

Extraction of Organosolv Lignin from Rice Husk under Reflux Conditions

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Abstract: The rice husk is a very abundant residue, being rich in cellulose and lignin, whose main destination in the southern Brazil is burning for power generation. This study aims at extracting the lignin from the rice husk, applying a methodology called Organosolv, in a modified process by the use of atmospheric pressure. As the extraction solution, a mixture of ethanol/water with ethanol concentrations of the 25 to 100% v/v were used. As the catalyst for extraction, concentrated sulfuric acid, in proportions of the 0.5 to 3.0% v/v under reflux and heating by 24 hours were used. The yields obtained were between 3 and 48% for the amount of Klason lignin analyzed. The tests, which applied smaller quantities of ethanol and catalyst (sulfuric acid), presented lower yields, while the highest yields was found in the extraction solutions with 75% v/v of ethanol and 3% of catalyst. The extracted lignin was characterized by spectroscopic, chromatographic and thermal analysis. The extracted samples showed great structural homogeneity, good thermal stability, low polydispersivity ($< 2,0$) and low presence of contaminants such as cellulose and hemicellulose. The studied procedure aims at the reuse of an abundant agro-industrial waste, in order to reduce the environmental impact of its burning and to obtain the lignin, a natural polymer with great potential for industrial application.

Keywords: Lignin, Organosolv, reflux, rice husk, waste.

1. Introduction

Among the lignocellulosic biomasses, it is possible to highlight the rice husk as a waste of abundant agro-industrial production, since rice is the second most cultivated crop in the world and 20% of its mass is made of its husk. This waste is currently burned in order to generate energy; such procedure causes an

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important environmental liability due to the air pollution generated. The main obstacles to extract the rice husk components are low porosity, high cellulose crystallinity, as well as the physical barrier originated from the fibrous structure and the high level of silica [1]. The growing interest in this waste comes from its chemical constitution, which presents compounds of great commercial interest such as lignin and cellulose. However, the amount of existent compounds on the husk depends on many factors such as soil, temperature and humidity during its growth.

The lignin, together with cellulose and hemicellulose, is one of the most abundant polymers on Earth, it is estimated that its annual production is around 10 to 50 billion tons⁷. In plants, it is found chemically bounded to cellulose and hemicellulose, with the function of providing rigidity and protection to the plant cell [2]. Its structure is formed by an aromatic “rings chain”, randomly connected by ether and C-C linkages and this makes its extraction and characterization extremely complex. Lignin is considered a subproduct of cellulose industry and it is used to generate energy through its burning [3].

The lignins are polymers that do not have a defined structure as the cellulose, they are considered an amorphous, random, three-dimensional and branched polymer, whose structure is difficult to determine, because its composition depends on many factors as the vegetable kind, type of the plat cultivation soil, climate, etc [4]. Other difficulties for its characterization concern the low solubility of these compounds in organic solvents and the difficulty of extracting them without structural change. The lignin is defined as a random polymeric chain formed by many units of “phenylpropanoids” interconnected [5], these structures can be seen in the figure (Fig. 1).

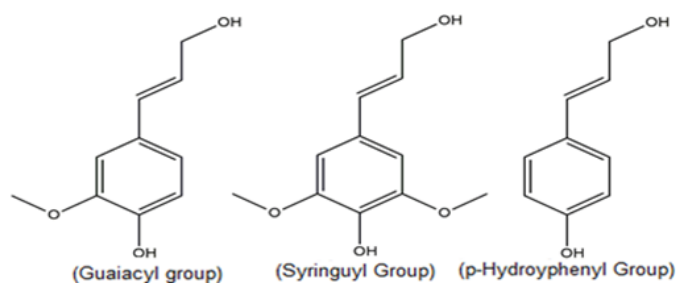


Fig. 1 Main units of “phenylpropanes” that form lignin.

In literature, there are few viable methodologies to extract lignin without changing its original structure. The chemical structure of the extracted lignin depends on the vegetable type and the extraction process [3]. Despite this, several studies were developed and suggested many application possibilities in adhesive production, chemical input, film production, as a dispersant agent in cement, as a chelating agent in the water heavy metal removal, among other possibilities [6]. Therefore, new extraction processes development and

study are becoming increasingly important, as well as the improvement of those studies already published, in order to seize all the compounds of the vegetable biomass: cellulose, hemicellulose and lignin.

