conversions above 90%. Similar results were obtained for the liquefaction of several agro-residues materials. For liquefied Douglas fir bark, 160°C was

suitable to attain an acceptable yield [38]. Similarly, Esteves et al. [12] with cork obtained a substantial increase from 150 to 160°C staying approximately constant subsequently. Zhang et al. [35] indicated a lower temperature of 150°C as the optimal temperature to liquefy agricultural wastes: rice straw, oilseed rape straw, wheat straw, and corn stover. Briones et al. [39] found that 170°C was the suitable temperature to liquefy rapeseed cake with above 90% liquefaction ratio.

The study of the liquefaction time is of great importance to find the shortest time to obtain the highest yield. Figure 3 presents the liquefaction time variation between 15 and 60 min at 200°C and a WS/solvent ratio of 1:10 for the <0.177 mm granulometry.

The liquefaction yield, as expected, increased with time until 30 min, where liquefied WS reached an 85% yield. The prolongation of the reaction time from 30 to 60 min resulted in a slight decrease of the liquefaction percentage to 83%. The reduction for 60 min reaction time is probably due to re-polymerization reactions of the liquefied components, similar to the observed for higher temperatures. This would slow the rate of the liquefaction process, producing a higher amount of residue [37,39]. Similarly, Soares et al. [40] found even smaller liquefaction yields due to the polycondensation of the liquefaction intermediates at higher reaction times on ecopolyol production from industrial cork powder via acid liquefaction at 150°C using polyhydric alcohols. The small reaction time obtained in this case not only allows reaching suitable liquefaction yields of about 85% but also is an economically advantage due to lower operational costs since more reaction time represents higher costs. More than 70% of WS were liquefied in the first 15 min. Studies carried out by Zhang et al. [41], on the liquefaction of nutshells of several species of Camellias, concluded that in the first stage of the reaction, most of
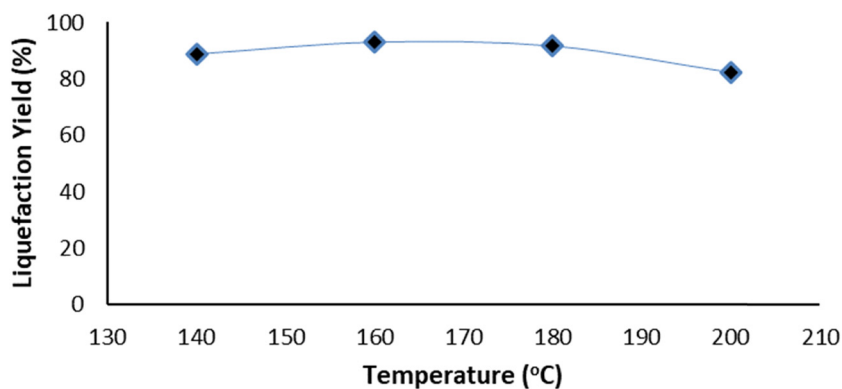

Figure 2: Liquefaction yield (%) with the temperature (°C) for walnut shells.
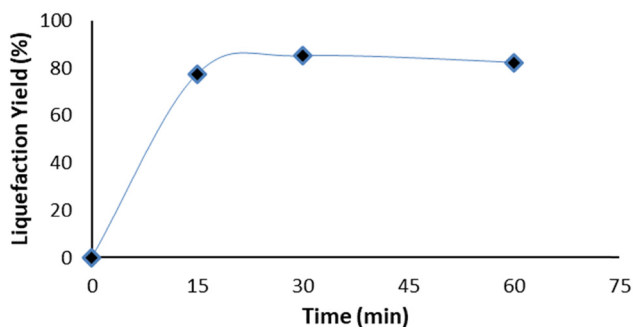
Figure 3: Liquefaction yield (%) with time (minutes) for walnut shells.

the hemicelluloses, some lignin and amorphous parts of cellulose are solubilized. These authors also stated that in the second stage, for longer times, there were re-condensation reactions between the liquefied intermediates that increased the residue amount. This phenomenon was also observed here. Kurimoto and Tamura [42] stated that re-condensation only happens when lignin and cellulose are both liquefied which means that there should have been some liquefaction for both compounds before. With respect to this, it can be said that 30 min is considered the most suitable reaction time for the liquefaction of WS.

Figure 4 presents the FTIR spectra of the original material (WS), the liquefied material, and the solid residue. The main conclusion that can be drawn from these spectra is that the FTIR spectrum of the liquefied material is very different from the FTIR spectrum of the original material and also from the solid residue obtained in the liquefaction reaction.

