Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Gilarranz, M. A. , Rodriguez, F. , Oliet, M. and Revenga, J. A.(1998) 'Acid Precipitation and Purification of Wheat Straw Lignin', Separation Science and Technology, 33: 9, 1359 — 1377
To link to this Article: DOI: 10.1080/01496399808544988
URL: http://dx.doi.org/10.1080/01496399808544988

SEPARATION SCIENCE AND TECHNOLOGY, 33(9), pp. 1359–1377, 1998

Acid Precipitation and Purification of Wheat Straw Lignin

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ABSTRACT

The acid precipitation and purification of lignin from wheat straw soda pulping effluent were studied. Prior to lignin precipitation, the suspended solids and dissolved silica were removed from the effluent to avoid lignin contamination. Suspended solids and dissolved silica were removed by centrifugation and selective precipitation at pH 5, respectively. After these treatments, the pH of the effluent was reduced to an optimum pH value of 3.5 with sulfuric acid in order to precipitate lignin. About 80% of the total lignin was recovered. Effluent color and COD were simultaneously reduced by 82 and 71%, respectively. Lignin precipitate purification was carried out by washing with aqueous acidic solutions. Only the time and the agitation rate influenced the washing process. The purity of the lignin was very high when the time and rate of agitation during washing were low. Under optimum conditions, lignin with a purity of 99.5% can be obtained.

INTRODUCTION

Soda and kraft pulps are produced by cooking lignocellulosic raw materials at high temperature in a solution known as white liquor. During the cooking

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process, white liquor dissolves lignin, which allows fiber liberation. At the end of this process, pulp and a highly concentrated solution, composed of organic matter and spent chemicals, are obtained. This solution (black liquor) is usually burned in the recovery furnace in order to produce energy for the mill and to recover the pulping chemicals.

In these mills, pulp production is limited by the amount of black liquor that can be burned in the recovery furnace. Therefore, in mills operating at or above their design capacities, black liquor spills often take place. To reduce biochemical oxygen demand (BOD) of the effluents, biological treatments are used. However, these treatments are not able to eliminate the lignin, and final effluents with high levels of chemical oxygen demand (COD) and intensive color are obtained (1).

In pulp mills using agricultural residues as raw material, the recovery of energy and chemicals is limited by the high silica content of the black liquor, which is often simply discharged (2, 3). The aim of this work is the separation and purification of lignin from wheat straw soda pulping effluents in order to recover this by-product. Also, the treatment allows reduction of both COD and color of the effluent. On the other hand, the lignin separated, which may have many uses (4, 5), could be sold to reduce the operating cost for effluent treatment. The soda pulping effluent was taken from the biological treatment plant.

Ultrafiltration and precipitation are the most commonly used methods to separate lignin from black liquors. Lignin precipitation is usually carried out by adding acids, alcohols, or salts with polyvalent cations. The purity of the lignin obtained will depend on the method used during the removal process.

Ultrafiltration

Ultrafiltration can separate solution components according to their molecular size and shape. In black liquor ultrafiltration, the water and small solute species (inorganic salts, carbohydrates, and low-molecular-weight lignin) pass through the membrane and are collected as permeate, while large solute species, mainly lignin, are retained by the membrane (6). Because lignin has a wide molecular weight distribution, the recovery efficiency will be mainly a function of membrane pore size (7, 8). Therefore, lignin separation involves its fractionation. To improve the lignin recovery efficiency, a multistage operation is usually employed (9). Lignin is obtained as a concentrate reject and is further isolated by other procedures (i.e., acid precipitation).

Precipitation

Due to the low solubility of lignin in acid media, CO_2 and H_2SO_4 can be successfully used to produce the precipitation of kraft lignin from black liquors. These chemicals have a low cost and are compatible with the pulping chemicals recovery system. Other acids, e.g., HCl, would introduce undesirable anions into the process. CO_2, which only allows the pH to be reduced to 8–9, produces a rather low precipitation yield: about 60–80% (2, 10, 11). In addition, CO_2 produces many problems in the following filtration stage because a colloidal precipitate is formed. To avoid these difficulties, some strong acids have been tested (7, 11, 12). Lower values of pH and higher recovery of lignin, up to 95%, can be achieved with these acids. The lignin precipitated with strong acids has also better filterability than lignin separated with CO_2. But in any case, the filtration stage is difficult. To improve the precipitation process, a two-stage process has been suggested (11). The first stage, acidification, is carried out with CO_2 at pH 9, while the second stage is carried out at pH between 2 and 4 with H_2SO_4. When a CO_2-rich flue gas is used, the two-stage method is cheaper than one-stage method with H_2SO_4.