One of the most recent processes of delignification, called Organosolv has limited application concerning the cellulose and lignin obtainment. It uses organic solvents, catalysts, pressure and high temperatures in the delignification process. The problems, especially of safety and cost end up limiting the use of this technique [7]. Here, the Organosolv method is tested with a low cost solvent (ethanol), an acid catalyst (sulfuric acid), atmospheric pressure and reflux during 24 hours to lignin extraction from rice husk. This procedure seeks to better take advantage of this waste use and generate a cheap and more chemically homogeneous lignin source.

2. Materials and Methods

2.1 Rice husk preparation and lignin extraction

The rice husk used is from the south of Brazil, all chemicals used were analytical grade reagents without previous treatment and the results were obtained in triplicate. The silica and the inorganics of the husk (ashes) were analyzed by the ASTM D1102 standard. The amount of lignin in the rice husk was determined through TAPPI standard, T 222 om-02 which applies the Klason method. The rice husk used was washed in distilled water for dirt removal. After, a procedure to remove the extractives (wax, proteins and lipids) of cell wall was held, it consists in exhaustive washes of the material with n-hexane and ethanol in Soxhlet extractor [8].

In order to extract the lignin from the rice husk, ethanol/water solutions with different concentrations of sulfuric acid as catalyst were used. this mixture of ethanol / water was applied in a concentration of ethanol 25 to 99%. As the catalyst for extraction, concentrated sulfuric acid, in proportions of the 0.5 to 3.0% v/v. The total volume of ethanol/water solution used in each experiment was of 100 mL and 5g of rice husk. The extraction solution, sulfuric acid and rice husk were kept under heating in reflux by 24 hours.

After the reflux, the extraction solution is filtered to remove the residual husk, the obtained filtered is evaporated and water is added up to the precipitation of all lignin extracted from the rice husk. The lignin is then washed and dried for characterization. The figure (Fig. 2) represents the complete extraction procedure applied.

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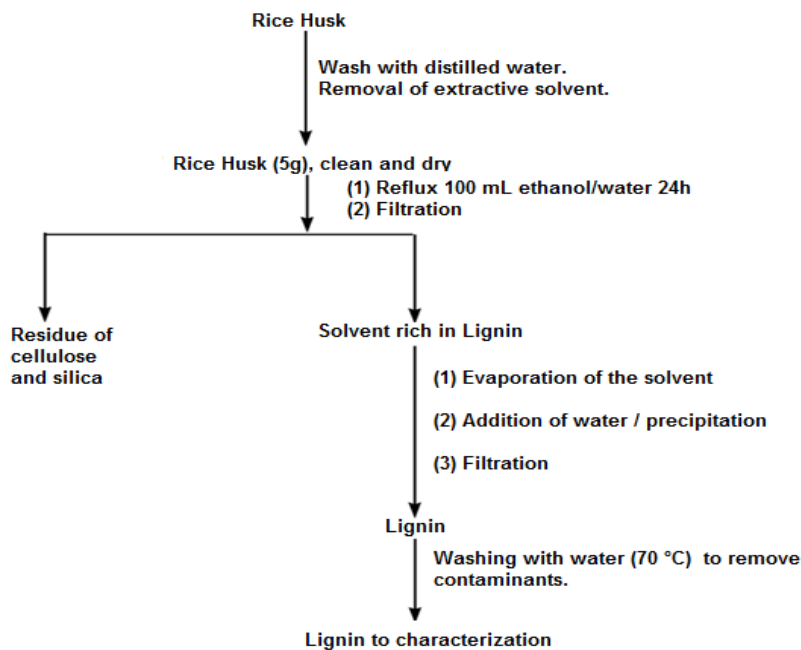


Fig. 2 Flowchart for lignin extraction from rice husk.

