Short Communication

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Microwave-assisted Liquefaction of Cork – From an Industrial Waste to Sustainable Chemicals

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Abstract

Cork wastes and by-products were used as raw materials to access sustainable biopolyols in a fast and clean manner. Contributing for the mitigation of a residue recorded as industrial residues in the European waste catalogue and hazardous waste list reducing, therefore, its environmental impact. Cork powder resulting from the cork industry as a waste and/or by-products with no commercial value was subjected to liquefaction in 2-ethyl hexanol/DEG in the presence of p-toluene sulfuric acid. Microwave radiation was used as the heating source. Pulsed microwaves from 150-300 W power were applied for 5-20 min. This alternative energy source was successfully applied leading to a high conversion of cork powder into liquid biopolyols. The efficiency of liquefaction increased with higher microwave power and shorter reaction time. This study evidenced that cork powder can be liquidized via microwave. ATR experiments indicated that microwave led to a more intense oxidized cleavage of the lignocellulosic material and more extensive liquefaction reaction when compared to the conventional procedure.

Keywords: Cork; Liquefaction; Microwave; Sustainable; Biopolyols

Introduction

Liquefaction of biomass, such as lignocellulosic residues, is a process that has been largely investigated, consisting in the conversion into polyols towards the depolymerization and solubilisation of biomass at high temperatures [1-5].

Being wood and forestry biomass a renewable, biodegradable, and abundant resource, it can be, and should be, seen as a source of raw materials for the chemical industry. In fact, throughout its liquefaction products rich in hydroxyl groups are obtained. Being extremely reactive, they can be readily used as starting materials for the production of environmental friendly polymeric products [6,7]. Polyurethane industry has been exploiting them in the formulation of new materials [4,6,8,9]. With different liquefaction reactants, this process can lead to a wide variety of reagents used in the formulations of biomaterials, resin and coatings and others. This means that could be possible to project different chemical structures of liquid wood aiming their final application [10]. The reaction mechanisms involved in liquefaction processes are quite unknown. Wood liquefaction involves wide number of reactions. Amongst them is esterification or etherification of free hydroxyl groups in cellulose or lignin along with reactions that decomposes cellulose into smaller units. This complex set of reactions is even more extensive due of the large number of minor wood components ranging from gums and resins to minerals and salts [11]. The polysaccharides are supposed to be firstly converted to its congener glycosides which are then hydrolyzed to levulinic glycosides [11,12]. The reaction pathway of lignin depolymerization is not known but it was shown that the presence of lignin plays a major role in the post-liquefaction re-condensation reactions, leading to insoluble precipitates [13].

Microwave irradiation is well known as an alternative to conventional heating of chemical processes. The very rapid heating of the volume of the reaction mixture, towards the applied electromagnetic field leads to higher reaction rates [14]. The use microwave irradiation for the liquefaction of biomass has been already reported with encouraging results [10,11].

Portuguese industry is responsible for half of the production of cork. Worldwide, the annual amount of cork involved in the whole industry ascend to 300000 tonnes. This outstanding bio-composite, which is the external bark of *Quercus suber* L. possesses a very interesting role of properties like elasticity, compressibility, low permeability of liquids and significant chemical/microbial resistance [15,16]. Cork major components are polysaccharides, lignin, suberin, and extractives (20, 22, 40, and 15 wt. %, respectively) [17,18]. This means that, structurally, cork has a strong relationship with lignocellulosic materials. The cork industry generates a residue considered problematic, obtained across multiple production phases, including granulation, that is, value-added operation of residues to manufacture alternative cork based wine closures, which is an important fraction of the total amount of wastes with no commercial value, this is the so called "cork powder". As the name suggests, cork powder includes small size particles, usually a size too small (<0,5 mm) for any possible reuse, due to its high surface. Even when used for agglomerates, inclusion of the dust is only possible under small amounts, therefore not incorporating significant volumes compared to the production. Moreover, not only cork dust but also other residues of this industry are recorded as industrial residues in the European waste catalogue and hazardous waste list therefore their accommodation is identified as potentially impacting environmentally. Several efforts have been made to reuse the "cork dust". Currently it is mostly applied as fuel for burning in furnaces: either in the cork industry or even in the ceramic industry. This is due to the fact that it presents a high calorific value, which is between 20.6 and 22.2 MJ/kg (ASTM D1989).

