LIGNIN RECOVERY FROM SPENT LIQUORS FROM ETHANOL-WATER FRACTIONATION OF SUGAR CANE BAGASSE

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The aim of the present work was to find the most adequate method of lignin recovery from two spent liquors from ethanol-water fractionations catalyzed with sulfuric acid. Different methodologies to separate lignin from liquors were assessed, based on the dilution and/or evaporation of the solvent. The carbohydrates, organic acids, ethanol and degradation products content of the spent liquors were analyzed by liquid chromatography. The yield of lignin recovery was quantified. The laboratory system, represented at an industrial scale by the reduction of ethanol concentration in the spent liquors through evaporation in a flash tank to 30% v/v, dilution 1:1 at 40 ºC and centrifugation, appeared as the best alternative for lignin recovery (45% of precipitate with a purity of 94%, yielding 42% pure lignin). The second feasible procedure involved lignin precipitation and recovery from the spent liquors by dilution with water, at room temperature. This method yielded 41% pure lignin, from a precipitate of 48% with 87% purity (much more contaminated, mainly with carbohydrates).

Keywords: lignin, recovery, spent liquors, ethanol-water delignification, sugar cane bagasse

INTRODUCTION

Organosolv lignins present potential uses in the manufacture of both phenol-formaldehyde resins (as a source of phenols) and biodegradable polyurethanes. Depending on the final use, the presence of carbohydrates in lignin may be problematic. As a consequence, the recovery of by-products from the spent liquors requires first lignin separation from the dissolved sugars.

Lignin recovery in alkaline organosolv pulping is not usual, because its precipitation is difficult. The process involves lowering of the spent liquor pH to values close to 2, which would require a large consumption of acid for precipitation. On the contrary, in acid organosolv pulping, lignin precipitation is carried out by diluting the spent liquor with water, which decreases the proportion of organic solvent, reducing significantly the solubility of lignin and producing its precipitation. The precipitated lignin corresponds to the fraction of high molecular weight, the other fraction remaining in the spent liquors.

All known recovery systems are based on lignin insolubility in water. One of the proposed systems, based on the dilution of spent liquors in water,[1-3] is characterized by low speeds of lignin removal and, in some cases, by the generation of a very stable colloidal suspension, difficult to filtrate or centrifuge. Another method consists in the recovery of the alcohol from spent liquors in a recovery tower (by vacuum), and subsequent precipitation of lignin in water.[4-5] This procedure is usually ineffective and difficult to control, since lignin tends to precipitate as a sticky tar in the internal surfaces of the recovery tower, fouling it and reducing the effectiveness of alcohol recovery. An alternative approach consists in the evaporation of 60 to 65% of the alcohol

in a flash tank, cooling of the spent liquor to a temperature above 70 ºC (to avoid lignin precipitation in the flash tank),[6] and dilution by injection of liquor in water through a Venturi tube.[7] Another alternative is to use ultrafiltration membranes to allow the recovery of lignin fractions of specific molecular weight, yet at a more expensive recovery.[8-10] The amount of water added to the spent liquor depends on the quantity of water used during fractionation. In all cases, precipitation of solids occurs in a conventional clarifier or in a settling tank. After that, the settled material is concentrated in a conventional centrifuge, forming a humid cake (the content of solids increases from 6-12% to 30-40%), then it is dried to form a uniform powder. In all methodologies, the efficiency of solvent recovery is critical in the general economy of the organosolv process.

Briefly, the recovery of lignin in an acid process consists of the following stages:[11-13]

- Precipitation of the lignin fraction with higher molecular weight;
- Separation of the precipitate by decantation, thickening, centrifugation or filtration;
- Washing with water to reduce impurities;
- Further thickening, to remove the water retained in the washing stage;
- Drying of lignin.

Although numerous papers have been devoted to the characterization of different organosolv lignins, each fractionation process produces spent liquors and lignins of diverse chemical characteristics, molecular weights, etc., representing unique cases. Also, only few articles refer to recovery yields and purities of lignins,[14] known as influencing their recovery costs and final applications.

