

Research Article

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Chemical composition and study on liquefaction optimization of chestnut shells

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Abstract: Chestnut shell (CS) is a by-product of some food sector companies. The aim of this study was to test the suitability of this material to be liquefied with polyalcohols, optimizing the main liquefaction parameters in order to use the liquefied material for the production of high added value products. As the chemical composition of the fruit shell depends on the variation in the soil, climate, and species, the chemical composition of CS was determined. Liquefaction was performed with 50:50 ethyleneglycol:glycerol catalyzed by sulfuric acid. Different tests were carried out and several parameters were tested: particle size, temperature 130–190°C, and time 15–120 min. Chemical composition of CSs was determined. The main component found was lignin with 47.0%, which is higher than α -cellulose with around 20.5%, hemicelluloses 15.2%, and extractives in ethanol 8.8%. For the tested parameters, the best liquefaction yield was obtained at 190°C, 30 min, and a 40–60 particle size.

Keywords: chestnut shells, chemical composition, polyalcohol liquefaction, biomass, agro-industrial residues

1 Introduction

Chestnut tree (*Castanea sativa* Mill.) is an angiosperm from the *Fagaceae* family, the seeds of which have been one of the most important food sources for centuries. Chestnuts are consumed worldwide, and thousands of tons of agricultural wastes are generated annually. In accordance to FAOSTAT (FAOSTAT 2020) during 2018, a

worldwide production of about 6,12,000 ha of chestnut, Asia represents the continent with more chestnut production (about 70.9% of world production), followed by Europe with about 19.5%. Portugal has about 38,000 ha of chestnut (representing 6.3% of world production). The production of chestnut in Portugal has increased from 17,290 to 34,165 tonnes since 1982–2018. Considering that the percentage of shell may vary between 10 and 15% of the weight of the whole chestnut, CS represented up to 5,125 ton in 2018 (FAOSTAT 2020). In Portugal, the production of chestnut is mostly centered in the north of the country 86.6%, specifically in Trás-os-Montes, with 81% of all national chestnut exports that generated around 53 million euros in 2016 and is still growing (INE 2017).

The wastes generated by the chestnut industry include leaves, pruning wastes, burrs, and chestnut shells (CSs). These residues are usually left in the soil and can cause damage to crops as they can promote the growth of insect's larvae (Vázquez et al. 2012). They are frequently burned in the fields polluting the atmosphere – some emissions are toxic, such as CO, NO_x, long-chain/aromatic hydrocarbons, and polychlorodibenzodioxins (Morana et al. 2017). In addition, pesticides and heavy metals from these wastes may remain in the soil from the ash when they are burned (Picchi et al. 2018). The chestnut industry waste frequently ends up in composting (Ventorino et al. 2016).

As biomass is the most abundant renewable resource, several studies have been made to replace products commonly made from fossil fuel. The CSs biomass is rich in cellulose (homopolymer), hemicelluloses (heteropolymer), and lignin, which can be used to produce a wide variety of products and high value chemicals (Morales et al. 2018). Through hydrolytic processes, it is possible to degrade the cell walls of lignocellulosic materials to obtain mixtures of oligomeric and monomeric sugars, such as glucose, xylose, mannose, galactose, and arabinose. Other high value-added products can be obtained, for example, bio-oil, biogas, or other bio-based chemicals with a wide range of industrial applications (Cherubini 2010; de Jong et al. 2012; Morales et al. 2018).

Gasification, pyrolysis, and liquefaction are thermochemical conversions of lignocellulosic materials that

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can lead to a series of different products (Zhang *et al.* 2010; Awalludin *et al.* 2015; Patel *et al.* 2016). From those, low to moderate temperature liquefactions are processes that can efficiently liquefy a solid lignocellulosic material consuming less energy. The liquefaction procedures are performed with a solvent or a mixture of solvents with acid or base catalysts. The resulting compounds are larger molecules than high temperature liquefaction processes but can be re-condensed through conventional polymerization techniques to produce adhesives, plastics, or polymers. These processes can be one of the best ways to produce chemicals in the future.

Mainly two different types of solvents are used: phenol (Zhang *et al.* 2005) and polyalcohols (Jin *et al.* 2011; Yu and Lee 2014; D'Souza *et al.* 2015; Esteves *et al.* 2015). The obtained liquefied material is different according to the liquefaction agent used. The advantage of polyalcohol liquefaction is that these compounds are not toxic and therefore easy and safe to use. In the past few years, there have been several lignocellulosic materials liquefied by these methods which include cornmeal (Wang *et al.* 2008), sugar bagasse (Hakim *et al.* 2011), or wood (Ertaş *et al.* 2014), for example.

