

Optimization of *Quercus cerris* Bark Liquefaction

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Abstract—The liquefaction process of cork based tree barks has led to an increase of interest due to its potential innovation in the lumber and wood industries. In this particular study the bark of *Quercus cerris* (Turkish oak) is used due to its appreciable amount of cork tissue, although of inferior quality when compared to the cork provided by other *Quercus* trees. This study aims to optimize alkaline catalysis liquefaction conditions, regarding several parameters. To better comprehend the possible chemical characteristics of the bark of *Quercus cerris*, a complete chemical analysis was performed. The liquefaction process was performed in a double-jacket reactor heated with oil, using glycerol and a mixture of glycerol/ethylene glycol as solvents, potassium hydroxide as a catalyst, and varying the temperature, liquefaction time and granulometry. Due to low liquefaction efficiency resulting from the first experimental procedures a study was made regarding different washing techniques after the filtration process using methanol and methanol/water. The chemical analysis stated that the bark of *Quercus cerris* is mostly composed by suberin (ca. 30%) and lignin (ca. 24%) as well as insolvent hemicelluloses in hot water (ca. 23%). On the liquefaction stage, the results that led to higher yields were: using a mixture of methanol/ethylene glycol as reagents and a time and temperature of 120 minutes and 200 °C, respectively. It is concluded that using a granulometry of <80 mesh leads to better results, even if this parameter barely influences the liquefaction efficiency. Regarding the filtration stage, washing the residue with methanol and then distilled water leads to a considerable increase on final liquefaction percentages, which proves that this procedure is effective at liquefying suberin content and lignocellulose fraction.

Keywords—Liquefaction, alkaline catalysis, optimization, *Quercus cerris* bark.

I. INTRODUCTION

THE Turkey oak (*Quercus cerris*) is a hardwood tree, which belongs to the family of *Fagaceae*, *Quercus* genus, *Euquercus* subgenus, from the section *Cerris*. The species is distributed naturally in the South of France, Italy, central Europe, Balkan Peninsula, Turkey and West of Syria and Lebanon [1]. There the species grows naturally between altitudes between 10 and the 1500 meters [2], [7]. The species is rare in Portugal only exists some samples inserted for decoration. It is characterized by its quick maturation, about

18 months, is very resistant to low temperatures and therefore particularly suited for planting in cold areas [1]. Is a medium-sized tree that reaches heights between 25 and 40 meters. The leaves are deciduous, dark green color [1], [3]. The length and width of the leaves are between 7-14 cm long and 3-5 cm, respectively [4]. The fruit has a length between 2.5 and 3.6 cm, with long ranges between 4-8 mm long [1], [4]. The bark is thick, approximately 5 cm [5], gray and contains deep longitudinal channels. The species was not valued as timber-producing, because wood has unwanted properties in end use, such as low dimensional stability, susceptible to cracks after drying, low durability and an irregular red color, usually used as firewood [6]-[8].

Given that society is increasingly made aware of sustainability, the liquefaction research of Cork bark has grown and aroused interest. The liquefaction of lignin and suberin present in the bark of trees, in particular conditions, can substitute the products currently derived from petroleum products.

The most effective method in liquefaction process is the use of one or a mixture of solvents and a catalyst, acidic or alkaline, where the solvent is part of the liquefied material at the end. In this process the temperature and pressure are the most important factors to consider. The longer the time and the liquefaction temperature, higher is the liquefaction yield. Use of catalyst permits the use of lower pressures and temperatures, 150-200 °C and 1-5 MPa respectively. The liquefaction at low temperatures and pressures may be one of the best ways to develop sustainable production of chemicals in a new future. There are also other liquefaction processes like the deoxy-liquefaction process that aims to obtain liquid fuels with ethanol, that consists in the reduction of oxygen atoms (O₂) combined with hydrogen atoms (H) in order to produce water (H₂O) in order to weaken the reduction of O₂ atoms as CO₂ and carbon monoxide (CO). There is also a process of liquefaction composed by two sequential steps, developed for production of polyols with high liquefaction yield. The first step consists of a liquefaction with acid catalyst followed by a liquefaction with basic catalyst. This process is interesting due to the fact that try to take advantage of the features of both steps [9]. Other solvents used in liquefaction processes are the cyclic carbonates (ethylene carbonate and propylene carbonate), phenols and polyhydric alcohols (ethylene glycol, propylene glycol, diethylene glycol and glycerol [10]-[15]). Therefore, factors such as the amount of solvents and catalytic converter, temperature and reaction time will influence the liquefaction process, being imperative to optimize these factors in order to obtain better yields. Of all the factors, it is known that the time of reaction is of the most significant, since the longer the time of liquefaction, less residue, and better yield can be obtained. Currently