The objective of our project was to study the technical and economic feasibility of producing unconventional by-products from sugar cane bagasse, using environmentally compatible and economically competitive technologies. In a previous work, we presented results of ethanol-water fractionations of sugar cane bagasse, catalyzed with acetic and sulfuric acids, at temperatures lower than usual.[15] Now, we discuss the methodologies for the separation and recovery of lignin from the spent liquors of the fractionations catalyzed with sulfuric acid. Different recovery techniques, based on dilution and/or evaporation of the liquor to precipitate the residual lignin, and its subsequent settling and removal, were evaluated.

EXPERIMENTAL

Sugar cane bagasse and ethanol were supplied by a local industry (San Javier Sugar Mill, Misiones, Argentina). Bagasse was first wet depithed to break its structure in a Bauer disc refiner, using a plate gap of 0.005 inches (0.13 mm), after which the bagasse pith was removed by screening, with a plate with 2 mm wide slits (Wenmber). Finally, depithed bagasse was centrifuged. Sulfuric acid (A.C.S. reagent grade) was used as a catalyst.

Bagasse delignification was carried out by an organosolv (ethanol-water) process, using a 7 L MK digester (M/K Systems, Inc., Maryland) with liquor circulation. Details on the methodology of bagasse characterization and of ethanol-water fractionations are provided in a previous study.[15] The conditions of fractionation were: 50/50 alcohol-water ratio (% v/v), 0.5 g/L sulfuric acid, maximum temperature: 150 and 160 ºC (F1 and F2, respectively), 30 min up to maximum temperature, 120 min at maximum temperature, 14/1 of liquor/bagasse ratio.

The experimental methodologies of fractionation and characterization of the obtained fractions and products are shown in Figure 1.

The lignin in the spent liquors was quantified by UV (Techcomp 8500 II Spectrophotometer) at 210 nm, on liquor aliquots diluted in ethanol. The lignin absorptivity applied was determined as 78.2 L/g. The values were corrected by subtraction of the absorptivity of furfural, obtained by HPLC. The quantities of carbohydrates, degradation products and organic acids in spent liquors were analyzed.

The purity of the recovered lignin was analyzed by identifying the carbohydrates, ethanol, degradation products and organic acids through HPLC chromatography (Waters Corp. Massachusetts, USA), as well as ashes at 525 °C (TAPPI T211). To quantify the organic impurities, HPLC chromatography was applied after hydrolysis with 3% sulfuric acid, using an AMINEX-HPX87H column, 4 mM H_2SO_4 as eluent, 0.6 mL/min of flow at 35 ºC, and the Refractive Index and Diode Array as detectors. Polyoses were converted into monomers by multiplying by the hydrolysis factor (hexoses to hexosanes: 0.900, pentoses to pentosanes: 0.880, acetic acid to acetyl groups: 0.683).

Lignin separation from the spent liquors was achieved by two basic approaches:

1) Dilution of the spent liquor in water, in mass:

- Method 1: Dilution of the spent liquor in water and centrifugation;
- Method 2: Dilution, flocculation by agitation for 30 min and centrifugation;

2) Ethanol evaporation:
- Method 3: Evaporation to 20% v/v and centrifugation;
- Method 4: Evaporation to 30% v/v + 1:1 dilution and centrifugation;
- Method 5: Evaporation to 30% v/v + 1:1 dilution, flocculation by agitation for 30 min and centrifugation.

The effect of dilution (alcohol:water – 1:1, 1:2 and 1:4) and temperature of treatment (20, 40 and 60 ºC) was sequentially studied for Method 1, the experiments showing better results. The pH of all sequences was 2.8.