Aiming at the recycling of this by-product, lately, cork powder has been investigated as a source of biomass for acid liquefaction using

polyhydric alcohols under conventional and ultrasounds-assisted methods [2,5]. Actually, this waste that is usually burned proved to be suitable for the production of biomaterials based on the polyols obtained from its liquefaction [6,19].

Herein, we envisaged to exploit microwave heating as the source of thermal energy in liquefaction of cork powder for the production of sustainable chemicals.

Experimental

Materials and chemicals

Cork Supply kindly supplied cork powder. The biomass was dried in an oven set to 120°C until no change in weight was observed. The reagents used were chemical grade (Sigma-Aldrich).

Liquefaction procedure

Microwave assisted liquefactions were carried out in a CEM microwave laboratory system (CEM Discover and Explorer SP). Samples were irradiated for 5, 10, and 20 min under 150, 225, and 300 W as starting microwave power. A typical procedure for the microwaves experiments was as follows: 10 ml reaction vessels were loaded with a mixture of solvents (2-ethylhexanol:diethylene glycol=4:1, w/w), 3% w/w of p-toluene sulfonic acid and 10% w/w of cork powder (both based on solvent mixture). The vessel was capped and subjected to microwaves irradiation. The sample temperature is controlled at 160°C. Concerning the conventional methodology the reactions mixtures were prepared as for microwave-assisted procedure, being then stirred at 160°C for the desired time. Ultrasounds-assisted experiments were performed as described by Mateus et al. [5]. Although glycerin is usually used as a polyhydric alcohol, 2-ethyl-hexanol was used instead since it leads to a less viscous product when compared with those obtained with glycerin. After liquefaction, the vessels were allowed to cool at room temperature.

Measurement of liquefaction extent

The conversion was gravimetrically evaluated based on the residue content (unreacted raw material). The reaction mixture was diluted with acetone and then filtered and washed with acetone and methanol. The filtrate was evaporated under reduced pressure by rotary evaporator system at 40-50°C temperatures to recover the bio-oil. The obtained solid residue was then dried in an oven set to 120°C until no change in weight was observed. The liquefaction yield was calculated according with equation 1.

$$\text{Liquefaction Yield} \left(\% \right) = \left(1 - \frac{M_R}{M_C} \right) \times 100 \qquad (1)$$

Where, M_C is the initial mass of cork, M_R the mass of the residue obtained.

Scanning electron microscopy (SEM) observations

Cork powder and liquefaction residues, were micro-graphed on a Hitachi S-2400 equipment, with a 15 kV beam were sputter coated with a thin layer of gold to avoid electrostatic charging during scanning.

Attenuated total reflectance (ATR) analysis

ATR spectra were collected using an ATR accessory. Spectra were collected on Thermo Nicolet Nexus instrument (128 scans with a resolution of 4 cm^{-1}).

Hydroxyl number and acid number

The acid number of the polyols was determined in accordance with the ASTM D4662-08 standard. The number of milligrams of KOH required to neutralize the acid of one gram of sample was calculated using equation 2.

$$\text{acid number} \left(\frac{mg_{KOH}}{g_{polyol}} \right) = \frac{\left[\left(A - B \right) \times 56.1 \times N \right]}{W} \qquad (2)$$

where A is the volume of KOH solution required for titration of the sample (mL); B is the volume of KOH solution required for titration of the blank (mL); N is the normality of the KOH solution; and W is the weight of the sample (g).