The liquefied materials have been used to produce different products. Polyurethane foams have been produced from liquefied cork (Gama *et al.* 2015; Esteves *et al.* 2017), cork-rich barks like *Pseudotsuga menziesii* and *Quercus cerris* (Cruz-Lopes *et al.* 2016; Esteves *et al.* 2018), coffee grains (Soares *et al.* 2014), corn stover (Wang *et al.* 2008), or wheat straw (Chen and Lu 2009). In addition, liquefied materials have been used as adhesives (Lee and Lin 2008; Esteves *et al.* 2019).

The objective of this study is to find a process to transform chestnut-derived waste into value-added products through liquefaction with a mixture of ethylene glycol and glycerol and to contribute to the scientific knowledge of the chemical composition of CS. The polyalcohols needed are available from renewable sources – glycerol is a by-product of biodiesel production and ethylene glycols can be produced from bioethanol – which emphasize the environmental advantages of this process.

2 Materials and methods

2.1 Material

CSs used in this study are wastes produced by the company Agromontenegro based in Portugal (Carrazedo de Montenegro), which is a forest management company. The samples were milled in a Retsch SMI mill and sieved

in a Retsch AS200 for 20 min at a speed of 50 rpm. Four fractions >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 afterwards.

2.2 Chemical composition

The chemical composition of CS was determined, including ashes, dichloromethane (DCM), ethanol and water extractives, α -cellulose, hemicelluloses, and lignin.

The fraction of 40–60 mesh was used for chemical analyses following Tappi T 264 om-97. The average chemical composition of each sample was determined in triplicate.

The extractives in all the solvents were determined by Soxhlet extraction according to Tappi T 204 om-88 (Prozil *et al.* 2012). The extractive content was determined by Soxhlet extraction using about 3 g of each sample:150 mL of DCM, ethanol, and water as solvents; 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.

Lignin was determined by Klason method in CS free from extractives with 72% H₂SO₄ (in accordance to Tappi T 204 om-88).

The holocellulose was determined by the acid chloride method. The α -cellulose was determined following holocellulose hydrolysis. The hemicelluloses content was determined by difference.

2.3 Polyalcohol liquefaction

Liquefaction was performed in a closed reactor. The samples (fractions >40, 40–60, 60–80, and <80 mesh) were liquefied in a CS/solvent ratio of 1:10 using a mixture of glycerol and ethyleneglycol 1:1, catalyzed by sulfuric acid (3% based on solvent mass). Temperature and time ranged from 130 to 190°C and 15 to 120 min, respectively. Liquefied samples were dissolved in methanol and filtered. The insoluble residue was determined gravimetrically.

3 Results and discussion

3.1 Chemical composition

The chemical composition was determined to better understand the potential of CSs for chemical conversion. Table 1 presents the CS chemical composition.

Table 1: Chemical composition of CS (% dry material)

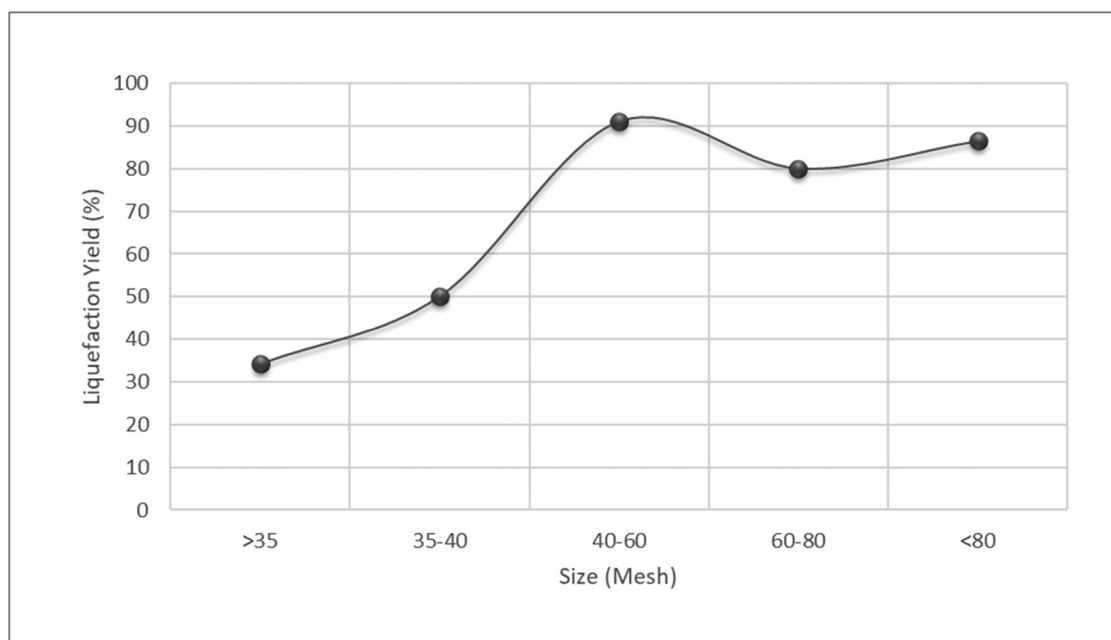
Parameters	Content (%)
Ashes	1.42
Extractives	
Dichloromethane	0.82
Ethanol	8.78
Hot water	6.31
Klason lignin	47.01
α -Cellulose	20.5
Hemicelluloses	15.16