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liquefaction techniques of cork as well as subsequent processing techniques (polyols) have great applicability in industry, due to the lack of research on this topic [15]-[17].

In this work, the bark of *Quercus cerris* was used. After the determination of chemical composition an optimization study in order to optimize liquefaction conditions with alkaline catalysis was performed.

II. EXPERIMENTAL

A. Sample Preparation

Quercus cerris (QC) cork was used in the tests. The samples were grounded and sieved into three fractions > 40 Mesh, 40-60 Mesh and < 60 Mesh. These fractions were dried in an oven at 100 °C for at least 24 hours before each essay.

B. Chemical Composition Determination

The QC was characterised regarding the ash content, extractives (in dichloromethane, ethanol and in hot water), suberin, proteins, tannins, cellulose, lignin and hemicelluloses.

The ashes content was determined by calcinations the QC (fraction <60 Mesh) at 525 °C, according to the standard procedure Tappi T 211 om-93.

The extractives content in dichloromethane, ethanol and hot water were determined by Soxhlet extraction according to the Tappi T 204 om-88 [10]. The determination of extractives in hot water was carried out with a solution of ammonium citrate (10 g/L) for 1 hour under reflux (liquid-to-solid ratio 100).

Suberin content was determined in extractive-free material by depolymerisation through methanolysis. A 1.5 g of extractive-free material was refluxed with 100 mL of a 3% methanolic solution of NaOCH₃ in CH₃OH for 3 h. After, the sample was filtered and washed with methanol. The filtrate and residue were refluxed with 100 mL CH₃OH for 15 min and filtrated again. Then, the combined filtrates were acidified to pH 6 with 2 M H₂SO₄ and evaporated to dryness. The residue was suspended in 50 mL water and the alcoholysis products recovered with dichloromethane in three successive extractions, each with 50 mL dichloromethane. The combined extracts were dried over anhydrous sodium sulphate (Na₂SO₄), and the solvent was evaporated to dryness [18]. Suberin extracts were quantified gravimetrically, and results were expressed in percent of cork dry weight.

Protein content in extractives-free, after extraction with acetone, was determined by treatment with 1% pepsin solution in 0.1 M HCl at 37°C for 16 hours [19].

Tannin content was determined in extractives and protein-free QC by refluxing with a solution of 0.3% NaOH (solid-to-liquid ratio 1: 100) under a nitrogen atmosphere for 1 hour. Then the extracted material was filtered, washed with hot water until obtaining neutral filtrate. Finally, it proceeded to drying at 60 °C until constant weight was achieved. The tannin content was determined by weight difference between starting and extracted material.

Lignin content in QC free of extractives, proteins and tannins was determined by Klason method with 72% H₂SO₄ (according to Tappi T 204 om-88).

The cellulose was determined by four consecutive treatments with HNO₃: EtOH mixture (1:4, v/v) under reflux for 1 h each according to the Kürschner and Höffer method [20].

C. Liquefaction

Liquefaction of QC cork was held on a double shirt reactor with heated oil using glycerol (G) catalysed by potassium hydroxide (KOH) at 6%. The liquefied bark was dissolved in methanol and filtered, determining the insoluble residue gravimetrically [21]. Trials were carried out at different particles size; different temperatures: 160, 180 and 200 °C and time ranged between 30-120 min.

III. RESULTS AND DISCUSSION

A. Chemical Composition of the Materials

Aiming a better understanding of the results, the general chemical composition of the QC has been done. Table I presents the QC chemical composition.