2.2 Characterization of the lignin samples

The obtained lignins were characterized through thermal, chromatographic and spectroscopic analysis. The differential scanning curves (DSC) were held in a Shimadzu (DSC-60, Japanese) using the nitrogen atmosphere in a flow rate of 50 mL/min, 4 mg of sample were heated from 20 to 600 °C with a 10 °C/min rate. The thermogravimetric analysis (TGA) was carried in a Shimadzu equipment (TGA-50 model, made in Japan), with the purpose to verify its thermal stability. All samples were analyzed under a nitrogen atmosphere in a flow rate of 50 mL/min, heating rate of 10° C/min, from ambient temperature to 600°C.

The lignin molecular weight was studied through gel permeation chromatography (GPC), in a Viscotek VE 2001 GPC with triple detector (Refractive Index, Viscosity and Light Scattering) Viscotek TDA 302. Equipped with gel columns of copolymer Styrene-Divinylbenzene. The columns were calibrated using polystyrene standard columns. THF was used as eluent in a flow of 1L/min and with lignin concentration of 1 mg/l.

For the Vibrational Spectroscopy Infrared Fourier Transform Spectroscopy (FTIR) a Shimadzu – IR PRESTIGE-21 spectrophotometer was used, the lignin was mixed with KBr (concentration 0,5%) and the readings taken from 500 to 2000 cm⁻¹. The spectroscopic analysis in the Ultraviolet-visible (UV-Vis) region was held in a Shimadzu (UV-2550 UV-Vis) equipment.

For the scanning electron microscopy (SEM), an electron microscope Jeol JSM 6060 was used, extensions from 500 to 5000 times were applied with accelerating power of 15 KeV.

3. Results and Discussion

3.1 Yields

The rice husk analyzed presented total ash and inorganics of 16,06 +/-1 wt% and the Klason lignin found in the husk was of 22,35+/-1,2 wt%. The yields in lignin are showed in the Table 1.

Table 1

Observed yields, considering the total lignin Klason analyzed.

1%	Ethanol*(%v/v)	Acid (% v/v)	Average Yield(wt. %)
1	25	0.5	< 3
2	25	1	< 3
3	25	1.5	< 3
4	25	3	< 3
5	50	0.5	< 3
6	50	1	19 ± 1.2
7	50	1.5	21 ± 1.7
8	50	3	23 ± 1.1
9	75	0.5	< 5
10	75	1	25 ± 1.3
11	75	1.5	36 ± 1
12	75	3	48 ± 1.5
13	100	0.5	< 5
14	100	1	16 ± 1.5
15	100	1.5	22 ± 2
16	100	3	39 ± 2

*Ethanol analytical grade 99%.

The obtained lignin yields vary between 3 to 48%, the reactions that occur during the delignification processes are difficult to analyze, because the lignin removal can happen in several ways and with reactions happening simultaneously, even after the extraction and solubilization of the substrate [7, 9, 10]. Therefore,

the yields are discussed by analyzing the variables separately (acid and ethanol concentration) only in the main results.

The extractions with 50% of ethanol (experiments 6, 7 and 8), show a very small yield growth ($19 \pm 1,2\%$); ($21 \pm 1,7\%$); and ($23 \pm 1,1\%$), if compared with the increase shown on the other concentrations. In others study's with ethanol concentration between 65 and 95% v/v [9], has a similar pattern when the water quantity of the extractor solution is raised. In these studies, it was stated that there is water/lignin colloidal systems formation that prevents precipitation and reduces yields. As we worked with reflux temperature, these conditions were also determining factors for the yields reduction in these experiments.

The experiments 14, 15 and 16 (100% v/v of ethanol) were expected to be primarily the ones with the best yields extraction. However, this was not observed experimentally. The phenomenon that results in a lignin lower yield with the raise of ethanol concentration [11], may be related to the decrease of the hydronium ion (H_3O^+) formation, resulting from the lower amount of present water (<1%). This specimen plays an essential role in the lignin depolymerization and solubilization. Thus, when the ethanol is raised, the amount of this ion available is reduced, which results in a lower lignin yield.

