

Article

Eco Valorization of *Eucalyptus globulus* Bark and Branches through Liquefaction

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Abstract: *Eucalyptus globulus* forest residues, bark, and branches, were characterized by wet chemistry methods and involved in the liquefaction process using a glycerol-ethylene glycol reaction mixture (1:1, v/v) catalyzed by strong mineral acid (3% H₂SO₄) or strong mineral base (6% KOH). The effect of the reaction conditions (temperature and duration) and the particle size on the yield of liquefied products have been evaluated. Acid catalysis revealed remarkably higher yields (25–50%) than when using basic catalyst. It was considered that bark was more vulnerable to liquefaction with respect to particle size than branches. Too high temperatures (>180 °C) are not advantageous regarding the liquefaction yields and, therefore, temperatures around 160–180 °C would be preferable. The best yield for the bark sample (>80 mesh fraction) was obtained at 180 °C for 60 min (61.6%), while for the branches the best yield was obtained at 160 °C for 60 min (62.2%). Under compromised conditions (180 °C for 60 min), the fine fraction (>80 mesh) of bark and branches did not show significant differences between their liquefaction yields and can be processed together while adjusting the suitable processing time. The main advantage of the use of these residues instead of solid wood is that it would bring the Forest managing companies a much higher income for their wastes that are usually burned and the use of lignocellulosic materials in detriment of petroleum-based materials for the production of polymers would make industry less dependent on oil prices fluctuations.

Keywords: bark; branches; *Eucalyptus globulus*; low temperature liquefaction; optimization; wastes



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1. Introduction

Eucalyptus globulus is the most important hardwood for the pulp and paper industry worldwide due to several features, such as fast-growing, easy adaptability to various types of soil and climate conditions (temperate, subtropical, and tropical), and the high-quality papers produced thereof. The plantations of this hardwood genus cover some 18 million hectares worldwide in 90 countries [1,2] with emphasis to *Eucalyptus globulus* Labill. being the dominant species in Southern Europe. It should be noted, however, that there are more than 700 different eucalyptus species [1], but only approximately a dozen species, including *Eucalyptus globulus*, are used for pulp production [2]. In Europe, in 2020, the

wood consumption for the pulp and paper industry was 146.4 million m³ and 8.6% of this value, 12.6 million m³, were eucalyptus [3].

Such *Eucalyptus globulus* forest residues as bark and branches resulting from debarking and pruning activities do not find industrial use and represent a considerable volume of wastes. These wastes are used to some extent for energy production, but often end up in landfills.

There are countless studies on the chemical composition of *Eucalyptus globulus* management wastes such as bark, stumps [4], and branches [5]. Thus, eucalyptus bark can be used for the extraction of phenolic compounds, since they are natural antioxidants [6] with a lot of applications in food and pharmaceutical sectors. Several studies have been carried out with the aim of improving the amounts of extractives removed from *Eucalyptus globulus* bark by supercritical fluid extraction [7–9] or using ultrafiltration membranes [10] for the recovery of polyphenolic compounds [11]. Other studies revealed the waste biomass from *Eucalyptus globulus* pulp production (e.g., bark) as a source of high-value triterpenic compounds [12,13]. However, after extraction, a lignocellulosic residue with unaltered macromolecular compounds is left as a residue.

Recently, several studies on the chemical composition of eucalyptus wastes related to the evaluation of the industrial bark as a biorefinery feedstock have been carried out [14]. Lima et al. reported the chemical and anatomical characterization and antioxidant properties of barks from 11 eucalypt species [15]. Similar works were carried out to evaluate the chemical composition and anatomical structure of *Eucalyptus globulus* stumps [16] and different pre-treatments to improve their delignification [17]. Regarding the chemical composition of the bark in 11 eucalyptus species, it was concluded that the chemical composition is specific to each species and differs in extractive content (from 5.5 to 18.6%), in Klason lignin (from 11.6 to 24.3%) and in glucose/xylose ratio (3.8 to 12.1) [15]. In another study, it is concluded that by applying pre-treatment, in a biorefinery context, *Eucalyptus globulus* stumps (with 11.9% extractives and 22.2% Klason lignin) could be successfully delignified and, therefore, used for the production of cellulosic pulp [17]. Regarding the chemical composition of *Eucalyptus globulus* stumps, it was found that the amount of ash in piled industrial stumps (19.2%) is much higher than in fresh stumps (3.5%) and that the extractive content is different in fresh stumps (7.5%) and on stacked stumps (4.1%) [16]. Recently, a study on the structural composition of lignin from *Eucalyptus globulus* bark revealed a H:G:S ratio of 1:26:73 [18]. This study also showed some structural units (*p*-coumaric acid, coniferyl acid, and sinapyl acid) in addition to the three main groups mentioned above. The identification of the components present in the extractives have also motivated several studies. Recently, 202 compounds were found in the lipophilic fraction of *Eucalyptus globulus*, of which, 189 were fully identified [19].

The most studied hydrothermal liquefaction takes places at high temperatures (200–370 °C) and pressures (4–20 MPa). However, at these temperatures and pressures, the obtained liquid has very small molecules and is mainly produced as a source for liquid fuels [20]. In the last few years, special attention has been given to liquefaction at lower temperatures and pressures where the resulting liquid has higher molecules than can easily be repolymerized into value added material. Since lignocellulosic materials are the most abundant natural material, many studies on their liquefaction from agricultural or forest residues have been done, such as wheat straw [21], corn stover [22–25], soybean straw [26], cotton stalks [27,28], olive pits [29], pine bark [30,31], *Quercus cerris* bark [32], cork [33], microalgae [34], lignin from enzymatic hydrolysis [35] and pure cellulose [36], pine wood sawdust [37], almond husk [38], rice husk [24,39], apricot stone [40], peanut shell [41], walnut shells [42], agricultural residues (rice straw, wheat straw, corn stover, and oilseed rape straw) [24], wheat straw [43], corn husks [44]; digested sewage sludge, hemp stalk hurd, and sugar beet pulp [45] were reported. The growing interest in the study of liquefaction of agroforest residues is due to these processes allowing the manufacture of value-added products similar to those traditionally made from petroleum. This is just one more path to

substitute petroleum-based products, similar to what's been done with liquid and solid biofuels [1].

