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Comparative study of lignin fractionation by ultrafiltration and selective precipitation

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ABSTRACT

The present work presents two different methods to fractionate the lignin resulting from the black liquor of the pulping process of *Miscanthus sinensis* (7.5% (w/w) NaOH, 90 min, 90 °C). The first method consists of selective precipitation, which is achieved by the gradual acidification of the black liquor, getting different precipitates according to the pH. The second employed technique is the ultrafiltration, which uses ceramic membranes of different cut-off (5, 10 and 15 kDa) to obtain different liquors containing lignins with specific molecular weight.

Using both methods, different lignin fractions have been obtained and characterized by the following analysis techniques: FTIR, thermal analysis, GPC and NMR. Obtained results have shown that the fractionation process applied affects the properties of the obtained lignin. Ultrafiltrated fractions are less contaminated by lignin–carbohydrate complex than the fractions obtained by selective precipitation. Ultrafiltration process also allowed controlling the molecular weight of the obtained fractions.

1. Introduction

Nowadays, life is based on petroleum. Nevertheless, as fossil fuel reserves are decreasing, the exploration of feasible pathways for the conversion of abundant and renewable biomass into clean fuels and high value added chemicals to supplement or gradually replace the petroleum-based industry is highly desirable [1].

The main components of lignocellulosic biomass are cellulose, hemicelluloses and lignin. Cellulose is the most abundant natural polymer. It has a linear structure and is made up of glucose monomers. Hemicelluloses are heteropolysaccharides and have an amorphous structure. The third main component of biomass is lignin. Lignin has a complex phenolic polymeric structure. Its structure results from the condensation of phenylpropane units. The precursors for lignin are p-hydroxyphenyl alcohol (H), guaiacyl alcohol (G) and syringyl alcohol (S). The structure of lignin varies depending on its origin and the extraction method used to obtain it. Lignin molecules are very heterogeneous; therefore, fractionation has become one of the best ways to obtain specific lignins. The aim of fractionation is to obtain specific molecular weight fractions with defined properties; so they can be then used as high added value products. Yang et al. [2] and Matsushita et al. [3] proposed the use of lignin as dispersant in cement and gypsum blends, Boeriu et al. [4] as emulsifier, Sena-Martins et al. [5] as a chelating agent for removing heavy metals from industrial effluents, Mohan et al. [6] found excellent adsorbent in lignin, even compared with the activated carbons and El Mansouri et al. [7] and Tejado et al. [8] proposed its use as a component of phenol–formaldehyde resins.

Different methods have been proposed to fractionate lignin. Mörck et al. [9] fractionated both softwood and hardwood Kraft lignins by successive extraction with organic solvents. Thring et al. [10] divided Alcell® hardwood lignin into three fractions by successive extraction with organic solvents increasing hydrogen-bonding capacity. They obtained similar results as Mörck et al. [9] concluding that the low molecular weight fractions had a lower polydispersity but a higher content of guaiacyl structures with saturated side chains than the higher molecular weight fractions. Yuan et al. [11] studied different procedures of fractionation by selective solvent.

Another possibility to fractionate lignin is the selective precipitation. Sun et al. [12] obtained and characterized five lignin fractions by precipitation from the black liquor of oil palm empty fruit bunches (EFB) fibre pulping after isolation of the polysaccharide degradation products. One lignin fraction was obtained directly from the black liquor by lowering the pH until 2 and was characterized prior to the isolation of the polysaccharide degradation products. Mussatto et al. [13] described the precipitation of lignin by acidification of the black liquor. The lignin mass precipitated for each pH condition was determined. The obtained liquors were evaluated in terms of their colouration and the concentration of soluble lignin, suggesting that each lignin-derived compound was differently affected by the pH alteration. Garcia et al. [14] studied

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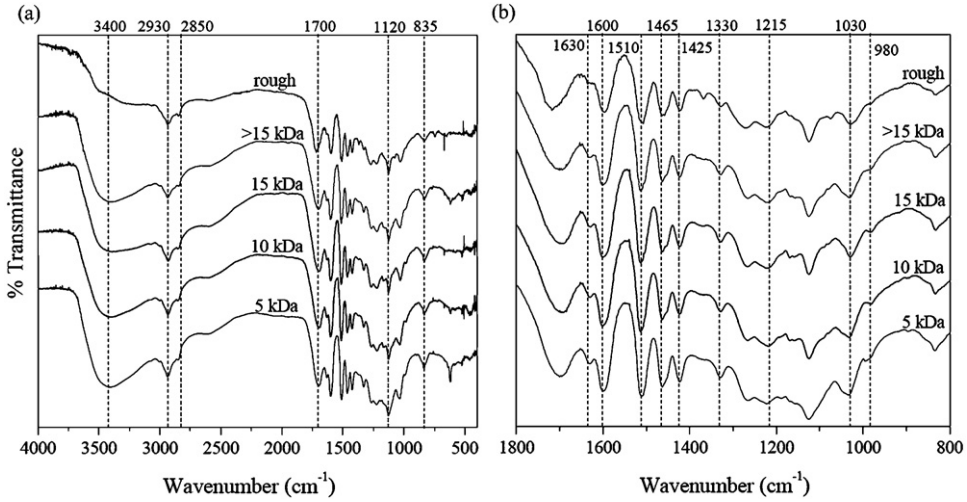