The samples that were extracted with a 75% of ethanol (10, 11, and 12) presented the best yields, showing the importance of the water to the extraction and proving the possibility of hydronium ion formation in order to improve the lignin cleavage and solubilization.

In all the experiments with the best yields, the acid raise represents an increase in the lignin extraction. The cleavage of α -ether bonding occur easily and account for the major part of the obtained lignin. To break the β -ether bonding it is necessary a more aggressive acid conditions, this can explain the reason why when the acid concentration is raised the lignin yield is raised [7]. The structure below (Fig. 3) shows where the breakage of the lignin bonding can occur.

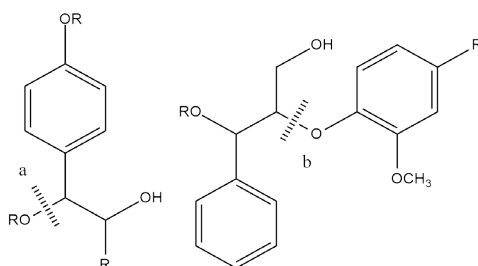


Fig. 3 Models of cleavage in lignin, a= α -ethers and b= β -ethers

3.2 Analysis results and characterization

The DSC curves showed a similar thermal behavior to all samples of lignin obtained in each conditions (Fig. 4, left curve). The endothermic transformations are present only at the beginning of heating and they are attributed to water loss up to 100°C [12]. The samples presented T_g (Glass transition temperature) between 80 and 90°C as the data of other organosolv lignins in literature [6,13]. About the contaminants, it is possible to see in the DSC curves a low contamination by carbohydrates or polysaccharides, because the presence of these compounds would cause some endothermic peaks, which are characteristic of these polysaccharides, between 200 and 400°C [14].

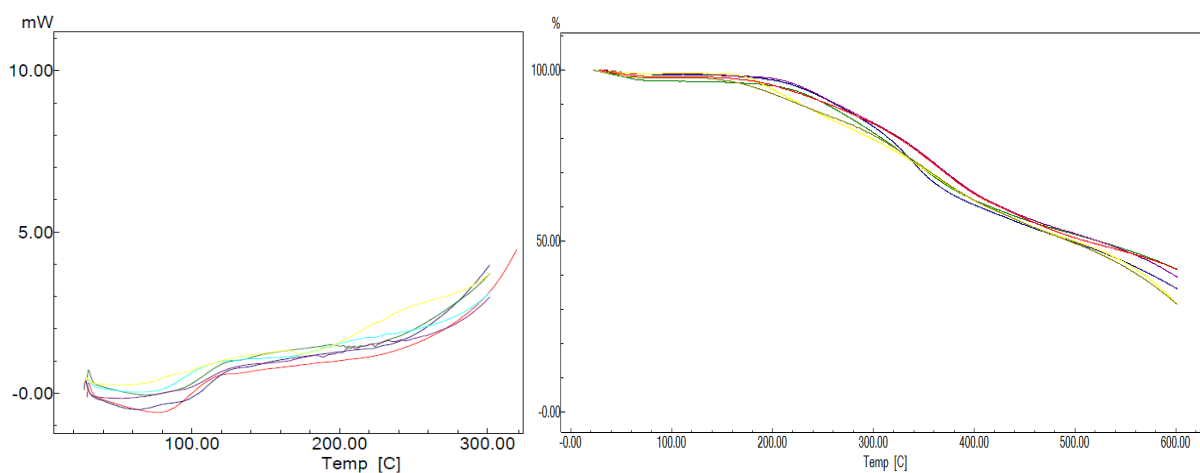


Fig. 4 DSC (left) and TGA (right) curves of the analyzed lignin samples.

It is possible to observe through TGA curve that the samples, besides presenting almost the same decomposition curve (Fig. 4, right curves), showed good thermal stability. Losing less than 6% of mass up to 200°C. The great degradation temperature range obtained in all extractions are the result of the stability supplied by the aromatic rings, besides the absence of contaminants that would result in changes in the curves slope.