In biomass liquefaction at relatively low temperatures and pressure, the most used solvents are phenol [46], ethylene glycol (EG) [23,47], polyethylene glycol (PEG) [27], and glycerol [20,26,36]. The function of the solvent in liquefaction is to dissolve the liquefaction products and prevent them from re-polymerization [20]. In the absence of a catalyst, liquefaction conditions require high pressure and temperatures (300–500 °C). In contrast, in the presence of a suitable catalyst, and at atmospheric pressure, the temperature range required for liquefaction of biomass is around 180 °C [46]. Both basic and acid catalysts can be involved in liquefaction reactions. The most used acid catalysts are organic acids, such as oxalic acid, *p*-toluenesulfonic and methanesulfonic acids, and inorganic acids, such as hydrochloric, sulfuric, or phosphoric acids [48,49]. Sulfuric acid was identified as the acid with the best catalytic efficiency [20]. The most common basic catalysts are potassium hydroxide [50] and sodium hydroxide [51]. The liquefaction of lignocellulosic materials comprises a complex set of reactions involving the three components of the plant cell wall: lignin, hemicellulose, and cellulose. Such reactions are basically of three types: esterification, etherification of cellulose, or lignin derivatives and different degradation reactions of biomass [22]. During liquefaction, the polymeric components of the cell wall are converted into smaller fragments, which can be used as macromonomers in the manufacture of polymers such as polyurethane foams [52], epoxy resins [53], and polyurethane adhesives [54].

Fernandes et al. [55] studied the liquefaction of *Eucalyptus globulus* sawdust using 2-ethylhexanol (2-EH) as a solvent, using *p*-toluenesulphonic acid (PTSA) (2.44%) as catalyst with a solvent:biomass ratio of 1:5. The optimal liquefaction results were found at 160 °C for 180 min. Furthermore, Mateus et al. [56] studied the liquefaction of *Eucalyptus globulus* bark using PTSA (3%) as catalyst and a mixture of 2-EH and diethylene glycol (DEG) (1:3) as solvent with a biomass:solvent ratio of 1:10. In this study, the best yield of liquefied products was achieved at 150 °C for 180 min. In another work, Vale et al. [57] liquefied the *Eucalyptus globulus* bark to prepare the polyurethane foams. In this work, the mixture of DEG and 2-EH was used as a solvent, in a mass proportion of 1:1:3 (biomass: DEG:2-EH), using PTSA (3%) as a catalyst. The best liquefaction yield was achieved at 160 °C for 120 min.

The objective of this study was to determine the optimal conditions for the liquefaction of the bark and branches of *Eucalyptus globulus*, in terms of reaction time, temperature, particle size, and type of catalyst (acid or base). These forest residues were also characterized as to their chemical composition in order to identify the possible ways of this biomass transformation to obtain value-added products (foams, polymers, and adhesives) while liquefaction is carried out at low pressure and temperature with an appropriate catalyst. The advantage of using these wastes over wood would bring higher revenue for Forest management companies and make polymer companies less dependent on oil prices fluctuations.

2. Materials and Methods

2.1. Sample Preparation

The bark and branch forest residues used in experiments are presented in Figure 1. These waste samples were supplied by Pedrosa & Irmãos, which is a Portuguese forest management company located in Leiria. Bark and branches were removed from *Eucalyptus globulus* trunks to produce logs to be used in pulp and paper industry.

After drying at room temperature, the samples were reduced to sawdust using a knives mill (Fritsch Pulversitte 19), followed by sieving for half an hour at 50 rpm (Retsh 5657 HAAN 1). The following fractions were obtained: >40 mesh (>0.425 mm); 40–60 mesh (0.425–0.250 mm); 60–80 mesh (0.250–0.180 mm), and <80 mesh (<0.180 mm). Afterwards these fractions were dried at 103 °C overnight.



Figure 1. *Eucalyptus globulus* forest residues: (a) bark and (b) branches.

2.2. Chemical Composition

Ash content determination was done in accordance with ISO 1762:2015 standard using the 40–60 mesh fraction. The sample was incinerated in a furnace at 525 °C for 3 h.

Moisture content of bark and branches was determined gravimetrically. The method used consisted in the determination of mass loss of the sample of 40–60 mesh fraction, dried in an oven at 105 ± 3 °C overnight.

Extractives were determined according to Tappi T 204 om-07 method [58]. Extractions were done sequentially in a Soxhlet apparatus with solvents of increasing polarity: dichloromethane (6 h), ethanol (12 h) and hot water (12 h).

The protein content was determined in the extracted sample with a 1% solution of pepsin in 0.1 M HCl (liquid-to-wood ratio 50). The resulting solution was left in the oven at 37 °C for 4 h and then filtered with warm water until neutralization. The remaining residue was dried at 60 °C until constant weight.

Tannin content was determined in a sample without extractives and proteins with a solution of NaOH at 0.3% (v/v). The resulting mixture was kept under a nitrogen atmosphere reflux during 1 h. The extracted material was filtered off, washed with hot water until neutralization and dried until constant weight at 60 °C.

Lignin content was determined from extractives-free samples such as a Klason lignin, according to Tappi T222 om-02 standard procedure [59]. This method consists in the direct determination of lignin and is based on isolation and determination of acid-insoluble lignin by two-step hydrolysis: first with concentrated sulfuric acid (72%), followed by hydrolysis with diluted sulfuric acid (3%).

The cellulose content was determined by the Kürschner and Hoffer method, which consists in the treatment of samples with nitric acid and ethanol (1:4, v/v). This method involves the sample free from extractives with a 50 mL solution of nitric acid and ethanol (1:4, v/v) for 3 h in reflux. At the end of each hour, the supernatant was removed by decanting and more 50 mL of ethanol and nitric acid solution were added (1:4, v/v). The insoluble residue obtained after 3 h is filtered off and washed with warm water until neutral reaction. The hemicellulose content was determined indirectly by the difference between the total polysaccharides content and cellulose.

2.3. Liquefaction

In order to study the optimal conditions for liquefaction of bark and branches of *Eucalyptus globulus* different liquefaction reaction time, temperature, type of catalyst (acid or base), and size of the biomass fraction were examined.