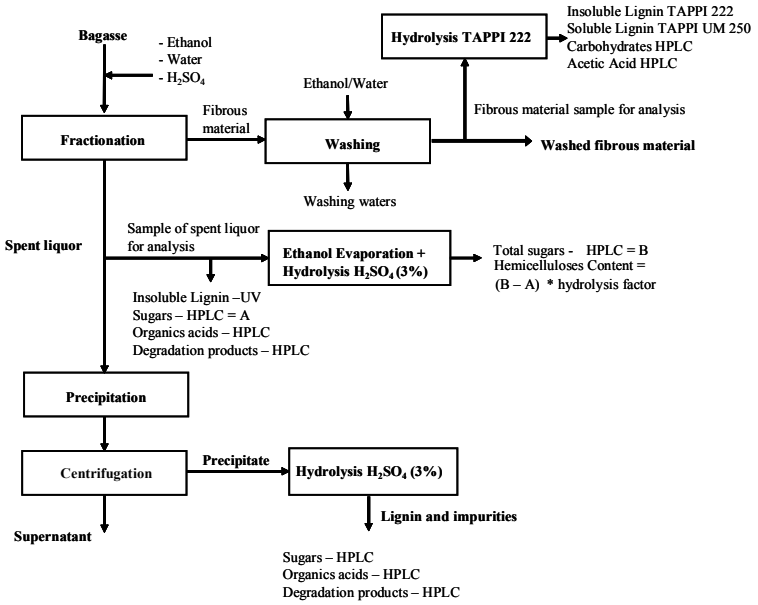

Figure 1: Diagram of the experimental methodologies of fractionation and characterization of the obtained fractions and products

The precipitated lignin was separated by centrifugation (3500 rpm, 15 min) and oven-dried at 105 ºC to constant weight. Percentages were calculated as follows:

- Yield of precipitation (% of precipitate): ratio of the amount of precipitate (g) and the lignin content (g) of the sample (of liquor used in the test) multiplied by 100;
- Purity of precipitated lignin (%): weight ratio of the precipitate free of impurities and the initial precipitate;
- Yield of lignin recovery: product between the precipitate (%) and purity (%), divided by 100.

To verify the influence of washing on the purity of the precipitate, a sequential washing was applied, by washing the precipitates first with 500 mL of water, followed by two other washing steps with 100 mL of water, each for 10 minutes. The precipitates were hydrolyzed and the impurities composition was determined by HPLC.

In some cases, the methods were replicated to verify the experimental errors. The results were statistically analyzed with the Statgraphics software.

RESULTS AND DISCUSSION

The chemical characterization of bagasse is presented in Table 1. Figure 2 shows the layout of fractionations F1 and F2, and the characterization of the different fractions obtained (fibrous material and spent liquor). The stronger conditions of fractionation F2 enhance delignification (10% more lignin in the spent liquor).

The experiments carried out by Method 1, made with spent liquors obtained in fractionation F1, demonstrated that high dilution improves the quantity of precipitate and lignin recovery, even if differences occur within the limit of statistical significance (Table 2).

The highest value was obtained at 1:4 dilution, at room temperature (68%). However, as high dilution may lead to excessive energy costs in the phase of ethanol recovery, a 1:2 ratio, at room temperature, could be an appropriate option (60%).

Table 1
Chemical characterization of bagasse (% o.d.b.)

Alcohol-benzene extractives	2.12
Hot-water solubility	2.73
1% Sodium hydroxide solubility	34.2
Ash at 525 °C	1.53
Total lignin	21.3
Total carbohydrates	70.2
Glucans	43.1
Xylans	23.8
Arabinans	1.66
Acetyls	1.66

% o.d.b.: on oven-dry bagasse

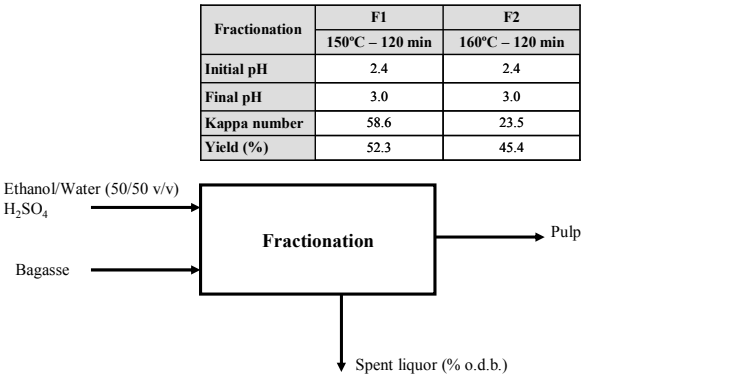

Figure 2: Diagram of fractionations F1 and F2, and characterization of the fractions obtained