TABLE I
CHEMICAL COMPOSITION OF QC (% DRY MATERIAL)

Parameters	Content (%)	
Ashes	2.32	
K	0.04	
Ca	1.27	
Mg	<0.01	
Na	<0.01	
Zn	<0.01	
Extractives	{ Dichloromethane	10.29
	{ Ethanol	3.10
	{ Hot water	2.25
Suberin	29.86	
Proteins ^a	9.44	
Tannins ^b	9.89	
Lignin <i>Klason</i> ^c	24.14	
Celluloses Kürschner - Höffner	8.71	
Hemicelluloses	22.81	

^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 chemical characterization showed that QC is a material in which suberin is the major component (with around 29.9%), followed by Klason lignin (with around 24.1%) and insoluble hemicelluloses in hot water (22.8%). It is important to highlight the high presence of extractives in dichloromethane (10.3%). The chemical analysis of the ash cations made to this bark shows high contents of K⁺ and Ca²⁺.

The ash percentage 2.3% obtained in this work is not much different than the presented by [22] with *Quercus cerris* (2.6%). Although the value obtained is a little lower in our case. The total extractives in dichloromethane (10.3%), in ethanol (3.1%) as well as the extractives in hot water (2.3%), are much similar compared with the results obtained by [22] 10.9, 3.4 and 2.4%, respectively. However, suberin (29.9%) presents higher value than those previously studied 28.5% and the lignin (24.1%) a lower value (28.1%). The lack of

information in relation to other analyses performed, proteins, tannins, etc., would allow a better comparison.

B. Liquefaction

The preliminary studies carried out on the influence of the filtration type of the liquefied product allows the conclusion that this is extremely important since there was an increase from 19.5% to 68.9% when the material was washed with methanol only or washed with methanol, followed by a water. This is because the solvent used in liquefaction reaction (glycerol) is very dense and it has been proved difficult to dissolve in methanol, increasing the residue amount. It appears that, for which addition of ethylene glycol to the glycerol (solvents) improves slightly the liquefaction yields, about 2% of the liquefaction time for less than 90 minutes. Optimal conditions in preliminary tests were used in all other tests.

Fig. 1 presents the liquefaction yield (%) variation with the different fraction (mesh). In these tests a temperature of 200 °C, a time of 60 minutes and the cork/solvent (glycerol) ratio of 1:10 was used.

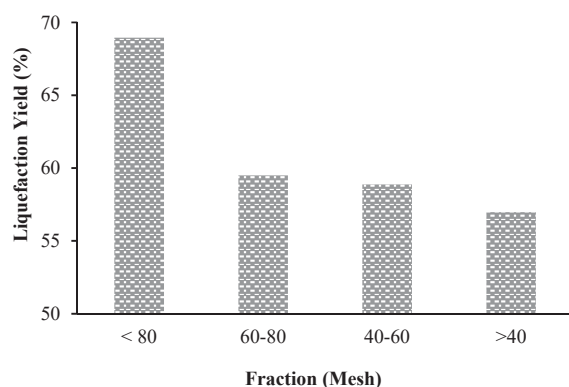


Fig. 1 Liquefaction yield (%) with fraction (mesh) for cork

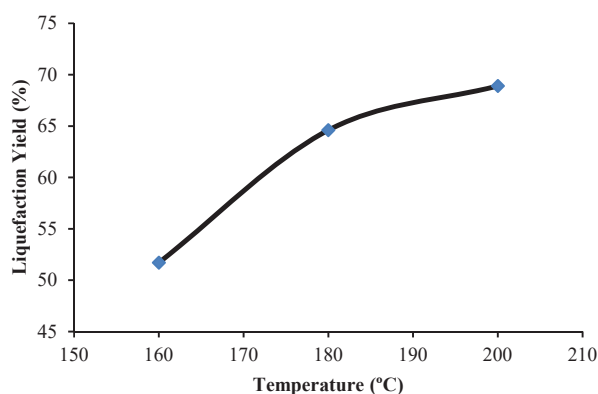


Fig. 2 Liquefaction yield (%) with the temperature (°C) for cork

Fig. 1 leads to the conclusion that the bark size affects the efficiency of liquefaction. Despite the fraction sizes 60-80, 40-60 and >40 showing similar liquefaction yields, between 55% and 60%, the fraction <80 shows a significantly higher yield of 68.9%.