The liquefaction was carried out in a double shirt reactor (600 mL) heated with oil (Reactor Parr LKT PED). The samples were introduced in the reactor with a mixture of glycerol and ethylene glycol (1:1, v/v) catalyzed with sulfuric acid (3%) or potassium hydroxide (6%). Liquid-to-solid ratio was 1:10 in all experiments, there is 100 g of solvent for each 10 g of solid material. Different temperature and time of liquefaction were tested, with temperatures ranging between 140 °C and 200 °C, and the liquefaction time from 15 to

120 min. After liquefaction, liquefied samples were dissolved in methanol and filtered with a filter paper in a Buckner funnel to determine the unreacted residue. The latter was then washed with hot water until neutral reaction and dried at 105 °C until constant weight.

The effect of particle size was studied for <40, 40–60, 60–80, and >80 mesh fractions. The catalysts examined were sulfuric acid (3% wt.) or potassium hydroxide (6% wt.).

3. Results and Discussion

3.1. Chemical Composition

The studied materials are wastes of a Forest management company that efficiently separates *Eucalyptus globulus* bark and branches before sending wood for the cellulose companies. The material dries in the sun and the initial samples had moisture around 17.5% and 10.6% for bark and branches, respectively. Since especially branches are mostly removed in the forest and afterwards transported to the company and chipped, there can be a vast diversity in the composition, such as bark, leaves, and possibly some sand, as mentioned before for *Pinus Sylvestris* forest residues shredded chips [60]. Bark and branches are heterogeneous materials, consisting of non-structural and structural components. Among the macromolecular structural components, the main ones are cellulose, hemicelluloses, and lignin. The non-structural components are low molecular weight compounds, which include mainly the extractives and inorganic compounds. It is known that the chemical composition of branches and bark varies from species to species, changing in various parts of the same tree (trunk, branches, roots, bark, and needles) and is also affected by the trees growing conditions [61]. Other factors influencing the chemical composition of the bark and branches includes the age of trees, tree cutting season, and time elapsed between cutting and carrying out the analyses. The results on the chemical composition of bark and branches used in this study are depicted in Table 1. The major component for both samples is cellulose, with 40.5% and 41.3% for bark and branches, respectively. Similar results for the cellulose content were presented by Vázquez et al. [62] for eucalyptus bark cellulose (41.6%) and Pereira et al. [5] for *Eucalyptus globulus* branches (41.2%). Miranda et al. [63] reported a 62.6% of holocellulose content in eucalyptus bark, which is not much different from the 63.6% obtained in this study. The second most representative component are hemicelluloses, with values are of 23.1% and 22.3%, for bark and branches, respectively (Table 1).

Table 1. Chemical Composition of barks and branches of *Eucalyptus globulus* (% dry material).

Parameter	Bark Composition (%)	Branches Composition (%)
Ashes	14.2 ± 1.2	10.6 ± 0.8
Dichloromethane	1.2 ± 0.2	3.0 ± 0.2
Extract. Ethanol	2.9 ± 0.3	3.1 ± 0.2
Hot water	4.4 ± 1.0	4.8 ± 0.5
Proteins ^a	--	0.3 ± 0.1
Tannins ^b	11.4 ± 6.8	16.8 ± 0.6
Klason Lignin ^c	15.6 ± 0.3	17.9 ± 1.6
Cellulose	40.5 ± 1.0	41.3 ± 3.7
Hemicelluloses	23.1	22.3

^a Corrected for the extractive content and ash, ^b Corrected for the extractive content, ash, proteins, ^c Corrected for the extractive content, ash, proteins and tannins.

The hemicellulose content was determined indirectly by the difference between the total polysaccharides and cellulose, which might justify the differences from other studies. Most of the studies report some smaller amount of hemicelluloses for eucalyptus bark (e.g., 20.8% [62] or 7.0–19.6% [5]). Pereira et al. [5] reported 17.8% of pentosans for eucalyptus branches. Klason lignin represented of 17.9% and 15.6% for branches and bark, respectively. Vázquez et al. [62] reported 16.7% of lignin in eucalyptus bark, which is quite similar to the data obtained in this work (Table 1). At the same time, Pereira et al. [5] obtained a lignin content of 21.8% for branches, which is considerably higher than that

found here. However, in that work, a contribution of tannins was not counted for the lignin content.

Extractives were determined with dichloromethane (non-polar), ethanol (semi polar), and water (polar). Bark presented 1.2% of non-polar, 2.9% semi-polar, and 4.4% of polar extractives, representing 8.5% of total extractives. There are not so many studies for extractives from eucalyptus bark using the same solvents. Nevertheless, Miranda et al. [63] reported 0.9%, 0.2%, 1.3%, and 4.1% for dichloromethane, methanol, ethanol, and water extractives, respectively, which is comparable to the results presented in Table 1. Pereira et al. [5] reported a similar percentage of total extractives in eucalyptus bark (6.3–8.5%). Other researchers reported somewhat higher values, as for instance Yadav et al. [64] that reported 7.2% for the extractives soluble in ethanol and 15.5% for water extractives.

Branches presented 3.0% extractives in dichloromethane, 3.1% in ethanol, and 4.8% in water. The similarity between bark and branches chemical composition was to be expected since branches have a high bark content. The high percentage of ashes obtained in this study, 14.2% and 10.6% for bark and branches, respectively, might be due to some contamination of the samples from some inorganic materials since these wastes are left outside in the field as stated before [65]. Other studies refer smaller amounts of ashes for eucalyptus bark as for instance 12.1% [63], 4.7% [62], or 4.5% [66] or even between 1.6 and 3.5% [5]. According to Neiva et al. [18], eucalyptus bark has a high mineral content dominated by Ca that corresponds to 75% of the mineral fraction, while in wood is just 19%. There is also a high amount of Fe (546 ppm) and Mn (731 ppm). These authors also mentioned that the HHV of eucalypt bark was 18.4 (MJ/kg), lower than the 19.3 (MJ/kg) for wood. The values for branches are difficult to find since they depend on the amount of leaves, bark, or wood in the sample.