Table 2
Lignin recovery by Method 1 using different variables, and impurity composition in precipitates (spent liquor F1)

Dilution-ethanol-temperature*	Precipitate (%)	Purity (%)	Recovered lignin (%)	Carbohydrates (%)**	Formic acid (%)**	Acetic acid (%)**	Ethanol (%)**
1:2-17-20	59.2	88.3	52.3	74.1	1.8	15.2	8.9
1:2-17-20	60.2	86.3	52.0	63.9	1.7	7.4	26.9
1:2-17-20	60.1	86.6	52.1	63.3	2.3	8.6	25.7
1:4-10-20	68.2	80.8	55.1	80.6	1.5	11.8	6.0
1:1-25-40	47.4	90.4	42.8	64.2	4.1	14.1	17.6
1:2-17-40	55.0	87.2	48.0	62.0	1.9	14.0	22.1
1:4-10-40	55.2	85.0	46.9	72.0	1.8	12.6	13.5
1:2-17-60	48.9	91.0	44.5	51.2	3.7	14.8	30.3

* Dilution (liquor:water)-ethanol (%)-temperature (ºC)
** Composition of impurities in precipitates, as percentage of total impurities

A substantial decrease was recorded in the recovered lignin at a dilution ratio of 1:1. Temperature decreased the precipitation and recovered lignin yields, but increased purity. The best results were obtained at room temperature (the mean lignin recovery was improved by 5.8%, by decreasing the dilution temperature from 40 to 20 ºC).

Impurities of the precipitates consisted mainly of carbohydrates (a global mean value of 66%), followed by ethanol (18%), acetic acid (13%) and a minor quantity of

formic acid (2.5%). While the carbohydrate content in impurities decreased slightly with the temperature of the treatment, the ethanol, acetic and formic acids content increased. Dilution had no effect on the composition of impurities. Ashes were not detected.

An experiment was performed at pH = 2.2 (dilution 1:2), yet the quantity of the precipitate was particularly low (43.7%). Even if lignin purity was high (91.0%), the recovered lignin was the lowest value obtained when using this spent liquor and method (39.8%). In the literature, 77.9% lignin recovery by water precipitation has been reported[14] for ethanol-water pulping of *Eucalyptus globulus*, (45% ethanol at 194 ºC for 104 min), after acidification at pH 2.

The methods of lignin recovery applied to the spent liquor from fractionation F2 are shown in Table 3. The yield of precipitation, the purity and the recovered lignin showed significant variations as to the methods and conditions applied ($p = 0.016$, $p = 0.056$ and $p = 0.019$, respectively). Method 1 (dilution 1:4, 20 ºC, pH 2.8) produced the highest precipitate (48%), followed by Method 4 (evaporation to 30% v/v + 1:1 dilution at 40 °C and pH 2.8), with a 45% yield. In contrast, the purity of the precipitate showed the highest value (94%) when using Method 4. Taking into account the precipitation yield and the precipitate purity, the best lignin yield was achieved with Method 4 (42%). At a laboratory scale, this system, representing an alternative for reducing ethanol concentration in the spent liquor by evaporation in a flash tank, followed by dilution in water and settling, has the advantage of a partial recovery of ethanol. The second option, Method 1, with a lignin yield of 41%, stands for the direct dilution of the residual liquor in water and subsequent centrifugation, although the solid fraction is much more contaminated, mainly with carbohydrates.

The impurities of the precipitated of the spent liquor F2 were composed by 60% carbohydrates, 7% acetic acid, 30% ethanol and 3.5% formic acid (global means). Ashes were not detected. The precipitates obtained by Methods 2 and 5 had a lower content of carbohydrates than the others, whereas acetic and formic acids and ethanol did not show any differences as to the applied methods.

