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Biorefining of lignocellulosic residues using ethanol organosolv process

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Non-woody lignocellulosic feedstock was used as raw material for cellulose, lignin and hemicelluloses obtaining in a biorefinery sense following economically and environmentally sustainable criteria. An integrated scheme composed by an ethanol organosolv pulping followed by an ultrafiltration module equipped with a set of ceramic membranes with different cut-offs was used to separate different lignin fractions. Furthermore, a distillation unit allowed the recycling of the solvents (ethanol and water) in order to reuse them favouring the economic aspect of the process and reducing its environmental impact. Products physico-chemical characterization (FTIR, GPC) was done to evaluate their potential possible industrial applications.

1. Introduction

The development of biorefinery processes in the last years is being boosted by the necessity of finding a substitute to the petroleum-based industry to produce both products and energy. Nevertheless, to become an actual alternative to fossil fuels and petroleum derivate products, biorefinery processes must be competitive and cost-effective. The 'Lignocellulose Feedstock Biorefinery', which makes use of 'nature-dry' raw material (wood, straw, forest and agricultural lignocellulosic residues) is a promising alternative due to the abundance and variety of available raw materials and the good position of the conversion products on the market (Kamm and Kamm, 2004). Process profitability is also dependent on the technology employed to alter the structure of lignocellulosic biomass in order to produce high value co-products from its three main fractions (cellulose, hemicellulose, and lignin) (Mosier et al., 2005). Technologies include enzymatic fractionating by cellulases and chemical hydrolysis by hot water treatment, steam explosion, ammonia fiber explosion, dilute or concentrated acid hydrolysis, alkaline treatment and organosolv processes. The latter group, which uses mixtures of water and organic alcohols or acids to fractionate the biomass, is well known in the pulp and paper industry (Hergert, 1998; Muurinen, 2000). Ethanol organosolv process, gained new relevance for biomass pre-treatment in a biorefinery sense (Lignol process) as it allowed recovering multiple co-products (cellulose, lignin,

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hemicellulose and extractive components of the lignocellulosic biomass) from different streams of the process (Pan et al., 2005). The complex structure of lignin, with a great variety of functional groups and over 10 different types of linkages, depends strongly on the original source and extraction method used (Lora and Glasser, 2002). Organosolv methods give rise to low molecular weight (LMW) lignins that are soluble in most common solvents (Belgacem et al., 2003). Their structure presents relatively high amount of phenolic hydroxyl groups and oxidized groups (e.g. Hibbert ketones) that favour their incorporation into polymer formulations and their chemical modification (Kubo and Kadla, 2004). Furthermore, oligomers and monomers hydrolysed from the hemicelluloses as well as the degraded hemicellulosic polymers could be used as a variety of chemicals for industry (Sun et at., 2005).

In this work, organosolv ethanol technology was used to fractionate non-woody biomass feedstock in order to obtain a solid cellulose stream and a liquid stream containing hemicellulosic sugars and lignin by a cost-effective renewable biorefinery process. Subsequent processing of those streams by separation and purification techniques (ultra filtration membrane) were design to obtain an enriched hemicellulose-derived sugar stream and a high quality lignin fraction with potential industrial applications.

2. Materials and methods

2.1 Materials

Characterization of original *Miscanthus Sinensis* fibres was done according to standard methods. Moisture content (6.1 wt %) was determined after drying the samples at 105 ºC for 24 h (TAPPI T264 cm-97). Chemical composition, given on an oven dry weight basis, was the following: 0.9±0.1% ash (TAPPI T211 om-93), 16±0.9% aqueous NaOH soluble matter (TAPPI T212 om-98), 4.2±0.4% hot water soluble matter (TAPPI 207 om-93), 2.0±0.5% ethanol–benzene extractives (TAPPI T204 cm-97), 20±0.1% lignin (TAPPI T222 om-98), 80±1.0% holocellulose (Wise et al., 1946) and 48±0.2% α-cellulose (Rowell, 1983).

2.2 Biorefinery process scheme

A flowchart of the integrated biorefinery process summarizing ethanol organosolv pretreatment, separation and purification stages as well as solvents (ethanol and water) recovery units is shown in Figure 1. Lignocellulosic raw material was milled and treated in aqueous ethanol, in a laboratory scale 20L batch reactor with temperature and pressure control. Experimental conditions used were: ethanol–water 60/40 w/w; temperature: 160ºC; reaction time: 90 min; liquid/solid ratio: 7:1. After cooking, the reactor content was cooled to room temperature. Solid and liquid fractions were then separated using a nylon mesh. The former was washed three times with 5L aqueous ethanol (60/40 w/w) at 45ºC and the filtrates combined with the original liquid fraction. The solid fraction was then separated from uncooked material by screening through a sieve of 1mm mesh. Its composition, mainly cellulose, could be post-treated by several processes, as saccharification and fermentation to obtain ethanol or pulp for paper production by refining.

