Cork fractionation via chemical approach and pressurized hot water

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1. Introduction

The cork industry, which is responsible in producing wine cork stoppers and thermal floorings from the cork oak tree (Quercus Suber) is producing an estimated 75,000 tons of byproducts annually.[1] The major composition of cork includes extractives, polysaccharides, suberin and lignin. For this reason, cork byproducts can be a promising resource stream for the production of valuable biobased materials.

Due to the myriad of substances and biopolymers present in cork, it actually represents a heterogeneous, complex biomass that requires a fractionation process to merit further handling and processing. Presently, conventional methods, such as alkali methanolysis and alkali hydrolysis, are hugely reliant on chemical approaches. Both processes entail very long reaction times and consumes huge amount of organic chemicals that is not appropriate for industrial valorization. The concepts of green chemistry and sustainable development has become more mainstream and is shaping the evolution and developments in chemical processing. In this context, it is highly desirable to develop processes that would shorten the processing time with the minimum number of steps possible and minimize, if not completely avoid the usage of organic chemicals.

Our group has been working on biomass fractionation via ultrafast hydrolysis under supercritical conditions. Supercritical water (SCW) is achieved as soon as the temperature and pressure exceed the liquid-vapor critical point, which is located at T_c = 647 K and P_c = 221 bar, upon which it assumes low viscosity, high diffusivity and low dielectric constant. We utilize a Sudden Expansion Micro-Reactor (SEMR) that allows continuous processing of biomass and enables residence times as short as 40 ms.[2] The SEMR has been recently demonstrated as an effective approach in valorizing lignocellulosic biomass, particularly cellulose, hemicellulose and lignin, in model compounds and actual biomass[3–6]. Thus, it is proposed to use SCW for cork fractionation.

This presentation will demonstrate the capability of SCW hydrolysis through SEMR for cork fractionation. The obtained cork fractions can serve as building blocks for biobased products. The knowledge gathered from the chemical approach for cork fractionation has helped in understanding SCW experiments. The overall scheme of the study is presented in Fig. 1.

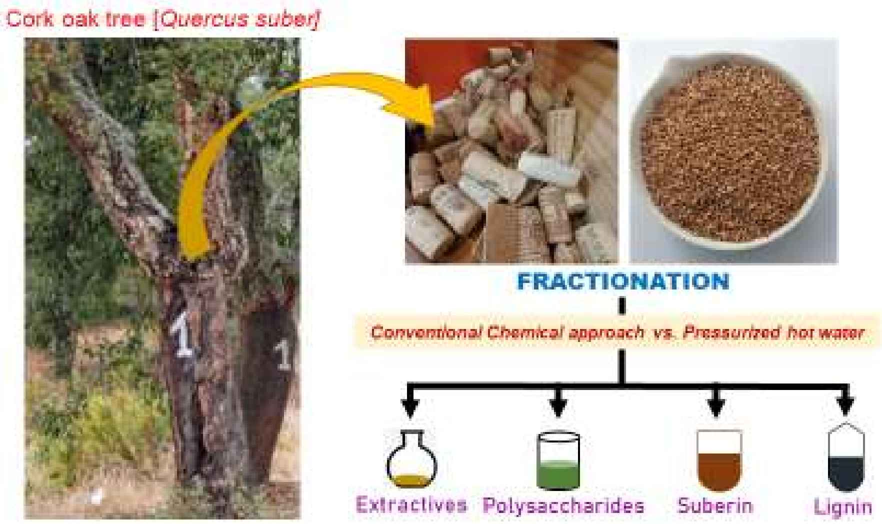

Figure 1. Overall scheme of the present study

2. Materials and Methods

Cork biomass between 40 – 60 mesh were subjected to hexane – methanol – water extraction using Sohxlet apparatus to obtain extractives. Then, suberin was obtained using alkali methanolysis and alkali hydrolysis. The protocols were adapted from Pereira et al[7] and Pinto et al.[8] respectively. Structural carbohydrates and lignin analysis were adapted from NREL[6] standard procedures. The individual products were characterized via HPLC, GC-MS and FTIR. Meanwhile, ultrafast hydrolysis process was carried out using the SEMR that has been reported elsewhere[5]. Cork suspension at an initial concentration of 40 g/L was prepared in water and was maintained under vigorous mixing until and during pumping onto the reactor. The typical reactor length used was 30 cm with an internal diameter of 4.5 mm.

3. Results and discussion

The components in the as-received cork was found to consists of 10.5 g total extractives, 47.7 g total suberin, 14.6 g polysaccharides and 21.1 total lignin per 100 g of oven dry cork, in agreement with previously published data. However, our total suberin value tends to have a higher value than previous reports as we have accounted for the glycerol which was previously excluded and discarded with water during partitioning. This is a one of the major contribution of this work. Hexane extractives were found to contain major tritepenes such as fredelan-3-one, γ-sitostenone, lup-20(29)-en-28-al and betulinic acid, docosanol and glycerol, ethanol extractives were found to contain mostly sugar derivatives such as levolglucosan, arabitol, xylose, myo-inositol, lactose, arabinopyranose, lactic acid, succinic acid and galactopyranose with palmitic acid, vanillin and vanillic acid while water extractives were enriched with arabinose, hexadecanoic acid, stearic acid and octadecanoic acid. Indeed, the conventional cork fractionation process involving alkaline hydrolysis or methanolysis required the use of a huge amount of chemicals (dichloromethane, ethanol, methanol, sodium methoxide, sodium hydroxide, sulfuric acid among others), long reaction time (2-3 days) and laborious work up procedure (9 steps at a minimum, in succession) only to generate small yields (few grams) that would only be suitable for characterization. Meanwhile, we have performed ultrafast hydrolysis in as short as 0.25 s. In a typical run, two product streams were recovered, named as liquid and solid matrix. The liquid matrix was found to contain about 30 μg/ml glucose and 33 μg/ml xylose. Through liquid-liquid extraction, it was found that docosanol and glycerol originating from hexane extractives, palmitic acid, vanillin and vanillic acid originating from ethanol extractives and stearic acid originating from water extractives are present. This result highlighted the low dielectric constant of SCW, similar to that of non-polar organic compounds, thus allowing dissolution of organic compounds. Meanwhile, the solid matrix was found to contain about 60% suberin and 20% lignin, and this increase is in agreement with the cork fraction that dissolved in the liquid matrix.

4. Conclusions

It was found that SEMR hydrolysis can significantly reduce processing time and chemical utilization in fractionating cork biomass compared with conventional approach. Extractives and carbohydrates were found in the liquid hydrolysis products. Suberin and lignin are concentrated in the solid matrix. This demonstrates that SCW is a promising and effective approach for fractionating even complex biomass such as cork due to its high diffusivity and low dielectric constant and could pave way for new applications for the cork fractions.

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