The hydroxyl number of the polyols was determined in accordance with the ASTM D4274-05 standard. The hydroxyl number was corrected and calculated according to equation 3.

$$\text{hydroxyl number} \left(\frac{mg_{KOH}}{g_{polyol}} \right) = \frac{\left[\left(B - A \right) \times 56.1 \times N \right]}{W} + C \qquad (3)$$

where, A is the volume of KOH solution used for titration of the sample (mL); B is the volume of KOH solution required the blank (mL); N is the normality of the KOH solution; W is the weight of the sample (g); and C is the acid number of the sample.

Results and Discussion

The work developed so far by our research group aimed to optimize the liquefaction of industrial residues from sludge to forestry biomass and even manure. Cork powder, which is produced in high amount by this Portuguese leading industry, is one of our main focuses. The yields of the liquefaction processes were determined and the products obtained characterized by SEM and ATR. The acid and hydroxyl number were also determined.

Effect of the reaction time and microwave power

The liquefaction extent of cork powder as a function of reaction time is shown in Figure 1 for conventional, ultrasounds- and microwave- assisted liquefaction. The time of the process decreased dramatically with the irradiation of microwave when compared with the conventional methodology. After 5 minutes, the conversion yields were already higher than 92%, reaching its higher value for the irradiation power of 300 W. Although for longer reactions, tar-type content appeared resulting in a small increase of the liquefaction residue. This could be attributed to recondensation reaction or decomposition products [20,21]. The liquefaction promoted by microwaves was also faster than that assisted by ultrasounds. Although the latter one afforded higher yields for longer reactions since it produces less decomposition and repolymerization products. The optimal reaction conditions for microwave-assisted liquefaction with the minimal residue content of 4.56% were obtained with an irradiation power of 300 W for 5 minutes. In contrast, the residue content reached 5.35% for conventional liquefaction only after 135 minutes. Compared with conventional liquefaction, microwave heating greatly accelerated the depolymerisation of cork. A different temperature regime caused by microwave heating is the main contributing factor to the acceleration of the reaction leading to a much rapid heating a more uniform temperature distribution.

