LIGNIN PURIFICATION WITH GREEN SOLVENTS

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Nowadays, lignin is gaining importance as a potential source for aromatic chemicals. Commercial lignins are usually contaminated with cellulose, hemicelluloses and other inorganic impurities, which constitute an obstacle in their direct processing for obtaining aromatic precursors. In this work, lignins obtained from *Malus domestica* by alkaline extraction (7.5% NaOH, 90 min, 90 ºC) and organosolv (60% ethanol, 90 min, 180 ºC) processes were treated with green solvents, to reduce their impurities. The green solvents used were water and [BMI][$MeSO_4$], and the obtained lignin was characterized by different techniques (ATR-IR, TGA, and HPLC). The results showed that soda lignin has more impurities than organosolv lignin, and that ionic liquid (IL) is the best purification method.

Keywords: lignin, ionic liquid, purification

INTRODUCTION

Lignocellulosic biomass is constituted principally of lignin, cellulose and hemicelluloses. Lignin is the second most abundant renewable biomaterial on earth,[1] being utilized as a low-value heating fuel, binder, dispersant, emulsifier and sequestrant; nowadays, lignin is gaining importance as a potential source for aromatic chemicals.[2] Lignin is an amorphous polyphenolic polymer, composed mainly of guaiacylpropane, syringylpropane and *p*-hydroxyphenylpropane.[3] Its complex and irregular structure is not completely understood.[4] Nowadays, several methods for obtaining lignin are in use, such as kraft process, alkaline treatment, steam explosion and organosolv processes. The lignin obtained by these industrial processes is always contaminated with cellulose, hemicelluloses and other impurities, so that its further purification is needed prior to its transformation into value-added products.[5,6]

To this end, green solvents are used. Currently, ionic liquids, as green solvents for biomass, are the most investigated ones. The first ionic liquid, $EtNH_3NO_3$, was discovered in 1914 by Paul Walden. Ionic liquids are liquid salts composed of ions, where one or both ions are large, the cation having a very low symmetry,[7] and low melting points, <100 ºC, which differentiate them from the classical molten salts.[8] Ionic liquids are used to substitute organic solvents, dut to their specific physico-chemical properties, particularly non-flammability and high thermal stability. Due to their very low vapor pressure, they do not emit volatile organic compounds,[9] which explains their low melting points. The ionic liquid has been described as a designer solvent, combining the appropriate anion with the cation, which permits to adjust properties, such as melting point, viscosity, density or hydrophobicity.[9] Due to their properties, and also to their versatile synthesis, ionic liquids are gaining interest as biomass solvents. Some ionic liquids, such as Bmin Cl (Butyl methylimidazolium chloride), have already been used for dissolving cellulose and for further depolymerization or reprecipitation.[10] Lignin is also solubilised by some ionic liquids, such as Bmin Cl, Amin Cl (1-Alyl-3-methylimidazolium chloride),[11] 1,3-dimethylimidazolium methylsulfate[3] and [BMI][$MeSO_4$] (butylmethhylimidazolium methylsulfate).[1] In the present study, soda and organosolv lignin, obtained from *Malus domestica*, were purified with [BMI][$MeSO_4$] and acidified water.

EXPERIMENTAL

Materials

The branches of *Malus domestica* used in the experiments were supplied by a local farmer. The ionic liquid [BMI][$MeSO_4$] was provided by Sigma-Aldrich and 96% (v/v) ethanol was supplied by Scharlab.

Methods

Analysis of raw material

The characterization of the original *Malus domestica* fibers was done according to standard methods.[12] Moisture content (8.80 ± 0.03wt. %) 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: 3.25 ± 0.24% ash (TAPPI T211 om-93), 16.73 ± 0.17% hot water soluble matter (TAPPI T207 om-93), 32.00 ± 0.57% aqueous NaOH soluble matter (TAPPI T212 om-98), 10.71 ± 0.47% ethanol-benzene extractives (TAPPI T204 cm-97), 26.15 ± 0.09% lignin (TAPPI T222 om-98), 57.44 ± 1.66% holocellulose[13] and 27.32 ± 0.23 α-cellulose.[14]

Organosolv pulping

Organosolv pulping was carried out using a 60% (v/v) ethanol solution with a solid-to-liquid ratio of 1:4 at 180 ºC for 90 min.[15] Lignin was recovered from the liquor by adding acidified water at pH 2, achieved by the addition of sulphuric acid at 72% w/w, after which the liquor was centrifuged at 4000 rpm for 15 min.[16] The precipitated lignin was separated and dried at 50 ºC.