Temperature optimization was done between 160°C and 200°C. In these tests the particle size of bark used was <80 mesh, a time of 60 minutes and the cork/solvent (glycerol) ratio of 1:10. The results obtained are described in Fig. 2.

Fig. 2 shows liquefaction yield increases with the temperature reaching a maximum value of 68.9% to 200°C. It is possible to predict that this increase will stabilize at higher temperatures and it is not energetically profitable doing tests at temperatures much higher than 200°C.

The last variable optimized was the time of liquefaction. Time optimization of liquefaction was made between 30 and 120 minutes, keeping constant the granulometry (fraction < 80 mesh), the temperature (200 °C) and the cork/solvent (glycerol) ratio of 1:10. The results obtained are given in Fig. 3.

The liquefaction yield increases, reaching a maximum at around 60 min (ca. 69%). The prolongation of the reaction does not increase liquefaction percentage, at 120 minutes is reached a maximum percentage of 70.4%.

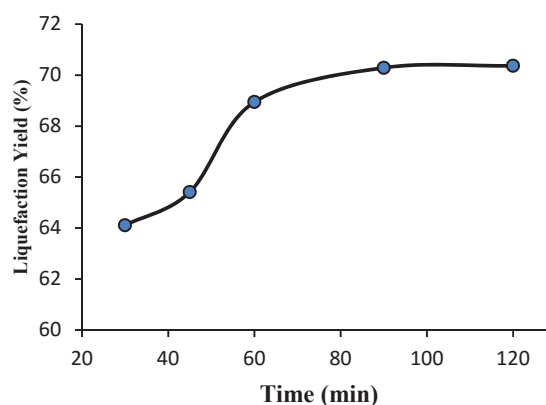


Fig. 3 Liquefaction yield (%) with time (minutes) for cork

IV. CONCLUSION

The study shows that this raw material is susceptible to liquefaction by polyols with alkaline catalysis process. The liquefaction will allow the use of these liqueurs for the production of high-value-added chemicals. The studies on the chemical composition of Cork bark of *Quercus cerris*, allowed to conclude that QC has 29.9% of suberin, 24.1% of Klason lignin and 22.8% insolvent hemicelluloses in hot water. The chemical analysis of the ash cations made to these cork shows high contents of K^+ and Ca^{2+} .

The studies carried out on the liquefaction of *Quercus Cerris* bark, allows us to conclude that the filtration step must be done by washing the residue with methanol and then with water when glycerol is used as solvent. The best conditions of liquefaction are obtained for a particle size < 80 mesh, temperature of 200 °C and a time of 60 minutes allowing to obtain a percentage of liquefaction of ca. 70%. Currently there is no utilization of the bark of *Quercus cerris*, however due to its rapid growth and substantial amount of cork tissue, this material could be used in this way to achieve high value added

products and become an asset to the Turkish economy (where it exists in large quantities).