As the thermal analysis, the FTIR spectroscopy showed a great similarity between lignin samples, figure (Fig. 5, right spectra) draws attention to it, as we can see spectra with the same peaks and just little differences in transmittance. The most important region to observe the main structures in the obtained lignin samples are between 2000 and 500cm⁻¹. The region in which is situated the major number of functional groups, becoming more evident the similarity between the found lignins in the different extraction conditions. Table 4 is an analysis of the main bands found in all the analyzed samples, based on the literature [15-17].

Therefore, functional groups are pointed for each band in Table 2. When referring to Guaiacyl, Syringyl and p-Hydroxyphenyl it was used G, S and G respectively.

Table 2

Attribution of each FTIR spectra wavelength (cm^{-1}).

Band Position (cm^{-1})	Assignment	Ref. on Fig. 5
1712	Unconjugated Carbonyl in G units	1
1589-1591	Aromatic ring in G and S units	2
1508-1512	Aromatic ring in G and S units	3
1417-1421	C-H stretching in the G and S rings in plane	4
1325-1327	C-O stretching in S units	5
1267	C-O stretching in G units	6
1219-1226	C-C, C-O and C=O stretching in G units	7
1159-1161	C=O stretching in ester grouping	8
1126-1128	Aromatic ring deformation in G unit	9
1091-1095	C-O stretching in secondary alcohols or aliphatic ethers	10
1033-1039	C-O stretching in methoxyl grouping	11
835-839	Deformation out of C-H plane in G and S units	12

Due to the several chromophore groups that exist in the lignin structure, the UV-vis spectra analysis is an important tool to determine the purity and to verify the presence of its major cinnamyl acids [18]. As it can be observed in figure (Fig. 5, left spectra), the curves are according what is expected for this type of organosolv lignin [19]. The highest band in 283nm is relative to conjugated and unconjugated phenolic groups. The second band in 313 nm is attributed to the ferulic acid and p-cumarylics [20] association. All the extractions resulted in absorptivity coefficient higher than 20 mg.cm/L , consequently in great purity of these lignins. Contaminants presence such as poliosis, silica, etc., result in a strong reduction in absorptivity of both band in 280 nm and 313nm [18].

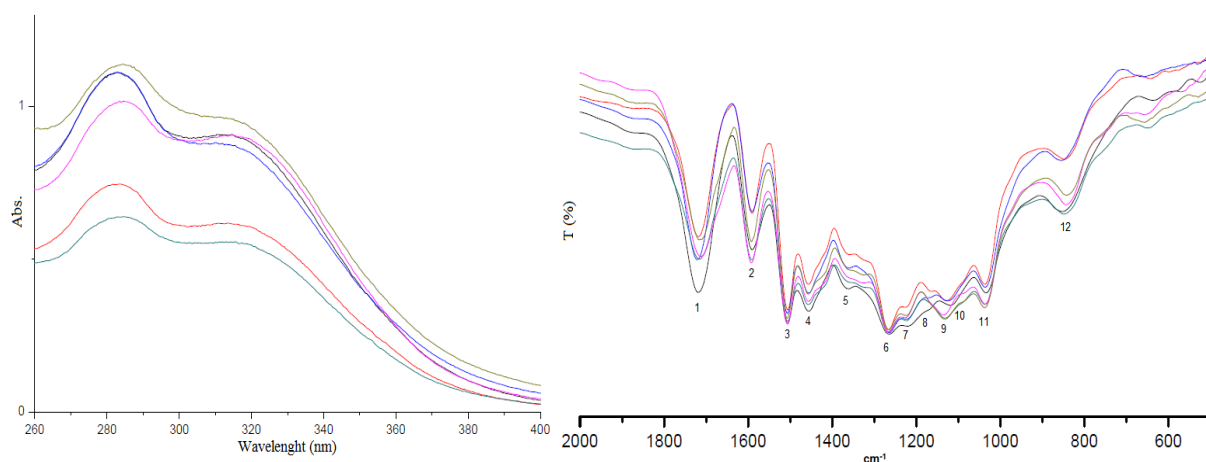


Fig. 5 UV-Vis (Left) and FTIR (Right) spectra of lignin samples, FTIR in the region between 2000 and 500 cm^{-1} .