The solid residue spectrum has a similar OH peak around $3,400 \, cm^{-1}$ to the original material spectrum, which probably shows that there is no substantial difference between OH groups in the initial material and the solid residue. The peaks at around $2,926$ and $2,870 \, cm^{-1}$, which represent stretching vibrations from methyl and methylene groups [43,44], seem to increase slightly with the peak around $2,920 \, cm^{-1}$ being still higher than the peak at $2,870 \, cm^{-1}$. The peak at $1,740 \, cm^{-1}$ (non-conjugated C=O bonds) shifts to around $1,700 \, cm^{-1}$ and increases in relation to the initial material. The peak at $1,600 \, cm^{-1}$ (conjugated C=O bonds) [43,44] increases slightly and is still higher than the peak for non-conjugated C=O bonds like in the initial material. There is also an increase in the peak around $1,450 \, cm^{-1}$ in the residue spectrum. The peaks between $1,400$ and $1,200 \, cm^{-1}$ are undistinguished in the residue spectrum due to a peak with a maximum absorption around $1200 \, cm^{-1}$. Lignin is known to have a higher absorption at $1,600 \, cm^{-1}$ due to benzene ring stretching vibrations [43,44] and also in the region between $1,200$ and $1,300 \, cm^{-1}$, which is linked to phenolic stretch vibration of single OH bond and aliphatic single bond CH deformation in methyl groups that has been stated earlier [38]. This might mean that there is a higher percentage of lignin in the residue and that existent lignin is probably in a different form. There is the appearance of a new peak at $1,107 \, cm^{-1}$ probably due to a decrease of the peak around $1,040 \, cm^{-1}$, generally attributed to the C–O–C group in polysaccharides [43,44]. This might be due to the decrease of
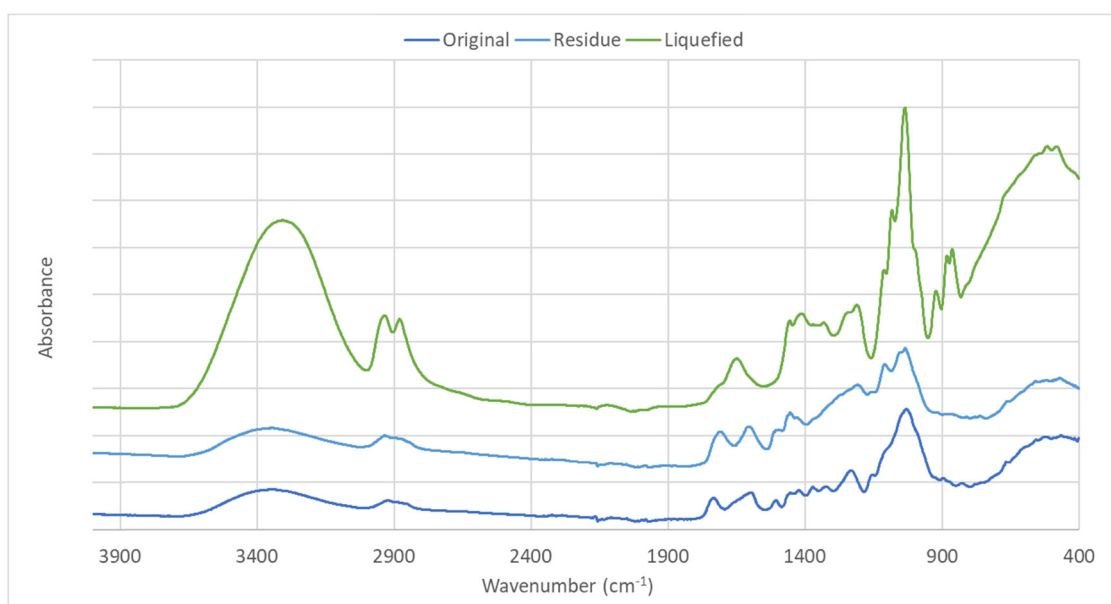

Figure 4: FTIR spectra for the original material (walnut shells), liquefied and solid residue.

hemicellulose and possibly amorphous cellulose in the residue when compared with the original material.

The OH band around 3,400 cm^{-1} increased considerably in liquefied WS, which can be attributed to the solvents, glycerol, and ethylene glycol used. The CH stretching bands around 2,926 and 2,870 cm^{-1} also increased which might be due to the existence of smaller molecules. The bands at 1,740 and 1,600 cm^{-1} disappear, and a new peak appear at around 1,660 cm^{-1}. Similar results were reported earlier by Jin et al. [37], noticing the absence of C=O groups after the liquefaction of enzymatic hydrolysis lignin. These results may possibly suggest that lignin content is lower, and the existent might be in a different form that corroborates the results obtained for the residue. The peak in the initial spectrum around 1,200 cm^{-1} also decreases.

There is an increase in the peak around 1,030 cm^{-1} confirming the existence of more C–O–C linkages and possibly higher sugar content. A new peak around 856 cm^{-1} emerges, which can be due to stretching in the pyranose ring [43].