The chemical composition showed that CSs have a high amount of Klason lignin (47%) that represents almost half of the chemical compounds in CS. Holocellulose was 35.6%, 20.5% from cellulose and 15.2% for hemicelluloses. In relation to extractives, the highest amount belongs to ethanol extractives with 8.8%, followed by water extractives with 6.3% and DCM 0.8%. Ashes represent 1.4% of the sample.

The high amount of Klason lignin obtained for CS is similar to that reported by Costa-Trigo et al. (2019) and López et al. (2012) with 44.3 and 45.9%, respectively. Differently, Yao et al. (2010) and He et al. (2016) obtained 28.5 and 23%, which is lower than that obtained here. Nevertheless, these authors did not mention how the results were obtained. In addition, the big differences in lignin content might be because of the extraction procedures performed before lignin determination, because if

tannins are not removed they can resist the acid treatment and can be accounted as lignin. The cellulose content was 20.50%, which is lower than the value obtained by He et al. (2016) (28%) or Maurelli et al. (2013) (28.4%), but not much smaller than the result obtained by López et al. (2012) (24.3%). It should be noted that the method used here was α -cellulose that gives smaller values than other methods because it mostly accounts for crystalline cellulose. The amount of hemicelluloses (15.2%) is similar to that reported by Costa-Trigo et al. (2019) (16.0%) and He et al. (2016) (16.7%).

The high amount of ethanol and water extractives means that, possibly, most of the extractives are polyphenolic and sugar compounds. The extractives are non-structural organic compounds and can be removed from the sample without changing their structure. Some are soluble in polar solvents, some in nonpolar or semi-polar, and others may be soluble in more than one type of solvent. Therefore, the extraction should be conducted along the same sequential order, which is agreed to be in ascending order of polarity, because if this order was amended the content of extractives obtained in each of the solvents would be different. As other authors did not use the same extraction sequence, some results are difficult to compare. However, the amount of ethanol extractives, 8.8%, is higher than that reported by Costa-Trigo et al. (2019) ($5.34 \pm 0.40\%$), lower than that reported by López et al. (2012) and He et al. (2016) (12 and 32%), but not much different from that obtained by Yao et al.

**Figure 1:** Liquefaction yield (%) with fraction (mesh) for CS.

(2010) (8%). The ashes content is in accordance to that reported by Blasi *et al.* (2019) (1.14%) and a little higher than the values obtained by Costa-Trigo *et al.* (2019) ($0.58 \pm 0.10\%$).

These results show that there are very different chemical compositions of CSs, which might be because of different growing parameters like plantation locations, spacing, terrain, chestnut maturation, and so on. The determination of the chemical composition can indicate the best applications for CS from this region.

3.2 Liquefaction

A basis was established for the main parameters in liquefaction, 190°C and 30 min, 40–60 mesh the CS/solvent (mixture of glycerol and ethyleneglycol 1:1) ratio of 1:10.

Figure 1 shows the liquefaction yield (%) variation with the different fraction (mesh). In these tests, a temperature of 190°C, a time of 30 min, and the CS/solvent (mixture of glycerol and ethyleneglycol 1:1) ratio of 1:10 was used.