The chromatograms for the lignin samples presented the same pattern for the retention volume in each sample, with a polydisperse and bimodal curve. Table 3 shows the Mn (number average molecular weight), Mw (weight average molecular weight) and Mw/Mn (polydispersity) values already calculated by the analysis equipment.

Table 3

Results of the average molar mass analyzed for the obtained lignin.

Conditions	Mn (Da)	Mw (Da)	Mw/Mn
75% Et. / 1% cat	1.542	2.599	1.685
75% Et. / 1.5% cat	1.462	2.732	1.869
75% Et. / 3% cat	1.359	2.360	1.737
100% Et. / 1% cat	1.222	2.067	1.691
100% Et. / 1.5% cat	1.160	2.066	1.781
100% Et. / 3% cat	1.107	1.966	1.776

According to the literature, Mn values for wooden organosolv lignin are between 500 and 5000 Da, with polydispersity from 1,5 to 2,35 [6]. Therefore, it is possible to realize that all the values were within the expected for this extraction methodology. The polydispersity value is really close to 1,0 and, therefore, indicated that the cleavages along the extraction and reflux resulted in molar mass compounds very similar for this methodology.

It is possible to see in SEM (Scanning Electron Microscopy) images that the lignin particles accumulated in large conglomerates. The sample images obtained with 75% v/v of ethanol showed spherical structures

more defined than the other extractions. While in the other samples the conglomerates are presented almost as unique structures, in Figure 6, it is possible to see the spherical structures that agglomerated in order to form bigger agglomerations. In other study was suggested that the amount of ethanol present in the extraction liquor can have a fundamental role in the morphology of the lignin obtained [21].

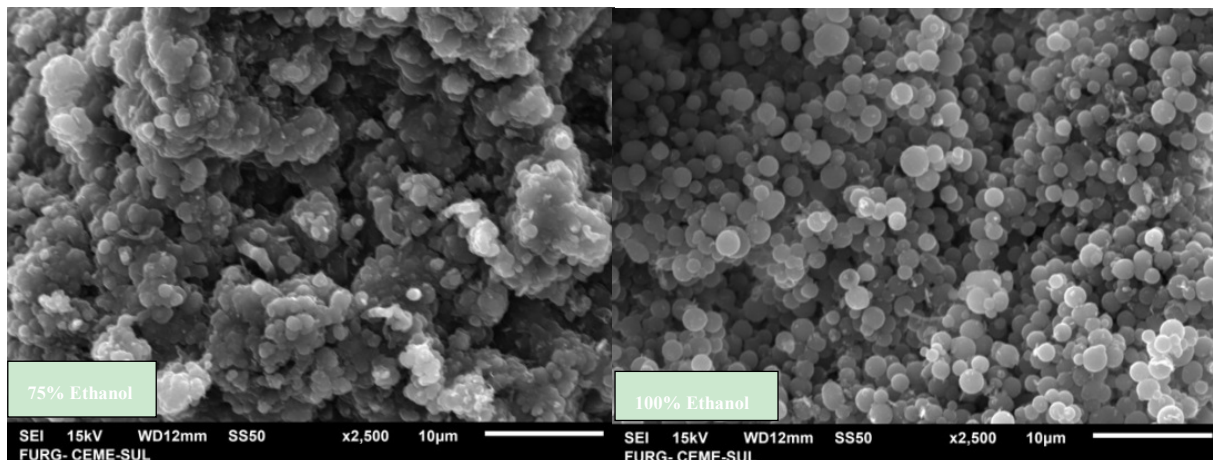


Fig. 6 Scanning electron microscopy image of four lignin samples extracted from rice husk.

4. Conclusion

Even with the limitations imposed by the husk resilience, it was possible to obtain lignin with low presence of contaminants, considering that a modified process with lower temperature and pressure was held. This extraction process can be considered very robust, because the lignins samples showed great similarity, even when were changed the conditions of extractions. The lignin obtained with relative low molar mass and low polydispersity can be used to obtainment of chemical compounds more important for industry, like phenols, benzene and toluene, and this justifies the proposed paper. Last of all, it is important to highlight that the process can be incorporated by industries as a pre-treatment on rice husk.

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