Soda pulping

Soda pulping was carried out with a 7.5% (w/v) NaOH solution, at a solid-to-liquid ratio of 1:10, at 90 ºC for 90 min.[15] Lignin was recovered from the liquor by adding 72% (w/w) sulphuric acid until the black liquor reached pH 2.[16] The liquor was centrifuged at 4000 rpm for 15 min and the precipitated lignin was separated and dried at 50 ºC.

Lignin purification with [BMI][MeSO$_4$]

Soda and organosolv lignins were oven-dried at 105 ºC for 24 h before treating them with ionic liquid, to avoid moisture adsorption. The dried lignin was introduced in a flask along with [BMI][$MeSO_4$] in a solid-to-liquid ratio of 1:25 at 50 ºC for 6 h under inert atmosphere, achieved by bubbling N_2 gas on the reaction vessel, to eliminate the water formed during the reaction. Further on, the ionic liquid solution was filtered and then acidified with water at pH 2 with 72% (w/w) sulphuric acid, to recover the lignin from the ionic liquid. The solution was centrifuged at 4000 rpm for 15 min. The recovered lignin and the residue separated in the filter were dried at 50 ºC.

Lignin purification under mild acid conditions

Organosolv and soda lignins were purified with acidified water at pH 2, attained with 72% (w/w) sulphuric acid at 50 ºC for 30 min, under constant magnetic stirring.

Lignin characterization

All lignin samples were characterized by attenuated-total reflectance infrared spectroscopy (ATR-IR), by direct transmittance in a single-reflection ATR System (ATR top plate fixed to an optical beam condensing unit with a ZnSe lens), with an MKII Golden Gate SPECAC instrument. Spectral data were recorded with 30 scans in the 4000-700 cm^{-1} range, at a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) of lignin was carried out under nitrogen atmosphere, using a Mettler Toledo TGA/SDTA RSI analyzer with a dynamic scan from 25 to 800 ºC, at a rate of 10 ºC/min. The lignin samples were treated with a 2% H_2SO_4 solution in reflux and filtered. To determine the content of sugars in the lignin samples, the filtered solutions were characterized by High-Performance Liquid Chromatography (HPLC) Jasco LC-Net II/ADC equipped with a photodiode array detector, refractive index detector and Rezex ROA-Organic Acid H+ (8%) column. As mobile phase, a dissolution of 0.005 N H_2SO_4 prepared with 100% deionised and degassed water was used (0.35 mL/min flow, 40 ºC and injection volume of 20 µL). High-purity xylose, glucose, galactose, mannose and arabinose purchased from Sigma–Aldrich were used for calibration. Standards were prepared at different sugar concentrations (0.1, 0.5, 1 and 2%, w/w). A linear calibration ($R^2 > 0.999$) was obtained for all sugars.

RESULTS AND DISCUSSION

The high content of lignin in *Malus domestica* (26.15 ± 0.09%) explains the selection of this raw material. The shortcoming of this raw material is its high holocelullose content (57.44 ± 1.66%), which leads to the obtaining of impure lignin. Soda lignin behavior is different from that of organosolv lignin. Unlike organosolv lignin, soda lignin is not soluble in ionic liquid, which explains why these lignin structures are very different. The low solubility of soda lignin in ionic liquid is due to the formation of inorganic salts during precipitation, and the ionic liquid cannot dissolve these inorganic salts.

Organosolv lignin solubility in the ionic liquid is of about 72%, while soda lignin solubility is of about 3.91%. The recovery of purified organosolv lignin from ionic liquid is of about 50%.