Results show that the CS particle size affects the efficiency of liquefaction. Overall liquefaction yield increases with the decrease in particle size at least until 40–60 mesh fraction from about 34% for the bigger particles

to around 91% for the 40–60 mesh fraction. Despite the fraction sizes <80, 60–80, and 40–60 showing similar liquefaction yields, between 80 and 91%, the fraction 40–60 has the highest yield. Similar results were presented before for cork liquefaction although only three different sizes were used (Esteves *et al.* 2017). The lower amount of liquefaction for lower particle sizes might be because of the different chemical composition of these particle sizes as shown before for other heterogeneous materials such as *Q. cerris* bark (Sen *et al.* 2020).

Figure 2 shows the liquefaction yield variation with reaction temperature that was performed between 130 and 190°C. In these tests, the particle size of shells used was 40–60 mesh, a time of 30 min, and the CS/solvent ratio of 1:10.

As expected, liquefaction yield increased with the increase in reaction temperature reaching a maximum value of 91% for 190°C. A fairly good liquefaction yield was obtained at 170°C (86%), whereas poor yields (under 70%) were obtained at lower temperatures. Similar reports were obtained before for the liquefaction of several lignocellulosic materials. For instance, for liquefied Douglas fir bark there was an increase in yield with the increase in temperature but smaller than the one found here (Esteves *et al.* 2018). Studies on liquefied cork showed that there was a big increase from 150 to 160°C staying approximately constant afterwards (Esteves *et al.* 2017). Different results were reported earlier by

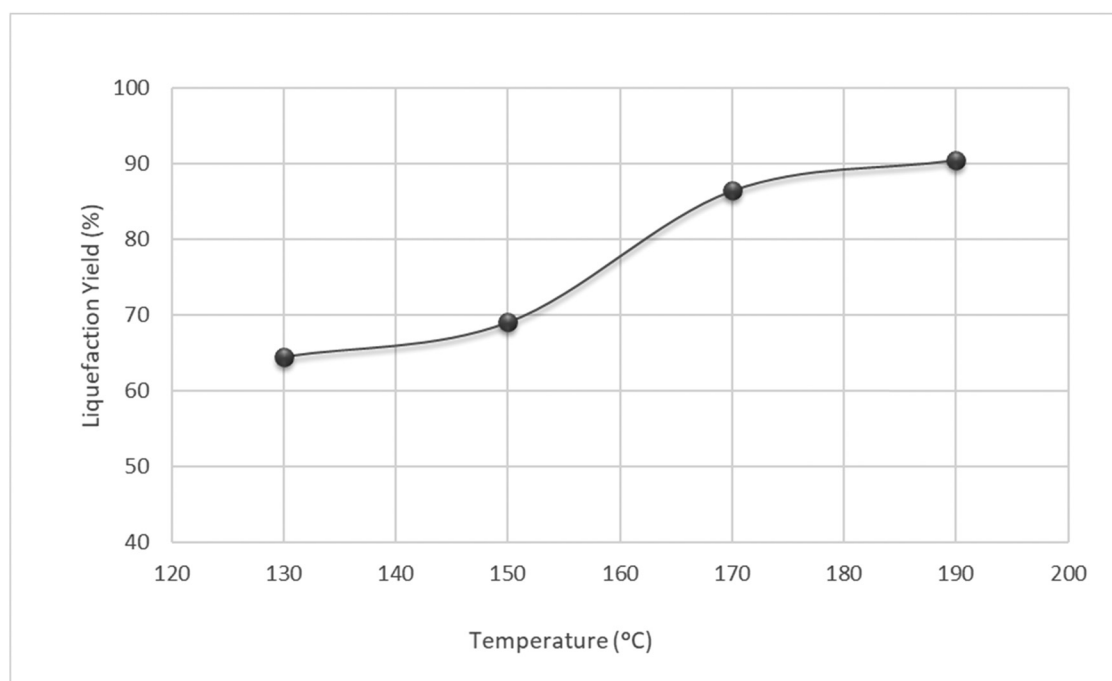


Figure 2: Liquefaction yield (%) with temperature (°C) for CS.