Lignin precipitation with acid in the presence of certain organic solvents which are immiscible with the black liquors has been proposed by several authors (13–15). In these methods the solid precipitate can be easily removed from the mother liquor by filtration. These procedures yield a high purity solid. However, these processes require a high efficiency solvent recovery stage in order to reduce both the solvent cost and the environmental effects, and therefore the investment is remarkably increased.

Salts with polyvalent cations, e.g., $CaSO_4$, can be used to produce the precipitation of lignin as a calcium salt because of its low solubility (16). Although $CaSO_4$ is very inexpensive, the precipitate obtained is a colloid, which gives rise to many problems in the following stage of filtration and a lignin with large amounts of calcium. To precipitate lignin, other chemicals, iron or alumina sulfates and chlorides, in combination with acids or separately have been used (3, 17). In these methods the cations have coagulation effect that improves the final stage of filtration. However, the precipitate contains large amounts of $Fe(OH)_3$ and $Al(OH)_3$ that contaminate the final product.

When alcohols are added to black liquors, precipitation of both lignin and carbohydrates takes place (18). Precipitation yield for these methods increases up to 60% when the alcohol/liquor ratio is 10/1. This process can be improved by employing calcium salts because they reduce both the required alcohol/liquor ratio and the filtration time. Under optimum operating conditions, a precipitation yield of 80% is achieved, but the final lignin contains a large amount of carbohydrates and inorganic contaminants. This method also requires an additional alcohol recovery stage.

Purification

The precipitated lignin usually needs a purification stage before it can be used (4). Acid-precipitated lignin from black liquors retains a substantial amount of mother liquor, including degraded carbohydrates and inorganic salts. For example, the lignin precipitated from kraft black liquor has high levels of organic acids (>1%) even after several purification stages (12). Nevertheless, if lignin comes from an effluent subjected to effective biological treatment, only inorganic contaminants are present in significant quantities.

There are few industrial methods to purify lignin. Some authors have propose that industrial purification of lignin could be carried out by washing with water or acid aqueous solutions (7, 11, 12). Other studies have focused on small-scale procedures: dialysis (19, 20), extraction (21, 22), or ion exchange (23).

If water is used as a washing agent, a considerable loss of lignin, up to 25%, is expected. This loss is due to an increase in the pH of the washing medium, in which part of the lignin is soluble (11). When acid solutions are used in the purification stage, the final lignin is contaminated by the corresponding anion (sulfate or chloride). On the other hand, acid washing allows a higher reduction of lignin sodium content because of the protonation of lignin functional groups associated with this cation (10, 12).

EXPERIMENTAL

Among the above-mentioned techniques, the present work focuses on lignin precipitation with strong acids. This precipitation is carried out in two stages. The first occurs at a medium pH level where separation of dissolved silica takes place. Then, at a lower pH level, the lignin precipitate is obtained. To purify this precipitate, washing with aqueous acidic solutions has been studied. The scheme of the proposed method to obtain high purity lignin is represented in Fig. 1.

Samples of wheat straw soda pulping effluent were employed in this study. Wheat straw is cooked in a sodium hydroxide white liquor (4% w/w). The cooking time and temperature are 150 minutes and 95°C, respectively. After cooking, black liquor is sent to a biological treatment plant (aerobic and anaerobic digestion processes). The characteristics of the effluent employed in the present work are shown in Table 1.

Reagents

All chemicals in the present study were A.C.S. reagent grade from Aldrich.

Procedure

Precipitation and washing runs were carried out in a Jar Test. The experimentation includes assays to study the removal of both the suspended solids and the dissolved silica and the precipitation yield as a function of pH. To