3.2. Liquefaction Optimization

The most important parameter in the liquefaction reaction is the catalyst in use, which allows the reaction to be developed at lower temperatures and pressures than non-catalyzed liquefaction. Catalyst promotes both the degradation of cellular macromolecular compounds and their reactions with the liquid medium, favoring their dissolution. In this work, sulfuric acid was used as an acid catalyst and potassium hydroxide as a basic catalyst. Figure 2 shows the liquefaction yields for the bark (a) and branches (b) in both alkaline and acid media. The results show that the acid catalyzed process led to higher liquefaction yields than for the base-catalyzed one for both bark and branches. The best liquefaction yield for bark in acid medium was around 60% for 60 min reaction time, while in basic medium, the highest yield of about 50% was obtained at 120 min reaction time. In relation to branches, the results were different since liquefaction percentage was higher with 61.7% for acid medium obtained at 60 min and 53.2% for basic medium at the same time. Alkaline medium is generally favorable for barks with high suberin content since it is known that suberin can be depolymerized by alkaline-catalyzed treatment in alcohol media as highlighted previously [18,32,50].

For instance, Esteves et al. [50] reported a liquefaction yield of around 60% for KOH and 30% for sulfuric acid catalyzed liquefaction of *Pseudotsuga menziesii* bark, which is a bark with high suberin content. The lower liquefaction yield obtained here for basic catalysis is probably due to the very low suberin content of eucalypt bark (<1%, [15]). Similar results were reported previously by other researchers [67,68].

Figure 3 presents the variation of the liquefaction yield in relation to the size of the particles. Results show that the particle size has no significant influence on the liquefaction yield and for the samples of bark and branches a similar yield of 61.6% and 56.0%, respectively, could be achieved using fractions of <80 mesh. The size of the samples is generally important when the chemical composition of the various fractions is very different, which happens, for example, in the bark of *Pseudotsuga menziesii*, which has a higher cork content in the larger particles than in the smaller ones. Results presented by Miranda et al. [63] show that the chemical composition of fine (F, <0.180 mm), medium (M, 0.250–0.450 mm),

and coarse (C, >2 mm) fractions differs mostly in the extractive content and there is only a smaller percentage of lignin and therefore higher holocellulose content in the coarse fraction. That work demonstrated that, theoretically, the coarse bark fraction would be more easily liquefied than the fine fraction by looking only at the chemical composition. However, in finer fractions, the reaction should be faster due to the better accessibility of the chemicals to the material. This equilibrium might justify the results presented in Figure 3, because there is a slightly higher liquefaction yield in the coarse (<40 mesh) fraction, decreasing further for the 60–80 mesh fraction, and increasing for the fine (<80) fraction.

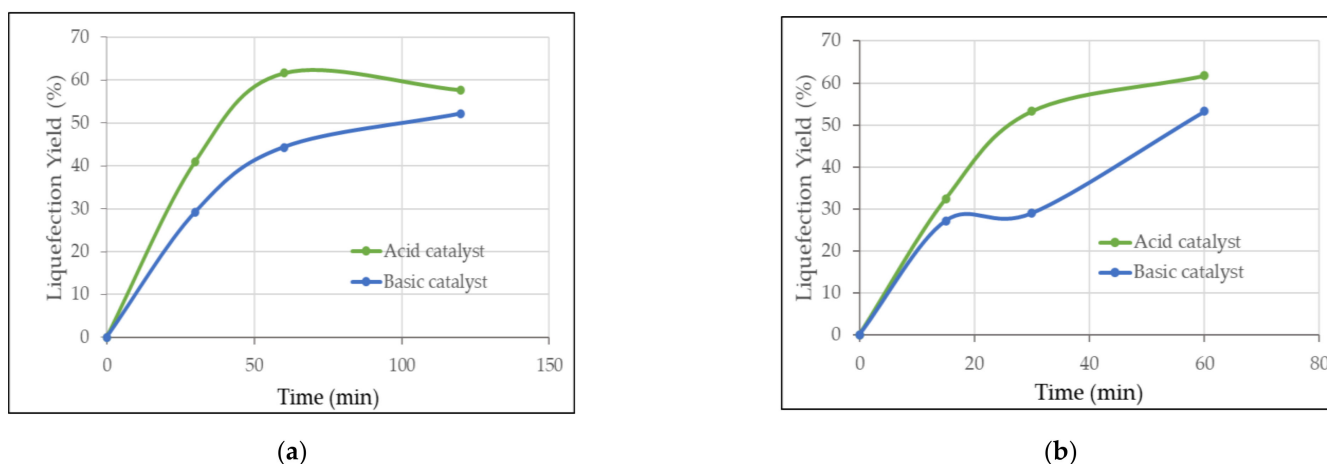


Figure 2. Effect of the catalyst on the liquefaction yields from (a) bark and (b) branches for the fraction > 80 mesh (powder) at 180 °C.

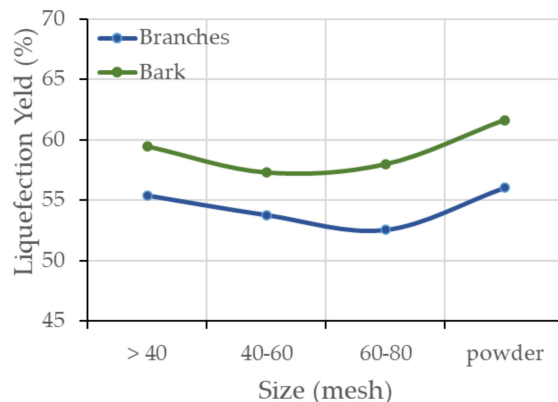


Figure 3. Effect of the bark and branches particle size to the liquefaction at 180 °C for 60 min with acid catalysis.

The best temperature to achieve the highest liquefaction was studied for 60 min reaction time. Figure 4 shows the liquefaction yields for reaction temperatures between 140 °C and 200 °C for both bark and branches. The best liquefaction yields were obtained for the bark at 180 °C (61.6%) and for the branches at 160 °C (62.2%). The different results between bark and branches can be attributed to the somewhat different chemical composition of both forest wastes. The poorer results obtained at 200 °C are probably due to some condensation reactions between the liquefaction products. Similar results were reported previously for the liquefaction of cork [69]. According to Kurimoto and Tamura [70], re-condensation happens at higher temperatures when both the cellulose and the lignin are liquefied. Nevertheless, these authors suggested that this reaction could be inhibited by the addition of low-molecular weight glycols, such as glycerol.