A comparison between the precipitation performance of spent liquors F1 and F2 using Methods 1 and 5 (without and with evaporation, respectively), under the same conditions, is shown in Table 4. In both cases, the quantity of the precipitate in the spent liquor of F1 was higher than in that of F2. Lignin yields showed the same behavior. On the contrary, purity did not show significant differences between spent liquors.

Table 3
Lignin recovery by different methods and variables,
and impurity composition in precipitates (spent liquor F2)

Method*	Dilution-ethanol-temperature**	Precipitate (%)	Purity (%)	Recovered lignin (%)	Carbohydrates (%)***	Formic acid (%)***	Acetic acid (%)***	Ethanol (%)***
1	1:4-10-20	47.7	86.8	41.4	66.1	2.4	2.1	29.5
2	1:2-17-40	43.6	93.1	40.6	54.1	4.7	9.7	31.5
2	1:2-17-60	39.7	91.1	36.1	52.6	2.7	2.2	42.6
2	1:2-17-60	39.6	91.4	36.2	57.9	2.7	2.4	37.0
3	- -20- -	44.9	87.6	39.3	65.9	4.9	9.9	19.4
4	1:1-15-40	45.2	93.6	42.3	62.9	2.8	14.0	20.3
5	1:1-15-60	41.5	90.7	37.6	54.9	2.9	2.5	39.8

* Corresponding to the numbers cited in the experimental part
** Dilution (liquor:water)-ethanol (%)-temperature (ºC)
*** Composition of impurities in the precipitates, as percentage of total impurities

Table 4
Comparison of precipitation performance of spent liquors F1 and F2, and impurity composition in precipitates

Method	Liquor	Dilution-ethanol-temperature*	Precipitate (%)	Purity (%)	Recovered lignin (%)	Carbohydrates (%)**	Formic acid (%)**	Acetic acid (%)**	Ethanol (%)**
1	F1	1:4-10-20	68.2	80.8	55.1	80.6	1.5	11.8	6.0
1	F2	1:4-10-20	47.7	86.8	41.4	66.1	2.4	2.1	29.5
5	F1	1:1-15-60	51.3	91.4	46.8	57.1	2.5	13.0	27.4
5	F2	1:1-15-60	41.5	90.7	37.6	54.9	2.9	2.5	39.8

* Dilution (liquor:water)-ethanol (%)-temperature (ºC)
** Composition of the impurities in precipitates, as percentage of total impurities

Table 5
Changes in lignin purity and impurities with sequential washing (spent liquor F2)

	Purity (%)	Carbohydrates (%)*	Formic acid (%)*	Acetic acid (%)*	Ethanol (%)*
Before washing	91.8	49.9	2.0	6.4	41.7
Before washing	92.2	51.3	2.1	6.9	39.6
1° Wash	91.2	54.4	2.8	5.9	37.0
2° Wash	91.1	50.7	2.7	5.8	40.7
3° Wash	92.2	56.4	2.2	6.3	35.1

* Composition of the impurities in precipitates, as percentage of total impurities