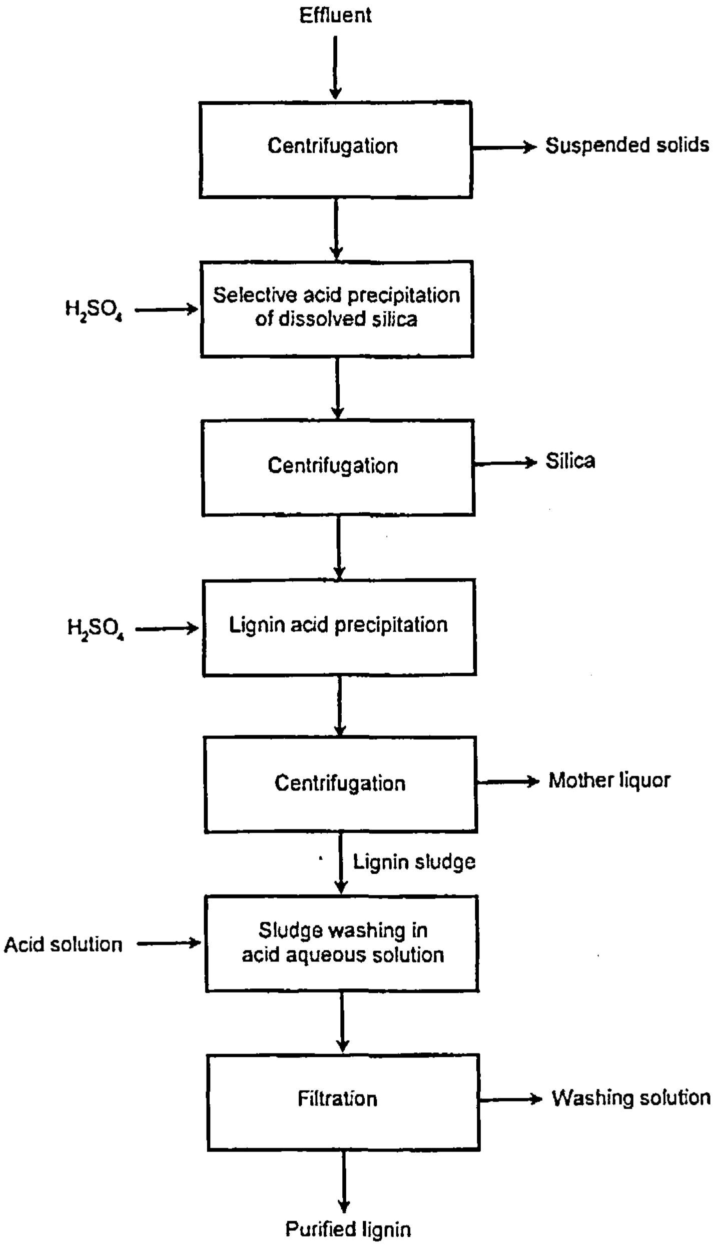

FIG. 1 Scheme of proposed lignin recovery method.

TABLE 1
Effluent Characteristics

pH	8.5
COD	7100 mg/L
BOD	<50 mg/L
Color	25,200 mgPt/L
Dissolved lignin	5.86 g/L
HCO_3	5.11 g/L
Dissolved SiO_2	0.17 g/L
Na^+	2.89 g/L
K^+	0.75 g/L
Ca^{2+}	0.061 g/L
Mg^{2+}	0.042 g/L
Suspended solids	0.36 g/L
Suspended SiO_2	0.22 g/L
Suspended $CaCO_3$	0.12 g/L

improve the lignin purity, a final stage of washing has been also studied. The operating conditions for these studies were as follows.

Removal of Suspended Solids. Two processes, coagulation–flocculation and centrifugation, have been compared. Coagulation–floculation conditions were: cation concentration, 50 ppm; agitation rate, 50 rpm; agitation time, 15 minutes; and sedimentation time, 6 hours. Centrifugation was carried out at 3500 rpm for 10 minutes.

Removal of Dissolved Silica. Precipitation of silica was performed by adjusting the pH of the effluent to the desired value. Then the silica precipitate was separated by centrifugation at 3500 rpm for 10 minutes.

Precipitation Yield. A set of runs was carried out in a pH range of 1.5–8. Precipitation yield was calculated from the difference between the initial lignin concentration in the effluent and the lignin concentration in the mother liquor.

Washing. The lignin precipitate used in the washing runs was obtained by effluent acidification to pH 3.5 with 5 N H_2SO_4 at an agitation rate of 25 rpm. The precipitate was isolated from the mother liquor by centrifugation and washed by resuspending it in the acid aqueous solution. The washed solid was separated by filtration under vacuum using a fritted disk funnel. The vacuum drop in the filtration system was considered as the filtration time end.