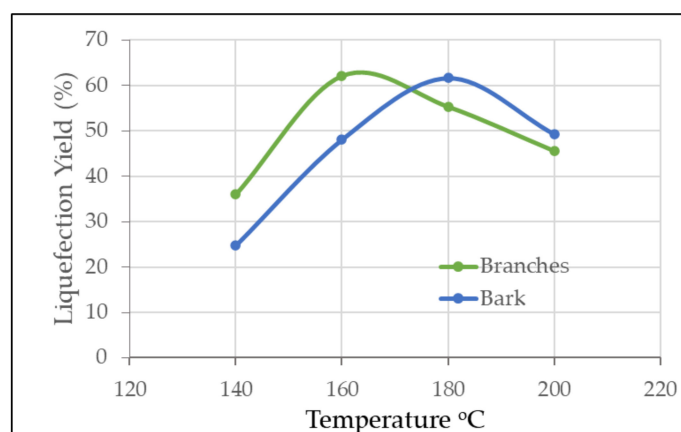


Figure 4. Effect of the reaction temperature on the liquefaction yield of bark and branches particles fraction > 80 mesh (powder) for 60 min with acid catalysis.

The variation of liquefaction yield along the treatment was studied for a liquefaction at 180 °C. Figure 5 shows the variation of bark and branches liquefaction yields for 15 min, 30 min, 60 min, and 120 min of treatment. It was found that for the bark sample, the best yield was obtained for 60 min and 180 °C (61.6%), while that for the branches the best yield was obtained for 120 min and 180 °C (61.2%). No significant difference was observed between bark and branches which is probably due to the relatively similar chemical composition of both residues as seen before. According to Hu et al. [71], in the first reaction stages, hemicelluloses, lignin, and amorphous cellulose are liquefied due to their better accessibility to chemicals while crystalline cellulose needs longer reaction time.

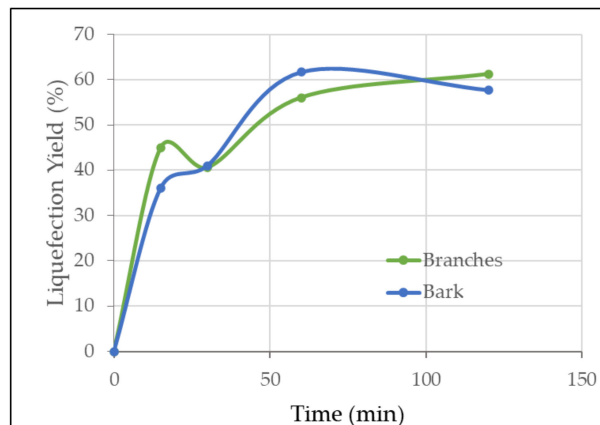


Figure 5. Effect of reaction time on yield of liquefaction products from the fraction of bark and branches particles > 80 mesh (powder) at 180 °C with acid catalysis.

The use of these wastes produced in forest management companies would bring a huge economic impact since these wastes are generally burned, and the possibility of using them to substitute wood in some products, derived from liquefied lignocellulosic materials, such as adhesives or polyurethane foams, would bring an important revenue for these companies. Another advantage is that the processing of these wastes is similar to the one used with wood and, therefore, no additional costs would be required to implementing this technology. Foams and adhesives are mostly produced from petroleum, which is becoming scarce. Lignocellulosic materials have been described as “the most abundant, economical, and highly renewable natural feedstock globally, with an approximate 200 billion tons yield” [20]. Another advantage is that since these materials are not derived from fossil fuels, they are not susceptible to oil prices fluctuations that are becoming more unpredictable every day [72].

4. Conclusions

Chemical analysis of the main forest residues of *E. globulus*, bark and branches, did not reveal significant differences in the abundance of their macromolecular components (cellulose, lignin and hemicelluloses). The highest liquefaction yields in the reaction mixture glycerol:ethylene glycol (1:1, v/v) for *E. globulus* bark and branches were obtained with acid catalyst. The best results for the bark powder were achieved at 180 °C for 60 min and for branches, (62.2% yield) attained with >80 mesh fraction at 160 °C for 60 min. Under certain conditions (e.g., at 180 °C for 60 min), the fine fraction (>80 mesh) of bark and branches did not show significant differences between their liquefaction yields. This means that both wastes can be mixed together for their processing as already practiced in most cases of other forest residues. Too high temperatures (>180 °C) are not advantageous regarding the liquefaction yields and, therefore, temperatures around 160–180 °C would be preferable for different bark/branches mixtures, while adjusting the suitable processing times. Overall, these results put in evidence that these lignocellulosic wastes can efficiently be converted into a liquefied material that can later be used for the production of added value materials. This study to test the ability of these liquefied materials to produce polyurethane foams and adhesives is ongoing.

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References

1. Penín, L.; López, M.; Santos, V.; Alonso, J.L.; Parajó, J.C. Technologies for Eucalyptus Wood Processing in the Scope of Biorefineries: A Comprehensive Review. *Bioresour. Technol.* **2020**, *311*, 123528. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Neiva, D.; Fernandes, L.; Araújo, S.; Lourenço, A.; Gominho, J.; Simões, R.; Pereira, H. Chemical Composition and Kraft Pulping Potential of 12 Eucalypt Species. *Ind. Crops Prod.* **2015**, *66*, 89–95. [\[CrossRef\]](#)
3. CEPI. *Key Statistics 2020 European Pulp and Paper Industry*; CEPI: Brussels, Belgium, 2020.
4. Gominho, J.; Lourenço, A.; Miranda, I.; Pereira, H. Chemical and Fuel Properties of Stumps Biomass from *Eucalyptus globulus* Plantations. *Ind. Crops Prod.* **2012**, *39*, 12–16. [\[CrossRef\]](#)
5. Pereira, H. Variability in The Chemical Composition of Plantation Eucalypts (*Eucalyptus globulus* Labill.). *Wood Fiber Sci.* **2007**, *20*, 82–90.
6. Coelho, A.L.R. Otimização Da Extração Sólido-Líquido de Antioxidantes de Subprodutos Florestais Pelo Método de Superfície de Resposta. Master's Thesis, Superior Institute of Technology of Porto, Porto, Portugal, 2013.
7. Santos, S.A.O.; Villaverde, J.J.; Silva, C.M.; Neto, C.P.; Silvestre, A.J.D. Supercritical Fluid Extraction of Phenolic Compounds from *Eucalyptus globulus* Labill Bark. *J. Supercrit. Fluids* **2012**, *71*, 71–79. [\[CrossRef\]](#)
8. de Melo, M.M.R.; Oliveira, E.L.G.; Silvestre, A.J.D.; Silva, C.M. Supercritical Fluid Extraction of Triterpenic Acids from *Eucalyptus globulus* Bark. *J. Supercrit. Fluids* **2012**, *70*, 137–145. [\[CrossRef\]](#)
9. Patinha, D.J.S.; Domingues, R.M.A.; Villaverde, J.J.; Silva, A.M.S.; Silva, C.M.; Freire, C.S.R.; Neto, C.P.; Silvestre, A.J.D. Lipophilic Extractives from the Bark of *Eucalyptus grandis* × *globulus*, a Rich Source of Methyl Morolate: Selective Extraction with Supercritical CO₂. *Ind. Crops Prod.* **2013**, *43*, 340–348. [\[CrossRef\]](#)
10. Pinto, P.C.; Mota, I.F.; Loureiro, J.M.; Rodrigues, A.E. Membrane Performance and Application of Ultrafiltration and Nanofiltration to Ethanol/Water Extract of Eucalyptus Bark. *Sep. Purif. Technol.* **2014**, *132*, 234–243. [\[CrossRef\]](#)
11. Baptista, M.E.A. Ultrafiltração de Extrato de Casca de *Eucalyptus globulus* Para Recuperação de Compostos Polifenólicos. Master's Thesis, University of Porto, Porto, Portugal, 2013.
12. Domingues, R.M.A.; Sousa, G.D.A.; Freire, C.S.R.; Silvestre, A.J.D.; Neto, C.P. *Eucalyptus globulus* Biomass Residues from Pulping Industry as a Source of High Value Triterpenic Compounds. *Ind. Crops Prod.* **2010**, *31*, 65–70. [\[CrossRef\]](#)