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REFERENCES

- [1] Kasaplıgil, B., "Past and present oaks of Turkey", *Phytologia*, vol. 49, 1981, pp. 95-146.
- [2] Abi-Saleh, B. e Safi, S., "Carte de la Végétation du Liban"; *Ecologia Mediterranea* XIV (1/2), 1988, pp. 123-142.
- [3] Yaltırıc, F., "Türkiye meşeleri teşis kılavuzu.", Tarım Orman ve Köyişleri Bakanlığı Genel Müdürlüğü Yayınları. Yenilik Basimevi. İstanbul. 1984.
- [4] Cotti, C., "Molecular markers for the assessment of genetic variability in the threatened plant species.", Tese de Doutorado, Università degli studi di Bologna, 2008.
- [5] Berkel, A. e Bozkurt, Y., "Untersuchungen über die makroskopischen und anatomischen holzmerkmale der wichtigsten Türkischen Eichenarten", İstanbul Üniversitesi Orman Fakultesi Yayinlari, Kutulmus Matbaasi, İstanbul, 1961, 78.
- [6] La Marca, O., Uzielli, L. e Zanuttini, R., "Possibilità di impiego del legname di cerro (*Quercus cerris* L.) in Italia. Indagini preliminari su alcuni popolamenti e prove sperimentali per l'industria dei compensati", *L'Italia Florestale e Montana* 1, 1983, pp. 33-62.
- [7] Bartha, S., "Cercatari Privind FActorii De Variatie A Caliatatii Lemnului De Cer Din Padurea Bobostea (Jud. Bihor)", Rezumatul tezei de doctorat, Universitatea Transilvania Din Brasov, 2011.
- [8] Todaro, L., Zanuttini, R., Scopa, A., Moretti, N., "Influence of combined hydro-thermal treatments on selected properties of Turkey oak (*Quercus Cerris* L.) wood", *Wood Science and Technology*, vol. 46, 2012, pp. 563-578.
- [9] Mun, S., Gilmor, I. e Jordan, P., "Effect of Organic Sulfonic Acids as Catalysts during Phenol Liquefaction of *Pinus radiata* Bark", *J. Ind. Eng. Chem.*, vol. 12, 2006, pp. 720-726.
- [10] Amorim. Diversidade e Aplicações. *Amorim*. (Online) 2015. <http://www.amorim.com/a-cortica/diversidade-de-aplicacoes/>.
- [11] Alma, H.M. e Bastiirk, M.A., "Co-condensation of NaOH-catalysed liquefied wood wastes, phenol, and formaldehyde for the production of resol-type adhesives", *Ind. Eng. Chem. Res.*, 2001, pp. 5036-5039.
- [12] Gandini, A., Neto, C.P. e Silvestre, A., "Suberin: a promising renewable source for novel macromolecular materials", *Prog. Polym. Sci.*, vol. 31, 2006, pp. 878-892.
- [13] Jin, Y.; Ruan, X.; Cheng, X.; Lü, Q., "Liquefaction of lignin by polyethyleneglycol and glycerol.", *Bioresource Technology*, 2011, pp. 3581-3583.
- [14] Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N., "Liquefaction of wood in the presence of phenolusing phosphoric acid as catalyst and the flow properties of the liquefied wood", *Journal of Applied Polymer Science*, vol. 52, 1994, pp. 1629-1636.
- [15] Mun, S., Hassan, E., "Liquefaction of lignocellulosic biomass with mixtures of ethanol and small amounts of phenol in the presence of methanesulfonic acid catalyst", *J. Ind. Eng. Chem.*, vol. 10, 2004, pp. 722-727.
- [16] Nasar, M.; Emam, A.; Sultan, M.; Hakim, A., "Optimization and characterization of sugar-cane bagasse liquefaction process", *Indian J. Sci. Technol.*, 2010, pp. 207-212.
- [17] Min, N., Zhao, G., Alma, H.M., "Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: a review", *Forestry Studies in China*, vol. 13, 2011, pp. 71-79.
- [18] Pereira, H., "Chemical composition and variability of cork from *Quercus suber* L.", *Wood Sci. Technol.*, vol. 22(3), 1988, 211-218.
- [19] Neto, C.P., Seca, A., Fradinho, D., Coimbra, M.A., Domingues, F., Evtuguin, D., Silvestre, A., Cavaleiro, J.A.S., Chemical composition and structural features of the macromolecular components of *Hibiscus cannabinus* grown in Portugal. *Industrial Crops and Products*, vol.5(3): 1996, pp. 189-196.
- [20] Browning, B.L., "Methods in Wood Chemistry", Vol. II. John Wiley& Sons, New York, USA, 1967, pp. 406-727.
- [21] Martins, J., Cruz Lopes, L., Esteves B., "Otimização da liquefação da madeira de *Pinus pinaster* com poliálcoois", *Silva Lusitana*. Nº Especial. Instituto Nacional de Investigação Agrária e Veterinária, vol. 21, 2013, pp. 177-185.
- [22] Şen, A., Miranda, I., Santos, S., Graça, J., Pereira, H., "The chemical composition of cork and phloem in the rhytidome of *Quercus Cerris*", *Industrial Crops and Products*, Vol.1 (2), 2010, pp. 417-422.