The TGA curves of the different lignins and their treatments are plotted in are plotted in Figure 1 and Figure 2, corresponding to organosolv lignin, shows that the range of maximum weight loss is between 300 and 400 ºC, assumed to be the lignin degradation peak.[17,18] The most significant change occurs in the lignin washed with IL. In this case, the peak is the sharpest, while the peak around 250 ºC, supposed to be the hemicelluloses degradation peak,[19,20] disappears; however, another peak appears at a lower temperature.

Apparently, the treatment with acidified water does not change the thermal behavior of the sample. The peaks and the shape of the curves are almost the same. Numerical data are shown in Table 1. Figure 2, corresponding to NaOH lignin, shows a different thermal behavior, compared to Figure 1. In this case, the maximum weight loss appears in the 200-300 ºC range. The sharpest peak, occurring in the lignin washed with acidified water at pH 2, is displaced at a higher temperature. In addition, a new peak appears around 400 ºC. The effect of IL is more or less the same as that of acidified water, even if it is less effective.

Table 1
TGA results of lignin degradation peak

Peak T (ºC)	Raw material	Water, pH 2	IL
Organosolv lignin	360.791	349.992	317.704
NaOH lignin	234.63	256.49	245.337

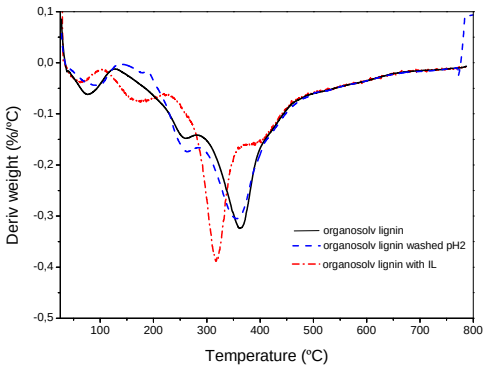

Figure 1: TGA of organosolv lignins and different purification treatments

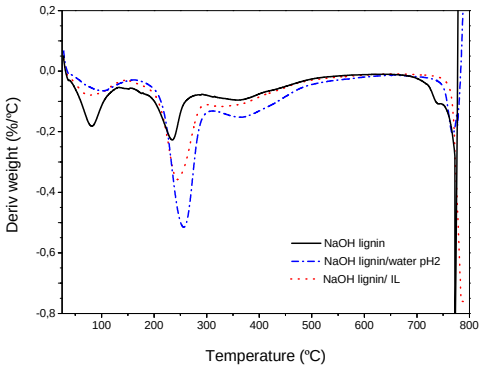

Figure 2: TGA of NaOH lignins and different purification treatments

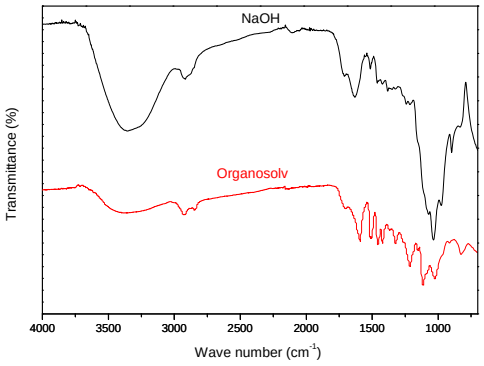

Figure 3: FTIR of organosolv and NaOH lignins

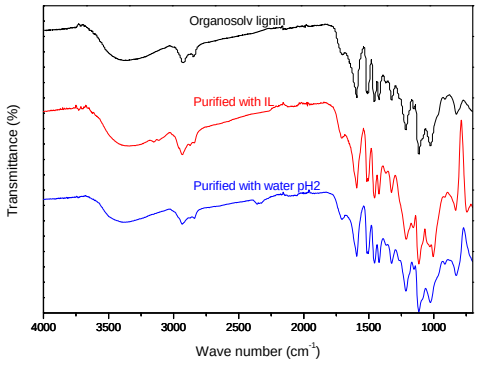

Figure 4: FTIR of organosolv lignins and lignin resulting from other purification treatments