13. Domingues, R.M.A.; Sousa, G.D.A.; Silva, C.M.; Freire, C.S.R.; Silvestre, A.J.D.; Neto, C.P. High Value Triterpenic Compounds from the Outer Barks of Several Eucalyptus Species Cultivated in Brazil and in Portugal. *Ind. Crops Prod.* **2011**, *33*, 158–164. [CrossRef]
14. Neiva, D.M.; Araújo, S.; Gominho, J.; de Carneiro, A.C.; Pereira, H. Potential of *Eucalyptus globulus* Industrial Bark as a Biorefinery Feedstock: Chemical and Fuel Characterization. *Ind. Crops Prod.* **2018**, *123*, 262–270. [CrossRef]
15. Lima, L.; Miranda, I.; Knapic, S.; Quilhó, T.; Pereira, H. Chemical and Anatomical Characterization, and Antioxidant Properties of Barks from 11 Eucalyptus Species. *Eur. J. Wood Prod.* **2018**, *76*, 783–792. [CrossRef]
16. Gominho, J.; Costa, R.A.; Lourenço, A.; Quilhó, T.; Pereira, H. *Eucalyptus globulus* Stumps Bark: Chemical and Anatomical Characterization under a Valorisation Perspective. *Waste Biomass Valor* **2021**, *12*, 1253–1265. [CrossRef]
17. Gominho, J.; Costa, R.; Lourenço, A.; Neiva, D.M.; Pereira, H. The Effect of Different Pre-Treatments to Improve Delignification of Eucalypt Stumps in a Biorefinery Context. *Bioresour. Technol. Rep.* **2019**, *6*, 89–95. [CrossRef]
18. Neiva, D.M.; Rencoret, J.; Marques, G.; Gutiérrez, A.; Gominho, J.; Pereira, H.; Río, J.C. del Lignin from Tree Barks: Chemical Structure and Valorization. *ChemSusChem* **2020**, *13*, 4537–4547. [CrossRef]
19. Gominho, J.; Lourenço, A.; Marques, A.V.; Pereira, H. An Extensive Study on the Chemical Diversity of Lipophilic Extractives from *Eucalyptus globulus* Wood. *Phytochemistry* **2020**, *180*, 112520. [CrossRef]
20. Wang, F.; Ouyang, D.; Zhou, Z.; Page, S.J.; Liu, D.; Zhao, X. Lignocellulosic Biomass as Sustainable Feedstock and Materials for Power Generation and Energy Storage. *J. Energy Chem.* **2021**, *57*, 247–280. [CrossRef]
21. Wang, H.; Chen, H.-Z. A Novel Method of Utilizing the Biomass Resource: Rapid Liquefaction of Wheat Straw and Preparation of Biodegradable Polyurethane Foam (PUF). *J. Chin. Inst. Chem. Eng.* **2007**, *38*, 95–102. [CrossRef]
22. Briones, R.; Torres, L.; Saravia, Y.; Serrano, L.; Labidi, J. Liquefied Agricultural Residues for Film Elaboration. *Ind. Crops Prod.* **2015**, *78*, 19–28. [CrossRef]
23. Xiao, W.; Zhang, X.; Wang, X.; Niu, W.; Han, L. Rapid Liquefaction of Corn Stover with Microwave Heating. *BioResources* **2015**, *10*, 4038–4047. [CrossRef]
24. Zhang, J.; Hori, N.; Takemura, A. Optimization of Agricultural Wastes Liquefaction Process and Preparing Bio-Based Polyurethane Foams by the Obtained Polyols. *Ind. Crops Prod.* **2019**, *138*, 111455. [CrossRef]
25. Jin, Y.; Lai, C.; Kang, J.; Lu, X.; Liu, J.; Lü, Q.-F. Liquefaction of Cornstalk Residue Using 5-Sulfosalicylic Acid as the Catalyst for the Production of Flexible Polyurethane Foams. *BioResources* **2019**, *13*, 6970–6982. [CrossRef]
26. 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*, 227–233. [CrossRef] [PubMed]
27. Hassan, E.M.; Shukry, N. Polyhydric Alcohol Liquefaction of Some Lignocellulosic Agricultural Residues. *Ind. Crops Prod.* **2008**, *27*, 33–38. [CrossRef]
28. Wang, Q.; Tuohedi, N. Polyurethane Foams and Bio-Polyols from Liquefied Cotton Stalk Agricultural Waste. *Sustainability* **2020**, *12*, 4214. [CrossRef]
29. Matos, M.; Barreiro, M.F.; Gandini, A. Olive Stone as a Renewable Source of Biopolyols. *Ind. Crops Prod.* **2010**, *32*, 7–12. [CrossRef]
30. D'Souza, J.; Yan, N. Producing Bark-Based Polyols through Liquefaction: Effect of Liquefaction Temperature. *ACS Sustain. Chem. Eng.* **2013**, *1*, 534–540. [CrossRef]
31. Jiang, W.; Adamopoulos, S.; Hosseinpourpia, R.; Žigon, J.; Petric, M.; Šernek, M.; Medved, S. Utilization Bark for Production of Particleboards. *Appl. Sci.* **2020**, *10*, 5253. [CrossRef]
32. Cruz-Lopes, L.P.; Silva, H.C.; Domingos, I.; Ferreira, J.; Lemos, L.T.; Esteves, B. Optimization of Quercus Cerris Bark Liquefaction. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* **2016**, *10*, 1073–1076.
33. Esteves, B.; Dulyanska, Y.; Costa, C.; Ferreira, J.V.; Domingos, I.; Pereira, H.; de Lemos, L.T.; Cruz-Lopes, L.V. Cork Liquefaction for Polyurethane Foam Production. *BioResources* **2017**, *12*, 2339–2353. [CrossRef]
34. Kim, K.H.; Jo, Y.J.; Lee, C.G.; Lee, E. Solvothermal Liquefaction of Microalgal Tetraselmis Sp. Biomass to Prepare Biopolyols by Using PEG#400-Blended Glycerol. *Algal Res.* **2015**, *12*, 539–544. [CrossRef]
35. Jin, Y.; Ruan, X.; Cheng, X.; Lü, Q. Liquefaction of Lignin by Polyethyleneglycol and Glycerol. *Bioresour. Technol.* **2011**, *102*, 3581–3583. [CrossRef] [PubMed]
36. Kosmela, P.; Hejna, A.; Formela, K.; Haponiuk, J.T.; Piszczek, L. Biopolyols Obtained via Crude Glycerol-Based Liquefaction of Cellulose: Their Structural, Rheological and Thermal Characterization. *Cellulose* **2016**, *23*, 2929–2942. [CrossRef]
37. Braz, A.; Mateus, M.M.; dos Santos, R.G.; Machado, R.; Bordado, J.M.; Correia, M.J.N. Modelling of Pine Wood Sawdust Thermochemical Liquefaction. *Biomass Bioenergy* **2019**, *120*, 200–210. [CrossRef]
38. Mateus, M.M.; Matos, S.; Guerreiro, D.; Debiagi, P.; Gaspar, D.; Ferreira, O.; Bordado, J.C.; Santos, R.G. dos Liquefaction of Almond Husk for Assessment as Feedstock to Obtain Valuable Bio-Oils. *Pure Appl. Chem.* **2019**, *91*, 1177–1190. [CrossRef]
39. Lee, W.-J.; Yu, C.-Y.; Chen, Y.-C. Preparation and Characteristics of Polyurethane Made with Polyhydric Alcohol-Liquefied Rice Husk. *J. Appl. Polym. Sci.* **2018**, *135*, 45910. [CrossRef]
40. Ertas; Fidan Biobased Rigid Polyurethane Foam Prepared from Apricot Stone Shell-Based Polyol for Thermal Insulation Application, Part 1: Synthesis, Chemical, and Physical Properties: BioResources. Available online: <https://bioresources.cnr.ncsu.edu/resources/biobased-rigid-polyurethane-foam-prepared-from-apricot-stone-shell-based-polyol-for-thermal-insulation-application-part-1-synthesis-chemical-and-physical-properties/> (accessed on 16 February 2021).