Characterization of the obtained products

Microstructure morphology of residues: The residues remained after the liquefaction process was analyzed by SEM. Figure 2 represents cork powder before liquefaction. Image B illustrates the morphology of the residues obtained for conventional heating, while micrographs C
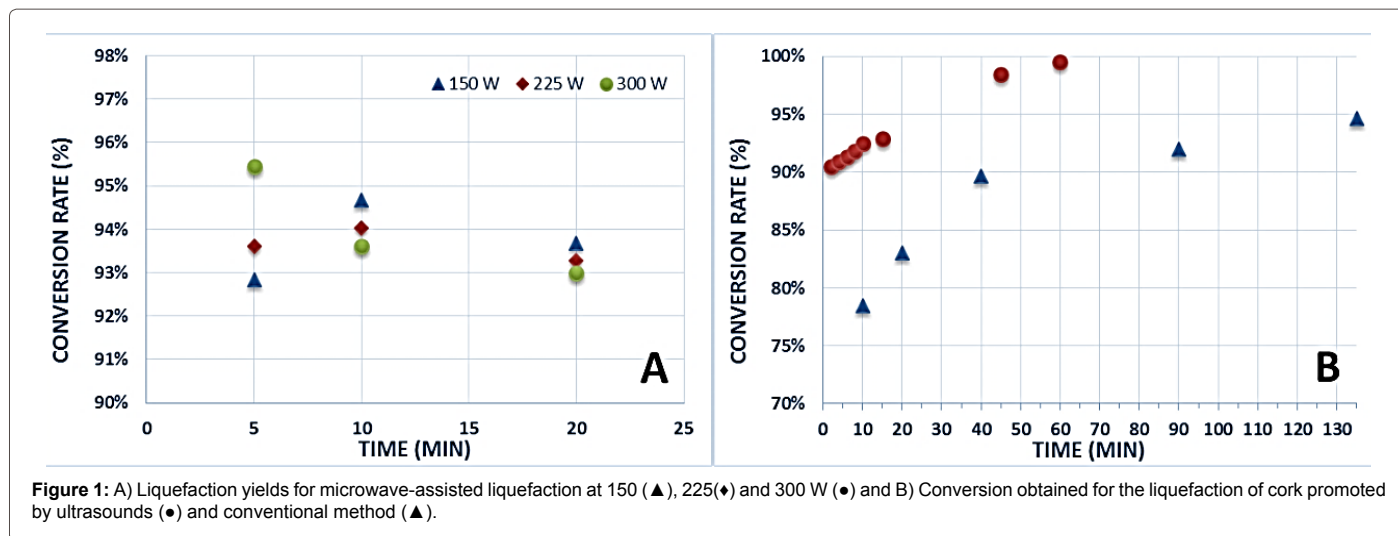
Figure 1: A) Liquefaction yields for microwave-assisted liquefaction at 150 (▲), 225(♦) and 300 W (●) and B) Conversion obtained for the liquefaction of cork promoted by ultrasounds (●) and conventional method (▲).
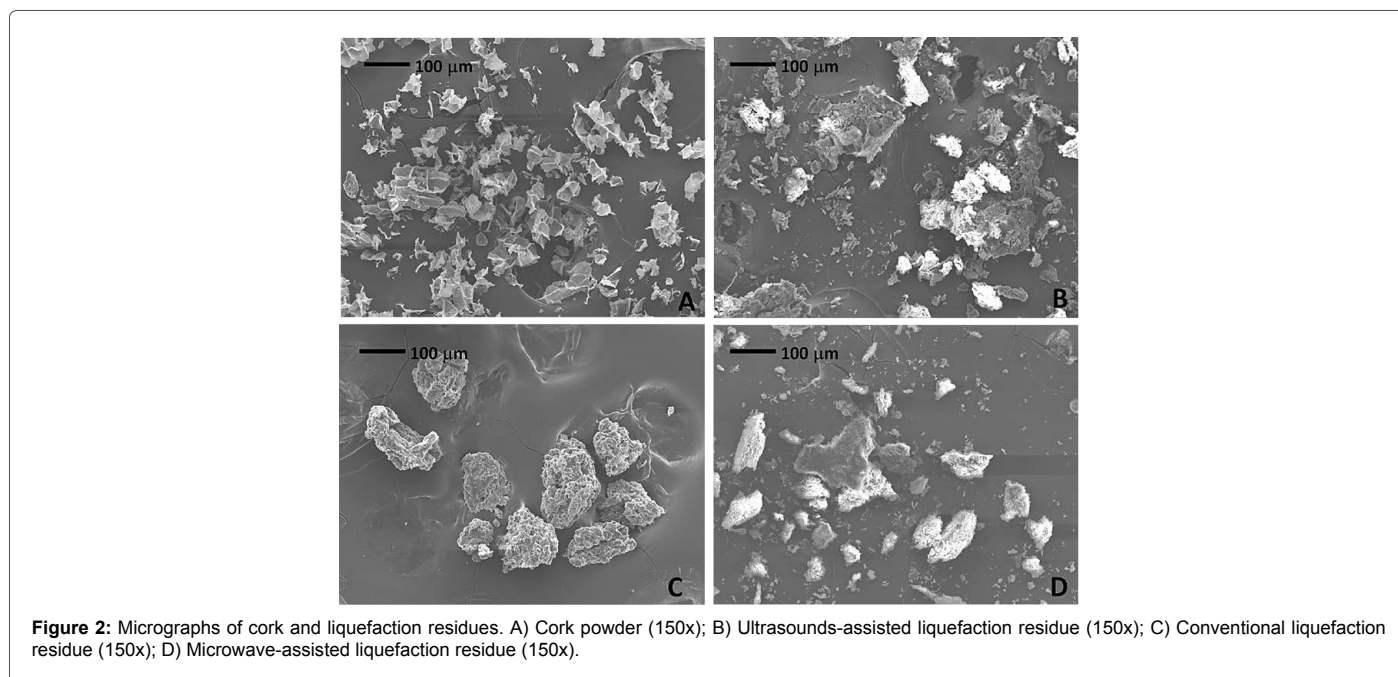

Figure 2: Micrographs of cork and liquefaction residues. A) Cork powder (150x); B) Ultrasounds-assisted liquefaction residue (150x); C) Conventional liquefaction residue (150x); D) Microwave-assisted liquefaction residue (150x).

and D show the morphology obtain for ultrasounds- and microwaves-assisted liquefaction, respectively.