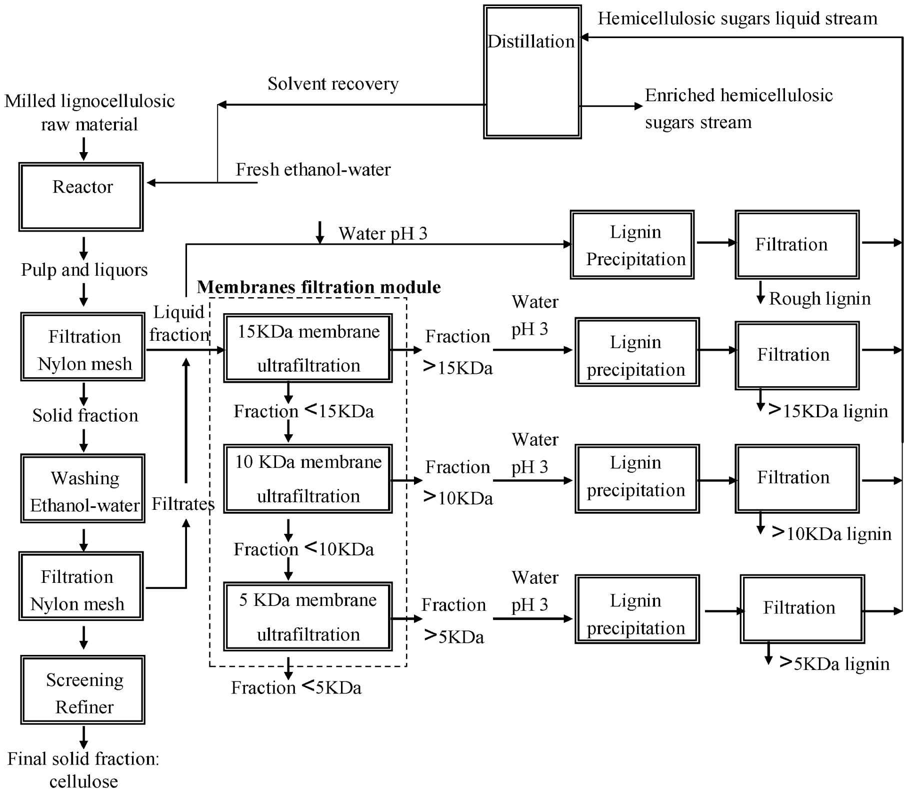

Figure1. Biorefining process scheme: ethanol organosolv pretreatment and membranes ultrafiltration process.

2.3 Membrane ultrafiltration unit

Ultrafiltration module used was a Pall Membralox XLab5 pilot unit equipped with a 3L 316 stainless steel tank with water jacket for temperature control, a recirculation pump and a set of tubular ceramic membranes of different cut-offs in the interval 5–15 kDa manufactured by IBMEM – Industrial Biotech Membranes, Germany. The diameter of the membrane tubes was 6 mm, the length 250 mm and the area of each membrane tube was 47 cm^2. Experiments were done at the following experimental conditions: trans-membrane pressure, TMP: 300 kPa; cross-flow velocity: 5.6 m/s and temperature: 60ºC.

2.4 Organosolv lignin

Lignin contained in the liquid fraction composed by the stream exiting the reactor mixed with the filtrates (ethanol-water) obtained from the washing of the solid fraction, was precipitated and conditioned (Ibrahim et al., 2004), as well as the lignin contained in the four streams exiting the membrane modules: lignin fraction>15KDa, 15KDa>lignin fraction>10KDa, 10KDa>lignin fraction>5KDa, lignin fraction<5KDa. Before being characterized by different techniques (FTIR, GPC) lignin samples were purified (Pan et al., 2005) and acetylated (Glasser et al., 1993). Characterization procedures were described elsewhere (González Alriols et al., 2008).

3. Results

3.1 Lignin characterization

3.1.1 Chemical Structure.

Lignin FTIR absorption spectra is presented in Figure 2.