To study the factors influence on the washing efficiency, a fractional factorial design containing 2^{6-2} runs was applied. Six factors (X_A, X_B, X_C, X_D, X_E, and X_F) and two levels for each factor were considered, as can be seen

TABLE 2
Factors Studied for the Washing Stage

Factor	Level –	Level +
X_A: Type of acid	HCl	H_2SO_4
X_B: Acid concentration	0.001 N	0.1 N
X_C: Agitation time	5 minutes	20 minutes
X_D: Agitation rate	50 rpm	180 rpm
X_E: Wash solution/lignin ratio[a]	200	400
X_F: Temperature	10°C	30°C

[a] Milliliters of wash solution per gram of lignin.

in Table 2 where the low and high levels are denoted by "–" and "+", respectively. The measured response was the ash content in the washed lignin. The experimental matrix employed and the experimental results are shown in Table 3. Analysis of variance for the experimental results is used to identify the significant effects.

Analysis

Lignin. The concentration of lignin in both the initial effluent and the precipitated mother liquors was determined by UV spectrophotometry at 280

TABLE 3
Experimental Matrix for 2^{6-2} Factorial Design and Ash Content

Run	X_A	X_B	X_C	X_D	X_E	X_F	Treatment combination	Ash content (wt %)
1	–	–	–	–	–	–	(1)	0.54
2	+	–	–	–	+	–	ae	0.80
3	–	+	–	–	+	+	bef	0.40
4	+	+	–	–	–	+	abf	0.52
5	–	–	+	–	+	+	cef	0.72
6	+	–	+	–	–	+	acf	1.14
7	–	+	+	–	–	–	bc	1.00
8	+	+	+	–	+	–	abce	1.16
9	–	–	–	+	–	+	df	0.77
10	+	–	–	+	+	+	adef	0.77
11	–	+	–	+	+	–	bde	0.56
12	+	+	–	+	–	–	abd	0.66
13	–	–	+	+	+	–	cde	1.29
14	+	–	+	+	–	–	acd	1.38
15	–	+	+	+	–	+	bcdf	1.94
16	+	+	+	+	+	+	abcdef	1.67

nm on a Varian Cary1E spectrophotometer. Prior to analysis, samples were dissolved in buffer solution (0.1 M boric acid adjusted to pH 12 with sodium hydroxide). Lignin standards were prepared using a high purity lignin sample obtained from the same effluent. The concentration of lignin (L) was calculated as

$$L\,(\mathrm{mg{\cdot}L^{-1}}) = -0.15 + 56.3Abs \tag{1}$$

where Abs is the absorbance value.

Sodium, Potassium, Calcium, and Magnesium Cations. Lignin solid samples were dissolved in a 0.01 N ammonium hydroxide solution and then diluted with water. Cation concentrations were measured by atomic absorption spectrophotometry on a Varian SpectrAA-100 spectrophotometer. Effluent analysis for these cations was carried out in the same way.

Silica. The silica content was calculated on the basis of SiO_2 after silicon content analysis by atomic absorption spectrophotometry. Samples were prepared in the same way as in the cation analysis.

Ash. Gravimetric determination after calcination at 600°C for 2 hours.

Bicarbonate Anion. The concentration of bicarbonate anion in the effluent was determined from measurement of inorganic carbon on a high temperature TOC analyzer (Rosemont Analytical DC-190).

COD. It was determined according to ASTM (D 1252-88) standard.

Color. The sample was adjusted at pH 7.6 and its color measured by spectrophotometry at 470 nm. K_2PtCl_6 standards were employed in color calibration.

Suspended Solids Content. It was calculated as described by ASTM (D 1888-78) standard.

Calcium Carbonate in Suspended Solids. The suspended solids recovered from effluent were leached with 0.1 N HCl. The carbonate content was determined as the difference between the initial sample weight and the leached sample weight. The procedure was verified by analysis of calcium in the leaching acid by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Removal of Suspended Solids and Soluble Silica

The effluent studied contains substantial amounts of suspended solids, composed mainly of calcium carbonate (33%) and silica (61%). Calcium carbonate is produced during the biological treatment of black pulping liquor whereas silica comes from wheat straw. During the precipitation stage, most of the acid is employed in the neutralization of calcium carbonate and sodium bicarbonate. Simultaneously, CO_2 is given off and persistent foams are formed. On the other hand, suspended silica is retained within the lignin precipitate.