4 Conclusions

During this study, the optimal temperature, particle size, and reaction time were determined to obtain liquefied bio-polyols based on WS with minimum residues. It was found that the liquefaction temperature, time, and particle size had great influences on the residue content.

Chemical composition showed that WS are mainly composed of lignin (35.0%), followed by cellulose (30.4%), the most representative polysaccharide, and hemicelluloses (24.9%). The amount of extractives is 10.2%, and most of them are attributed to polar extractives. The high amount of lignin makes this residue suitable to produce adhesives that can give an increased value for the walnut exploitation sector.

More than 70% of the material is liquefied in the first 15 and 30 min, which was enough to achieve a high liquefaction yield of 85% at 200°C. Nevertheless, an economic study must be made to determine the best conditions to achieve a good product at lower costs.

FTIR-ATR spectra showed that all the different chemical compounds suffered some kind of degradation, but they seemed to indicate that there is a higher degradation of polysaccharide compounds related to lignin.

The results reported here show that WS can be successfully liquefied, which might allow their utilization for the synthesis of bio-polyols. The high lignin content indicates that WS could be used as a bio-fuel or adhesives.

References

[1] Kar Y. Co-pyrolysis of walnut shell and tar sand in a fixed-bed reactor. Bioresour Technol. 2011;102:9800–5.

[2] FAO. Food and Agriculture Organization of the United Nations; 2019.

[3] Almeida C. Walnut production and marketing in Portugal and in the world context. Rev Bras Ciênc Agrár. 2020;43:10–6.

[4] Demirbas A. Effect of temperature on pyrolysis products from four nut shells. J Anal Appl Pyrolysis. 2006;76:285–9.

[5] Demirbaş A. Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Convers Manag. 2000;41:633–46.

[6] Pan H. Synthesis of polymers from organic solvent liquefied biomass: a review. Renew Sustain Energy Rev. 2011;15:3454–63.

[7] Cruz-Lopes LP, Domingos I, Ferreira J, Esteves B. Chemical composition and study on liquefaction optimization of chestnut shells. Open Agric. 2020;5:905–11.

[8] De Bhowmick G, Sarmah AK, Sen R. Lignocellulosic biorefinery as a model for sustainable development of biofuels and value added products. Bioresour Technol. 2018;247:1144–54.

[9] Arevalo-Gallegos A, Ahmad Z, Asgher M, Parra-Saldivar R, Iqbal HM. Lignocellulose: a sustainable material to produce value-added products with a zero waste approach – a review. Int J Biol Macromol. 2017;99:308–18.

[10] Alma MH, Yoshioka M, Yao Y, Shiraishi N. Preparation of sulfuric acid-catalyzed phenolated wood resin. Wood Sci Technol. 1998;32:297–308. doi: 10.1007/BF00702897.

[11] Domingos I, Ferreira J, Cruz-Lopes L, Esteves B. Polyurethane foams from liquefied orange peel wastes. Food Bioprod Process. 2019;115:223–9. doi: 10.1016/j.fbp.2019.04.002.

[12] Esteves B, Dulyanska Y, Costa C, Ferreira JV, Domingos I, Pereira H, et al. Cork liquefaction for polyurethane foam production. BioResources. 2017;12:2339–53. doi: 10.15376/biores.12.2.2339-2353.

[13] Esteves B, Martins J, Martins J, Cruz-Lopes L, Vicente J, Domingos I. Liquefied wood as a partial substitute of melamine-urea-2 formaldehyde and urea-formaldehyde resins 3. Maderas-Cienc Tecnol. 2015;17:3.

[14] Lin R, Sun J, Yue C, Wang X, Tu D, Gao Z. Study on preparation and properties of phenol-formaldehyde-chinese fir liquefaction copolymer resin. Maderas Cienc Tecnol. 2014;16:159–74.

[15] Niu M, Zhao GJ, Alma MH. Thermogravimetric studies on condensed wood residues in polyhydric alcohols liquefaction. BioResources. 2011;6:615–30.

[16] Yamada T, Ono H. Characterization of the products resulting from ethylene glycol liquefaction of cellulose. J Wood Sci. 2001;47:458–64. doi: 10.1007/BF00767898.

[17] Xie T, Chen F. Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from the liquefied product. J Appl Polym Sci. 2005;98:1961–8. doi: 10.1002/app.22370.

[18] Yao Y, Yoshioka M, Shiraishi N. Water-absorbing polyurethane foams from liquefied starch. J Appl Polym Sci. 1996;60:1939–49.

[19] Gama NV, Soares B, Freire CS, Silva R, Brandão I, Neto CP, et al. Rigid polyurethane foams derived from cork liquefied at atmospheric pressure: Rigid polyurethane foams derived from cork liquefied. Polym Int. 2015;64:250–7. doi: 10.1002/pi.4783.