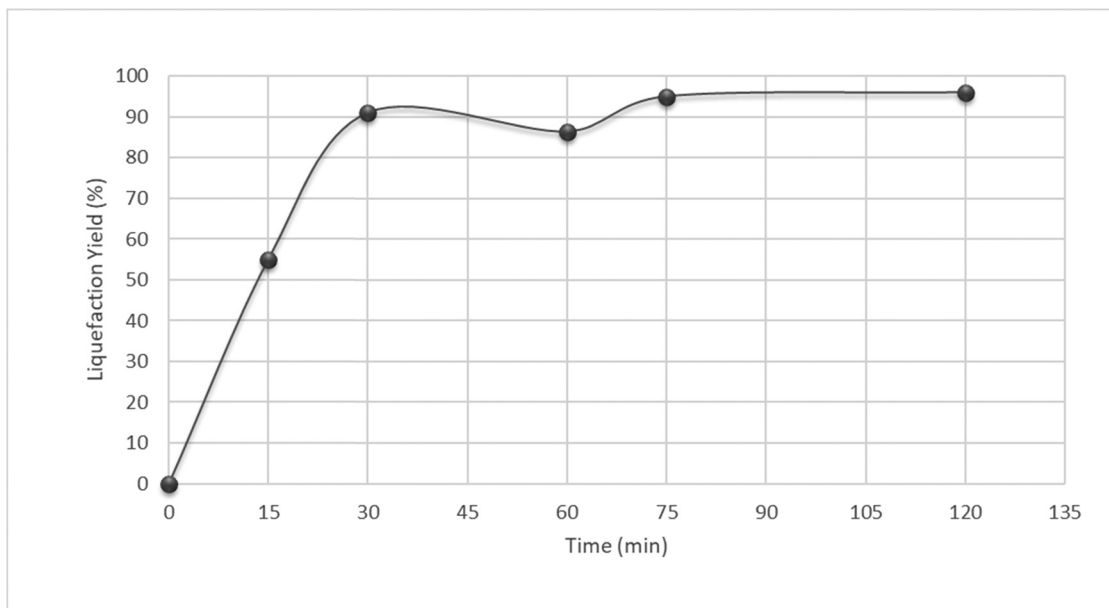


Figure 3: Liquefaction yield (%) with time (minutes) for CS.

Soares et al. (2014) by testing cork powder via acid liquefaction using a mixture of PEG 400 and glycerol. These authors reported that liquefaction yield increased from 150 to 160°C but decreased when the temperature reached 170°C which was attributed to condensation reactions between liquefied intermediates. Nevertheless, they reported that it was possible because of the higher percentage of PEG 400 (90%) in relation to glycerol (10%) because Kurimoto and Tamura (1999) stated that a higher amount of low molecular weight glycols such as glycerol would prevent these re-condensation reactions. Therefore, once the liquefaction of CSs was conducted only with glycerol, these re-condensation reactions might have been inhibited.

The liquefaction time was studied between 15 and 120 min, keeping constant the granulometry (40–60 mesh), the temperature (190°C), and the CS/solvent ratio of 1:10. The achieved results are shown in Figure 3.

As expected, the liquefaction yield increased with time staying approximately constant after 75 min (95%). The prolongation of the reaction time did not increase significantly the liquefaction percentage at 120 min (96%). This is important because of operation costs as more time represents more money spent in the process. Probably the liquefaction time could be reduced if a higher temperature was used, but then more money would be spent to increase the temperature. The increase in liquefaction yield with time has been reported before (Soares et al. 2014; Esteves et al. 2017, 2018). In the first 15 min, more than 70% of CS was liquefied. In accordance

to Zhang et al. (2016), who studied polyalcohol liquefaction of nut shells of several *Camelia* species, in the first stage of liquefaction most of the hemicelluloses are solubilized. At the same time, there is also some solubilization of lignin and of amorphous parts of cellulose. The high amount of lignin in CS suggests that there is a significant solubilization of lignin in the first stage of liquefaction. In the second stage, Zhang et al. (2016) stated that for longer times there are re-condensation reactions between liquefied products that increase the residue amount. This phenomenon was not observed here possibly because of the high amount of glycerol used as stated before.

4 Conclusions

Chemical composition showed that CSs mainly contain Klason lignin (47%), followed by α -cellulose (20.5%), hemicelluloses (15.2%), and extractives in ethanol (8.8%). The high amount of lignin suggests that this material might be used to produce adhesives giving the chestnut exploitation sector an increased value product.

More than 55% of the material is liquefied in the first 15 min, which is probably because of the liquefaction of hemicelluloses, lignin, and ordered parts of cellulose. On the contrary, 30 min was enough to achieve a high liquefaction (91%) at 190°C. Nevertheless, an economic study must be made to determine the best conditions to achieve

a good product with lower costs. Results show that it is possible to reach a good liquefaction percentage at lower temperatures.

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