Fig. 1. (a) FTIR spectra of the fractions obtained by ultrafiltration. (b) Magnified region of FTIR spectra of the fractions obtained by ultrafiltration.

the characteristics of the lignin obtained by selective precipitation and the physico-chemical properties of the different lignin fractions obtained.

Membrane technology is another fractionation technology that can be considered because it allows obtaining lignin fractions with defined molecular weight distributions by free-reagent treatment. The effectiveness of the fractionating process using membrane technology lies on the selection of the proper cut-off. Ultrafiltration allows the separation of macromolecular solutions, so, theoretically, it is suitable for lignin fractionation as lignin is a macromolecule. Jönsson et al. [15] studied the influence of membrane cut-off, transmembrane pressure and cross-flow velocity during ultrafiltration of cooking liquor and black liquor. Colyar et al. [16] focused their study on the ultrafiltration of the liquid stream containing a variety of soluble lignin species, taking into account permeance decline, total organic carbon recovery (TOC) sodium recovery and the average molecular mass of organic compounds rejected and permeated.

In the present work, lignin was obtained from black liquor resulting from the soda pulping process of *Miscanthus sinensis* (7.5% (w/w) NaOH, 90 min, 90 °C). Two different processes were considered to fractionate lignin: selective precipitation and ultrafiltration. Obtained lignin fractions by both procedures were characterized to establish the relationship between lignin properties and the fractionation method applied.

2. Materials and methods

2.1. Black liquor obtaining

Black liquor was obtained by pulping *M. sinensis* in a 20 L glass reactor, at a temperature of 90 °C for 90 min, with 7.5% sodium hydroxide solution (w/w), a solid/liquid ratio of 1/18 (w/w) and a constant stirring rate. After reaction, the separation of liquid and solid fractions was carried out, and the resultant black liquor was characterized. The raw material, *M. sinensis*, was kindly supplied by SPE – Straw Pulping Engineering (Zaragoza, Spain).

2.2. Fractionation processes

The first fractionation method used was ultrafiltration (UF) membrane technology. The UF module used in the present work was supplied by IBMEM – Industrial Biotech Membranes (Frankfurt, Germany). The membranes (5, 10 and 15 kDa) are made of

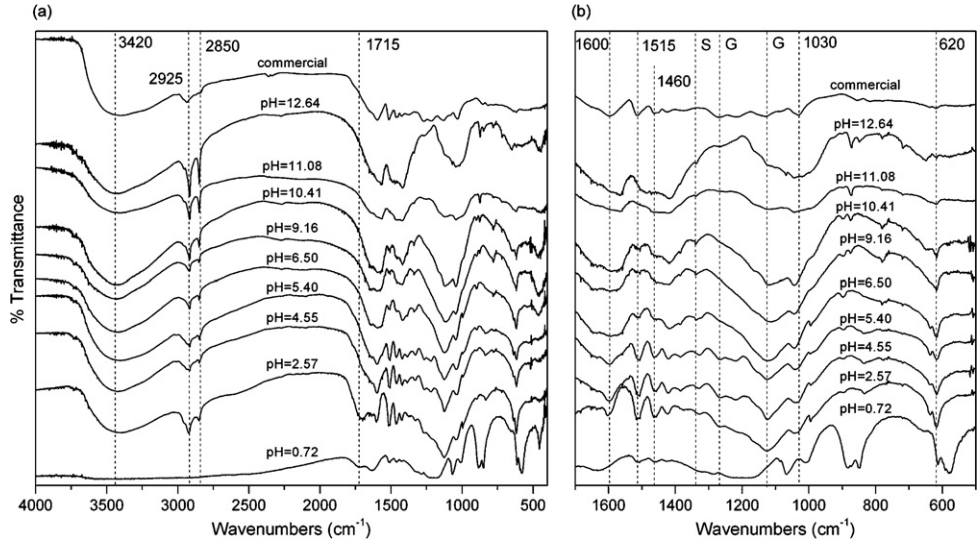

Fig. 2. (a) FTIR spectra of the fractions obtained by selective precipitation. (b) Magnified region of FTIR spectra of the fractions obtained by selective precipitation.