41. Zhang, Q.; Zhang, G.; Han, D.; Wu, Y. Renewable Chemical Feedstocks from Peanut Shell Liquefaction: Preparation and Characterization of Liquefied Products and Residue. *J. Appl. Polym. Sci.* **2016**, *133*, 43361. [\[CrossRef\]](#)
42. Członka, S.; Strąkowska, A.; Kairytė, A. Application of Walnut Shells-Derived Biopolyol in the Synthesis of Rigid Polyurethane Foams. *Materials* **2020**, *13*, 2687. [\[CrossRef\]](#)
43. Chang, C.; Liu, L.; Li, P.; Xu, G.; Xu, C. Preparation of Flame Retardant Polyurethane Foam from Crude Glycerol Based Liquefaction of Wheat Straw. *Ind. Crops Prod.* **2021**, *160*, 113098. [\[CrossRef\]](#)
44. Briones, R.; Rodriguez, J.; Labidi, J.; Cunningham, E.; Martin, P. Liquefaction of Corn Husks and Properties of Biodegradable Biopolyol Blends. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 2973–2982. [\[CrossRef\]](#)
45. Jasiūnas, L.; Skvorčinskienė, R.; Miknius, L. Wet and Coarse: The Robustness of Two-Stage Crude Glycerol Mediated Solvothermal Liquefaction of Residual Biomass. *Waste Biomass Valor* **2020**, *11*, 2171–2181. [\[CrossRef\]](#)
46. Yip, J.; Chen, M.; Szeto, Y.S.; Yan, S. Comparative Study of Liquefaction Process and Liquefied Products from Bamboo Using Different Organic Solvents. *Bioresour. Technol.* **2009**, *100*, 6674–6678. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Martins, J.; Lopes, L.C.; Esteves, B. Otimização Da Liquefação Da Madeira de Pinus Pinaster Com Poliálcoois. *Silva Lusit.* **2013**, *21*, 177–183.
48. Niu, M.; Zhao, G.J.; Alma, M.H. Thermogravimetric Studies on Condensed Wood Residues in Polyhydric Alcohols Liquefaction. *BioResources* **2011**, *6*, 615–630. [\[CrossRef\]](#)
49. Pan, H.; Zheng, Z.; Hse, C.Y. Microwave-Assisted Liquefaction of Wood with Polyhydric Alcohols and Its Application in Preparation of Polyurethane (PU) Foams. *Eur. J. Wood Wood Prod.* **2012**, *70*, 461–470. [\[CrossRef\]](#)
50. 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. [\[CrossRef\]](#)
51. Alma, M.; Shiraishi, N. Preparation of Polyurethane-like Foams from NaOH-Catalyzed Liquefied Wood. *Eur. J. Wood Wood Prod.* **1998**, *56*, 245–246. [\[CrossRef\]](#)
52. Yao, Y.; Yoshioka, M.; Shiraishi, N. Water-absorbing Polyurethane Foams from Liquefied Starch. *J. Appl. Polym. Sci.* **1996**, *60*, 1939–1949. [\[CrossRef\]](#)
53. Kobayashi, M.; Tukamoto, K.; Tomita, B. Application of Liquefied Wood to a New Resin System-Synthesis and Properties of Liquefied Wood/Epoxy Resins. *Holzforschung* **2000**, *54*, 93–100. [\[CrossRef\]](#)
54. Juhaida, M.F.; Paridah, M.T.; Mohd Hilmi, M.; Sarani, Z.; Jalaluddin, H.; Mohamad Zaki, A.R. Liquefaction of Kenaf (*Hibiscus cannabinus* L.) Core for Wood Laminating Adhesive. *Bioresour. Technol.* **2010**, *101*, 1355–1360. [\[CrossRef\]](#)
55. Fernandes, F.; Matos, S.; Gaspar, D.; Silva, L.; Paulo, I.; Vieira, S.; Pinto, P.C.R.; Bordado, J.; Galhano dos Santos, R. Boosting the Higher Heating Value of *Eucalyptus globulus* via Thermochemical Liquefaction. *Sustainability* **2021**, *13*, 3717. [\[CrossRef\]](#)
56. Mateus, M.M.; Guerreiro, D.; Ferreira, O.; Bordado, J.C.; Galhano dos Santos, R. Heuristic Analysis of *Eucalyptus globulus* Bark Depolymerization via Acid-Liquefaction. *Cellulose* **2017**, *24*, 659–668. [\[CrossRef\]](#)