[20] Hakim AA, Nassar M, Emam A, Sultan M. Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol. Mater Chem Phys. 2011;129:301–7.

[21] Soares B, Gama N, Freire CS, Barros-Timmons A, Brandão I, Silva R, et al. Spent coffee grounds as a renewable source for ecopolyols production. J Chem Technol Biotechnol. 2015;90:1480–8.

[22] Hu S, Wan C, Li Y. Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. Bioresour Technol. 2012;103:227–33.

[23] Alma M, Shiraishi N. Preparation of polyurethane-like foams from NaOH-catalyzed liquefied wood. Eur J Wood Wood Prod. 1998;56:245–6.

[24] Chen F, Lu Z. Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products. J Appl Polym Sci. 2009;111:508–16.

[25] Cruz-Lopes LP, Silva HC, Domingos I, Ferreira J, Lemos LT, Esteves B. Optimization of Quercus cerris Bark Liquefaction. Int J Chem Mol Nucl Mater Metall Eng. 2016;10:1073–76.

[26] Domingos I, Fernandes AP, Ferreira J, Cruz-Lopes L, Esteves BM. Polyurethane foams from liquefied Eucalyptus globulus branches. BioResources. 2019;14:31–43.

[27] TAPPI. Solvent extractives of wood and pulp. TAPPI T204 cm-07. GA, USA: TAPPI Press Atlanta; 2007.

[28] TAPPI. T 222 om-02. Acid-insoluble lignin in wood and pulp. Atlanta, GA, USA: TAPPI; 2002.

[29] TAPPI. Alpha-cellulose in paper, Test Method T 429 cm-10; 2010.

[30] Domingos I, Ayata U, Ferreira J, Cruz-Lopes L, Sen A, Sahin S, et al. Calorific power improvement of wood by heat treatment and its relation to chemical composition. Energies. 2020;13:5322.

[31] Queirós CS, Cardoso S, Lourenço A, Ferreira J, Miranda I, Lourenço MJV, et al. Characterization of walnut, almond, and pine nut shells regarding chemical composition and extract composition. Biomass Convers Biorefin. 2020;10:175–88.

[32] Pirayesh H, Khazaeian A, Tabarsa T. The potential for using walnut (Juglans regia L.) shell as a raw material for wood-based particleboard manufacturing. Compos Part B Eng. 2012;43:3276–80.

[33] Yang J, Qiu K. Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. Chem Eng J. 2010;165:209–17.

[34] Demirbaş A. Fuel characteristics of olive husk and walnut, hazelnut, sunflower, and almond shells. Energy Sources. 2002;24:215–21.

[35] Zhang J, Hori N, Takemura A. Optimization of agricultural wastes liquefaction process and preparing bio-based polyurethane foams by the obtained polyols. Ind Crop Prod. 2019;138:111455.

[36] Sen A, Miranda I, Esteves B, Pereira H. Chemical characterization, bioactive and fuel properties of waste cork and phloem fractions from Quercus cerris L. bark. Ind Crop Prod. 2020;157:112909. doi: 10.1016/j.indcrop.2020.112909.

[37] Jin Y, Ruan X, Cheng X, Lü Q. Liquefaction of lignin by polyethyleneglycol and glycerol. Bioresour Technol. 2011;102:3581–3. doi: 10.1016/j.biortech.2010.10.050.

[38] Esteves B, Cruz-Lopes L, Ferreira J, Domingos I, Nunes L, Pereira H. Optimizing Douglas-fir bark liquefaction in mixtures of glycerol and polyethylene glycol and KOH. Holzforschung. 2018;72:25–30. doi: 10.1515/hf-2017-0018.

[39] Briones R, Serrano L, Labidi J. Valorization of some lignocellulosic agro-industrial residues to obtain biopolyols. J Chem Technol Biotechnol. 2011;87:244–9.

[40] Soares B, Gama N, Freire C, Barros-Timmons A, Brandão I, Silva R, et al. Ecopolyol production from industrial cork powder via acid liquefaction using polyhydric alcohols. ACS Sustain Chem Eng. 2014;2:846–54.

[41] Zhang J, Du M, Hu L. Factors influencing polyol liquefaction of nut shells of different camellia species. BioResources. 2016;11:9956–69.

[42] Kurimoto Y, Tamura Y. Species effects on wood-liquefaction in polyhydric alcohols. Holzforschung. 1999;53:617–22.

[43] Rodrigues J, Faix O, Pereira H. Determination of lignin content of Eucalyptus globulus wood using FTIR spectroscopy. Holzforschung. 1998;52:46–50.

[44] Michell A, Higgins H. Infrared spectroscopy in Australian forest products research. Melbourne, Australia: CSIRO Forestry; 2002. p. 60.