Due to liquefaction the cork cells become completely disintegrated and disrupted. Irregular particles of cork fragments or products of the polycondensation process that can occur at the end of the liquefaction processes are observed for the liquefaction residues. Although is clear that the ultrasounds or microwave systems led to smaller, but similar artifacts than those for the conventional heating.

Acid and hydroxyl number: The acid numbers obtained (Table 1) for both methods are in accordance with the same range of those reported in the literature [22,23]. This acidic character may be due to catalyst used in the liquefaction process and the acidic substances generated by the decomposition of the cork powder components, mainly cellulose and hemicelluloses. Regarding the hydroxyl numbers obtained in this study (Table 1), which are quite low when compared to those reported for other polyols obtained from other lignocellulosic

materials, there is a remarkable difference between microwave assisted liquefaction and the other methodologies.

The lower hydroxyl number obtained for product obtained from the microwave driven liquefaction, can be inferred to the oxidation since microwaves are able to promote more efficiently those reactions as well as recondensation reactions between the liquefaction solvents and cork components which consumed plenty of hydroxyl groups [21,24]. The specific composition of cork itself can also justify the lower values. The fatty acids from suberin which is the major component of cork suffers esterification with the hydroxyl groups present in the mixture leading to aliphatic linear-chain polyols esters and a decreased hydroxyl number. This is not quite a surprise since p-toluene sulfonic acid is commonly used to catalyze esterification reactions. Lignin can also be involves in the decrease of the hydroxyl value. The high output of energy generated by microwaves can promote the formation of a "lignin-based polymer" resulting from the condensation reactions

Liquefaction Method	Reaction time (min)	Liquefaction Yields (%)	Acid number (mg KOH/g)	Hydroxyl number (mg KOH/g)
Conventional	135	94	6	725
Ultrasound-assisted	60	99	10.7	532
Microwave-assisted	5	96	9	180

Table 1: Comparison of the acid and hydroxyl number of the conventional, ultrasound- and microwave- assisted reactions.
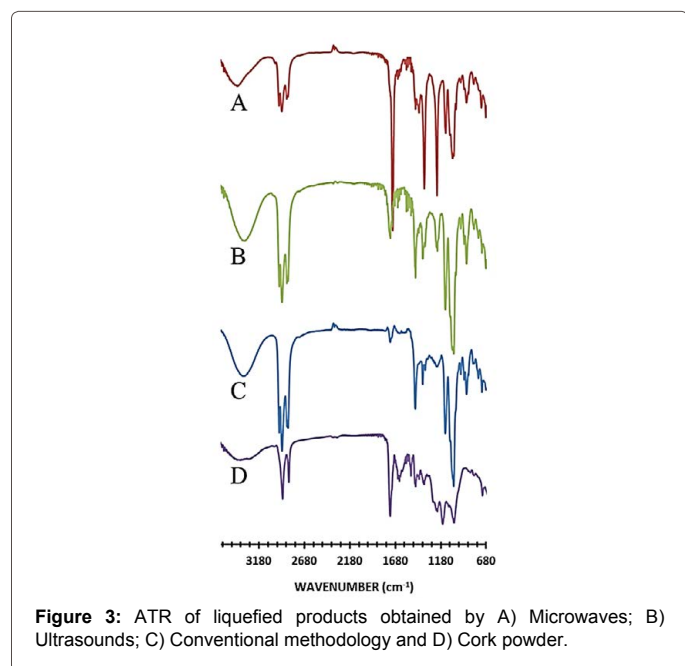

Figure 3: ATR of liquefied products obtained by A) Microwaves; B) Ultrasounds; C) Conventional methodology and D) Cork powder.

between the solubilized lignin with the hydroxyl groups present in the medium. Other concurrent degradation and condensation reactions between the lignin degradation fragments and 2-ethylhexanol may also occur contributing to the decrease of the OH number [25].