The FTIR spectra evidence numerous differences between the NaOH and organosolv treatments (Fig. 3).The main difference is that the peak at 2850 cm^{-1}, which is associated with C-H aliphatic bonds, disappears in the spectra of NaOH lignins. In addition, typical lignin structure bands are more defined in organosolv lignins.[21] The changes observed in the spectra of lignin subjected to different treatments are not numerous. The most important difference refers to the peak at 821 cm^{-1} in both samples previously purified with IL and with acidified water, which is typical of sulfate vibration (Fig. 4). As seen in Figure 5, the differences between spectra are not very important; the only change is the displacement of the peak at 1650 cm^{-1} to a lower wavenumber,

which corresponds to carbonyl stretching – para-substituted aryl ketone. Moreover, in the spectra of NaOH lignin and of lignin purified with IL, the peak at 850 cm^{-1} is very significant, being less intense when treated with water.[21]

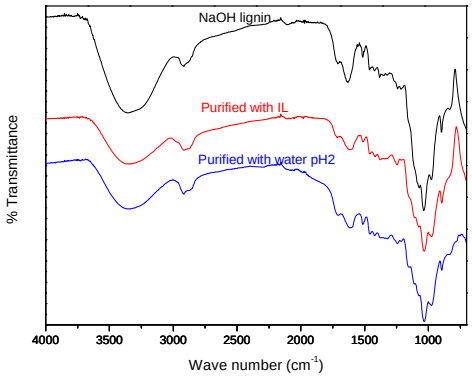

Figure 5: FTIR of NaOH lignins and different purification treatments

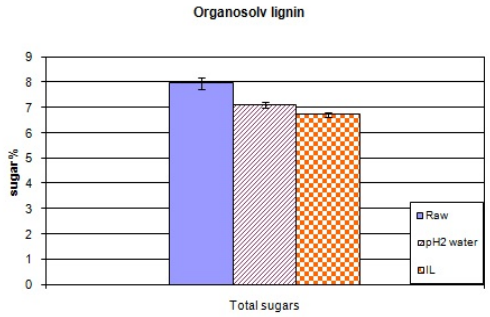

Figure 6: Sugar content comparison in organosolv lignins

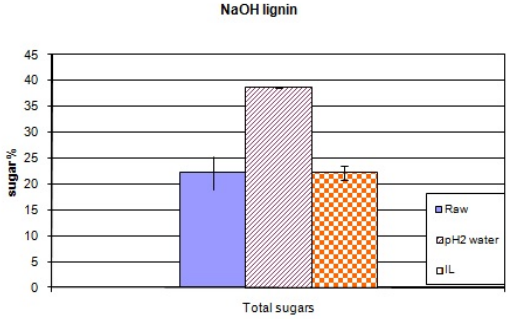

Figure 7: Sugar content comparison in soda lignins

The total amount of sugars in the different lignin samples is shown in Figures 6 and 7, which evidence different behaviors, as depending on the lignin involved in the treatment.

Figure 6 shows that the sugar content in organosolv lignin samples decreases in both treatments. The most significant decrease occurs when lignin is treated with IL. Figure 7 shows that the sugar content in soda lignin samples increases when lignin is treated with acidified water, such an abnormal behavior being explained by the presence, in the sample, of other components with the same retention time as that of the measured sugars. Further experiments will be carried out to elucidate this aspect. The experiment showed that the use of IL did not improve soda lignin purity. The organosolv process applied to obtain lignin is less aggressive and the product is purer. The treatment of organosolv lignin with IL shows good results and future works will be carried out to improve this purification treatment.

CONCLUSIONS

Considering different techniques for the purification of various types of lignins, the present study shows that soda lignin has more impurities than organosolv lignin, which makes more difficult the process of its purification, especially considering that the structures of both lignins are different and the amount of sugars in soda lignin is very high, as shown by TGA analysis and HPLC characterization. On the other hand, organosolv lignin is purer, so that it can be better purified by an IL treatment.

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