57. Vale, M.; Mateus, M.M.; Galhano dos Santos, R.; Nieto de Castro, C.; de Schrijver, A.; Bordado, J.C.; Marques, A.C. Replacement of Petroleum-Derived Diols by Sustainable Biopolyols in One Component Polyurethane Foams. *J. Clean. Prod.* **2019**, *212*, 1036–1043. [\[CrossRef\]](#)
58. TAPPI. *Solvent Extractives of Wood and Pulp*. TAPPI T204 Cm-07; TAPPI Press: Atlanta, GA, USA, 2007.
59. TAPPI. T 222 Om-02. *Acid-Insoluble Lignin in Wood and Pulp*; TAPPI: Atlanta, GA, USA, 2002.
60. Roman, K.; Barwicki, J.; Rządziejewicz, W.; Dawidowski, M. Evaluation of Mechanical and Energetic Properties of the Forest Residues Shredded Chips during Briquetting Process. *Energies* **2021**, *14*, 3270. [\[CrossRef\]](#)
61. Kilulya, K.F.; Msagati, T.A.M.; Mamba, B.B.; Catherine Ngila, J.; Bush, T. Effect of Site, Species and Tree Size on the Quantitative Variation of Lipophilic Extractives in Eucalyptus Woods Used for Pulping in South Africa. *Ind. Crops Prod.* **2014**, *56*, 166–174. [\[CrossRef\]](#)
62. Vázquez, G.; Fontenla, E.; Santos, J.; Freire, M.S.; González-Álvarez, J.; Antorrena, G. Antioxidant Activity and Phenolic Content of Chestnut (*Castanea Sativa*) Shell and Eucalyptus (*Eucalyptus globulus*) Bark Extracts. *Ind. Crops Prod.* **2008**, *28*, 279–285. [\[CrossRef\]](#)
63. Miranda, I.; Gominho, J.; Mirra, I.; Pereira, H. Fractioning and Chemical Characterization of Barks of *Betula Pendula* and *Eucalyptus globulus*. *Ind. Crops Prod.* **2013**, *41*, 299–305. [\[CrossRef\]](#)
64. Yadav, K.R.; Sharma, R.K.; Kothari, R.M. Bioconversion of Eucalyptus Bark Waste into Soil Conditioner. *Bioresour. Technol.* **2002**, *81*, 163–165. [\[CrossRef\]](#)
65. Roman, K.; Roman, M.; Szadkowska, D.; Szadkowski, J.; Grzegorzewska, E. Evaluation of Physical and Chemical Parameters According to Energetic Willow (*Salix viminalis* L.) Cultivation. *Energies* **2021**, *14*, 2968. [\[CrossRef\]](#)
66. Akuyuz, M.; Sahin, A.; Alma, A.; Bektap, I.; Usta, A. Conversion of Tree Bark into Bakelite-like Thermosetting Materials by Phenolation. In Proceedings of the XII World Forest Congress, Québec City, QC, Canada, 21–28 September 2003; p. 0425-A1.
67. Yona, A.M.C.; Budija, F.; Kričej, B.; Kutnar, A.; Pavlič, M.; Pori, P.; Tavzes, Č.; Petrič, M. Production of Biomaterials from Cork: Liquefaction in Polyhydric Alcohols at Moderate Temperatures. *Ind. Crops Prod.* **2014**, *54*, 296–301. [\[CrossRef\]](#)
68. Maldas, D.; Shiraishi, N. Liquefaction of Wood in the Presence of Polyol Using NaOH as a Catalyst and Its Application to Polyurethane Foams. *Int. J. Polym. Mater.* **1996**, *33*, 61–71. [\[CrossRef\]](#)

-
69. Soares, B.; Gama, N.; Freire, C.; Barros-Timmons, A.; Brandão, I.; Silva, R.; Pascoal Neto, C.; Ferreira, A. Ecopolyol Production from Industrial Cork Powder via Acid Liquefaction Using Polyhydric Alcohols. *ACS Sustain. Chem. Eng.* **2014**, *2*, 846–854. [[CrossRef](#)]
 70. Kurimoto, Y.; Tamura, Y. Species Effects on Wood-Liquefaction in Polyhydric Alcohols. *Holzforschung* **1999**, *53*, 617–622. [[CrossRef](#)]
 71. Hu, S.; Luo, X.; Li, Y. Polyols and Polyurethanes from the Liquefaction of Lignocellulosic Biomass. *ChemSusChem* **2014**, *7*, 66–72. [[CrossRef](#)] [[PubMed](#)]
 72. Kahlerras, Z.; Irinislimane, R.; Bruzaud, S.; Belhaneche-Bensemra, N. Elaboration and Characterization of Polyurethane Foams Based on Renewably Sourced Polyols. *J. Polym. Environ.* **2020**, *28*, 3003–3018. [[CrossRef](#)]