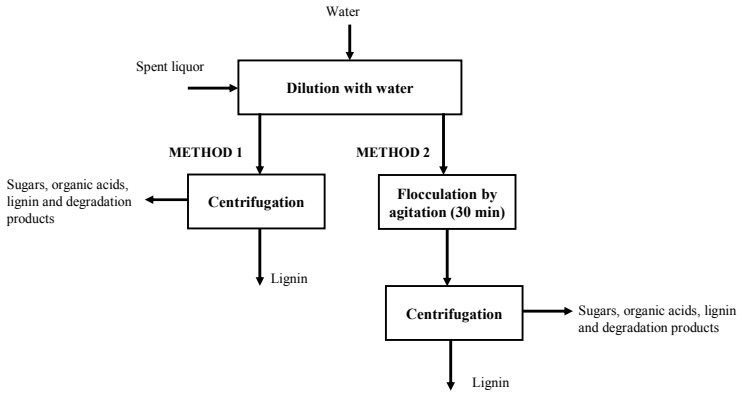

Figure 3: Diagram of Methods 1 and 2 for lignin recovery by mass dilution

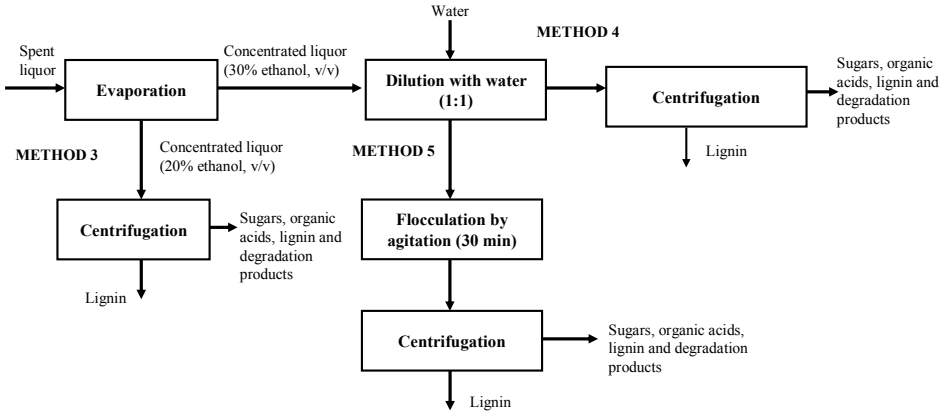

Figure 4: Diagram of Methods 3, 4 and 5 for lignin recovery by gradual dilution of the spent liquor

The carbohydrate and formic acid contents showed no significant differences between the precipitates of both spent liquors, although differences in carbohydrates content under conditions of dilution-ethanol-temperature of dilution – 1:4-10-20 – are noticeably higher in F1 than in F2. A reason may be that, at low fractionation temperatures, the first hydrolyzed fraction is composed of small lignin fragments linked to carbohydrates as lignin-carbohydrate complexes. On the contrary, acetic acid was significantly higher in F1, with a mean value of 12.4% compared to 2.3% of F2 ($p = 0.004$), while ethanol was slightly higher in F2. Figures 3 and 4 summarize the methods applied. Schemes of Methods 1 and 2 for lignin recovery by mass dilution are shown in Figure 3, whereas Methods 3, 4 and 5, based on an initial stage of partial evaporation of the residual ethanol in the liquor, are presented in Figure 4.

The effect of washing on the changes of purity in lignins is presented in Table 5. Sequential washing did not improve lignin purity (differences fall into the experimental error domain), which indicates that sugars should be linked to lignin, forming lignin-carbohydrate complexes.

Based on these results, it was decided that the best method to precipitate lignins from spent liquors involved dilution with water (dilution factor 1:2), at room temperature and pH 2.7. The lignins obtained by this method, under seven different fractionation conditions, were characterized chemically and physico-chemically by High Pressure Liquid Chromatography (HPLC), Fourier Transform-Infrared Spectroscopy (FTIR), UV Spectroscopy, Size-Exclusion Liquid Chromatography (HPSEC), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results are presented in another work.[16]

CONCLUSIONS

The laboratory-scale representation of a system involving the reduction of ethanol concentration in the spent liquors by evaporation in a flash tank to 30% v/v, dilution 1:1, at 40 ºC, and centrifugation, appeared as the best alternative for lignin recovery (45% of precipitate with a purity of 94%, yielding 42% pure lignin).

The second feasible procedure involved lignin precipitation and recovery from the spent liquors by dilution with water, at room temperature. Although the best dilution was 1:4, it is practicable to a dilution ratio of 1:2, as a higher dilution leads to high-energy consumption in the ethanol recovery stage. This method yielded 41% pure lignin, yet from a precipitate of 48% with 87% purity (much more contaminated, mainly with carbohydrates).

The temperature of the treatments affects the recovery process. In both cases, the most suitable dilution conditions involved room temperature or 40 ºC.

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