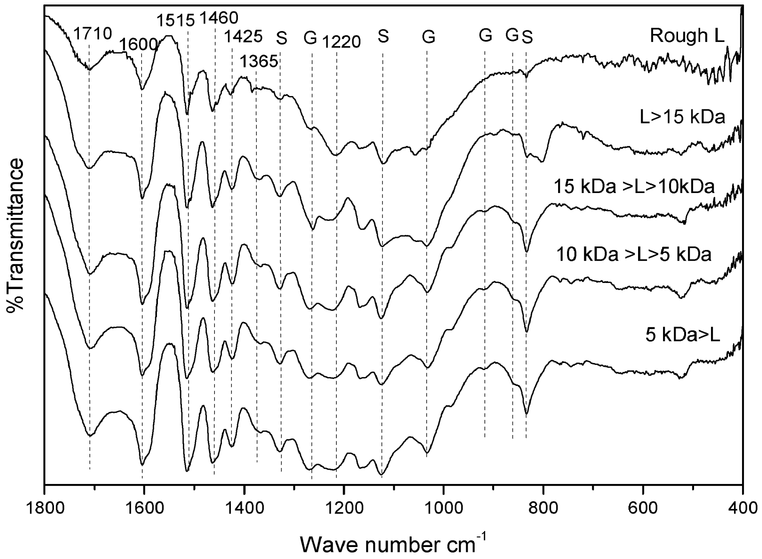

Figure 2. FT-IR spectra of lignin samples

Typical lignin structure bands were identified, as aromatic and aliphatic hydroxyl groups (3400cm^{-1}), aromatic phenylpropane skeleton vibrations (1600, 1515 and 1425cm^{-1}), C–H aliphatic bonds (2925, 2850 and 1460cm^{-1}), ether bridges (1220cm^{-1}) and stretching of conjugated (1660 cm^{-1}) and non-conjugated (1710cm^{-1}) carbonyl groups with the aromatic ring. Furthermore, several bands were attributed to syringyl (S) and guaiacyl (G) structures; S bands: S ring breathing with C–O stretching (1330 cm^{-1}), S-type aromatic C–H in plane deformations (1118 cm^{-1}), out-of-plane C-H bending in S units (833cm^{-1}) and G bands: G ring breathing with C–O stretching (1265 cm^{-1}), aromatic in-plane bending in G units (1033 cm^{-1}), out-of-plane C-H bending in G units (915 and 855 cm^{-1}). Although G and S bands could be observed in all analyzed lignin samples, their intensity varied. S bands presented higher intensity as the cut-off of the lignin sample diminished, being maximum in the <5kDa lignin sample. On the contrary, G signals were more intense in the >15kDa lignin sample. This fact was related with the chemicals bonds between lignin structural units. β-O-4 and C–C links are the most common bonds between lignin structural units (specially those involving C5 of the aromatic ring). G units are able to form C5 bonds, but this is not possible in S units as they have C5 position substituted by a methoxy group. This feature affects lignin's molecular weight (MW), as C–C bonds are so stable that are not cleaved during wood pulping. As a consequence, the higher G percentage in lignin composition, the higher MW they are expected to present (Tejado et al., 2007). This analysis seems to be valid for the lignin samples studied in this work meaning that membrane fractionation system allowed the obtaining of different cut-off lignin groups.

3.1.2 Lignin molecular weight.

Molecular weight distribution (Weight average MW -M_w-, number average MW -M_n- and polydispersity -M_w/M_n-) of acetylated lignin samples analysed by GPC is presented in Table 1. Rough lignin M_w value was in good concordance with organosolv lignins published data (Sun et al, 1997) and lower than those reported for kraft and soda lignins (Tejado et al., 2007). Lignin fractions obtained by the membrane filtration system presented lower polydispersity and the smaller was the cut-off of the used membrane the smaller were the M_w and M_n of the lignin fraction. This fact corroborated the results obtained by FTIR and demonstrated that the membrane filtration system allowed the purification of narrower lignin fractions with similar molecular weights which could be used in several industrial applications as polymer formulation (Kubo and Kadla, 2004) or as antioxidants (Pan et al, 2006).

Table 1. Weight average MW (M_w), number average MW (M_n) and polydispersity (M_w/M_n) of acetylated lignin samples analysed by GPC.

Sample	**M_w**	**M_n**	**M_w/M_n**
Rough L	2180	1150	1.9
L >15KDa	2390	1500	1.6
15KDa>L>10KDa	1900	1360	1.4
10KDa>L>5KDa	1750	1350	1.3
5KDa>L	1357	1130	1.2

4. Conclusions

Non-woody biomass feedstock has been satisfactorily converted in cellulose, lignin and other products with significant potential market value by organosolv pretreatment and membrane fractionation processes. The possibility of recycling the solvents allowed the cost-effectiveness of the process while obtained products high quality (lignin low molecular weights and polydispersity) ensured their actual industrial applications.

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