ATR-FTIR analysis for the liquefied products: The liquefaction products arising from the conventional, ultrasounds-, microwave-assisted liquefaction and cork powder were subjected to ATR FTIR experiments to study the functional groups present in the samples, Figure 3 shows the spectra obtained. Concerning the cork powder, the spectra display a broad band at 3100-3500 cm^{-1} representative from the OH stretching vibration. Two bands at 2925 and 2857 cm^{-1} typical of C–H stretching vibrations were also detected along with a sharp band which is representative of C=O from esters at 1710 cm^{-1} and two sharp bands at 1160 and 1044 cm^{-1} from the stretching vibrations of C–O. In addition to this, the microwave assisted liquefaction spectra presents bands arising from the solvents used in the liquefaction can be observed at 2958 and 2874 cm^{-1}, both from the C–H stretching vibrations, 1360, 1220 and 1127 cm^{-1} due to C–O stretching vibrations can be observed.

Comparing the spectra for the conventional, ultrasounds- and microwave-assisted liquefaction the relative intensity of the bands at 3100-3500 cm^{-1} (O–H stretching) decreased significantly for the microwave heating liquefaction as expected from the hydroxyl number results. The CH stretching bands at 2925, 2958, 2857, and 2874 cm^{-1}, and 1044 cm^{-1}, CO stretching band, are higher in liquefied products resulting from conventional and ultrasounds reactions indicating the presence longer carbon chain and higher hydroxyl content. On the other hand, the stretching band of C=O is clearly stronger in

microwave assisted liquefaction than that for other procedures. This band indicates a higher content of carbonyl function resulting from the oxidation of hydroxyl groups [21,26,27]. Along with decreased hydroxyl number this results supports that oxidation reactions are indeed favored by microwaves. The lower intensity of the carbonyl band on the conventional methodology is not necessarily a surprise since under lower energy the glycosides formation with the polysaccharides derivatives from cork may be favored justifying the intensity of C-H aliphatic bands at 2925, 2958, 2857, and 2874 cm^{-1}.

Conclusions

In conclusion, we have described a highly efficient microwave-induced modification of conventional heating procedure for the liquefaction of cork powder proving that cork powder can be liquidized, at 160°C in the presence of 2-ethyl hexanol/DEG and p-toluene sulfuric acid as catalyst towards microwave technology. This environmentally friendly and safe protocol presented high product yields and short reaction time even when compared with the ultrasounds-assisted depolymerization. Irradiating the reaction mixture during 5 minutes with a microwave power of 300 W was set as the optimal conditions. ATR characteristics of the products indicate that microwave led to a more intense oxidized cleavage of the lignocellulosic material when compared to the other procedures. SEM micrographs demonstrate extent of the reaction promoted by microwaves since smaller particles were observed when compare to those obtained to the conventional methodology. Thus, microwaves are a promising substitute for traditional heating method in cork liquefaction. This industrial waste that is usually burned in Biomass Steam boilers can be used as a source of added value, sustainable and environmentally friendly chemicals. The obtained complex mixture of liquefied products, whose composition was not studied can then be used as polyols from the formulation of PU foams [6], adhesives [19] and others polymeric materials as well as bio-fuels.

The work present herein has contributed to demonstrate that the liquefaction can indeed be applied to cork residues. Needed to say that there are only handfuls papers regarding cork as raw materials for this kind of processes and none focused on microwaves, so it is needed to study the performance of these methodologies using this lignocellulic product, in particular, as raw material. Moreover, it was proved that microwaves could play a crucial role in the reaction time, leading to more efficient, fast, and cleaner liquefaction of cork. Being produce annually, tons of these residues, cork powder threatens the safety of the industrial plants and those working on it. The studies concerning the mitigation of these residues contribute strongly for the safety of the industry and offers an alternative that can generated added-value chemicals turning a worthless waste into valuable products increasing the business profits.

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