TABLE 4
Removal of Suspended Solids from Effluent

Treatment	Suspended solids removal (%)	Lignin silica content (% w/w)
No treatment	—	5.27
Flocculant: $FeCl_3$	40	3.47
Flocculant: $Fe_2(SO_4)_3$	24	3.97
Flocculant: $AlCl_3$	68	2.27
Flocculant: $Al_2(SO_4)_3$	81	1.77
Centrifugation	100	0.71

Hence, if previous removal of these solids is carried out, the consumption of acid will be reduced and the purity of the final lignin will be increased.

Table 4 shows the silica content for several samples obtained after removal of suspended solids by different methods. From Table 4 it can be seen that centrifugation is able to remove suspended solids completely. The lignin silica content is determined in this case by soluble silica, which coprecipitates with lignin at an acidic pH. The centrifugation of suspended solids reduces the lignin silica content by 87%. The use of several flocculants was also studied. However, the results showed that there was only a low reduction of suspended solids even after a sedimentation time of 6 hours. This time is too long for industrial volumes. Besides, the ashes from lignin obtained with iron flocculants had a red color, which suggests a high retention of iron by the lignin. This retention is due to both the lignin capacity to adsorb cations (24, 25) and the coprecipitation of $Fe(OH)_3$ (17). Although silica from suspended solids is totally removed by centrifugation, when effluent acidulation is carried out to precipitate lignin, dissolved silica coprecipitation still takes place. Therefore, the final solid lignin still has a significant amount of silica.

Dissolved silica can be removed from the effluent by a previous stage of precipitation. A set of runs at different pH values was carried out to reduce the dissolved silica concentration in the effluent. This new stage will improve the lignin purity. Results from these experiments are shown in Fig. 2. According to these results, silica precipitates effectively at pH 5 without lignin coprecipitation, so the lignin subsequently precipitated has a low silica content. With this procedure, the amount of dissolved silica that coprecipitates with lignin is reduced by 58%. However, if the pH is lower than 5, a significant precipitation of lignin takes place during the dissolved silica removal stage, and the final lignin recovered from the treated effluent has a higher silica content.

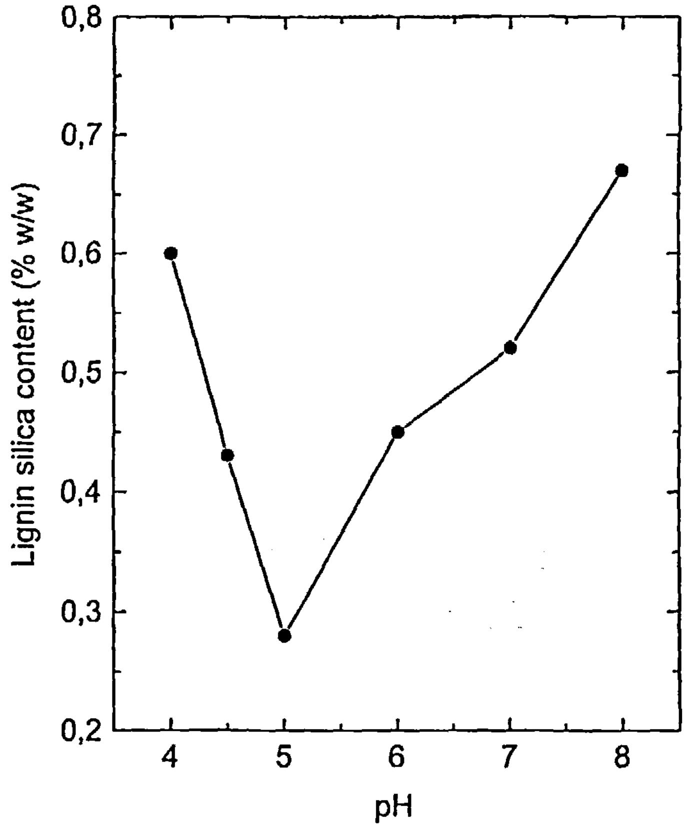

FIG. 2 Results of dissolved-silica removal stage at different pH values.

Precipitation Yield

The effluent pH (8.5) is lower than the black liquor pH. This is due to the process of carbonation that takes place during aerobic digestion of the black liquor. Because of this, the pH cannot be reduced with CO_2, and the use of strong acids is required.

As can be seen in Fig. 3, the precipitation yield and acid consumption depend on the pH. From this figure an optimum pH value, close to 3.5, can be selected for this stage. This value causes a high precipitation yield with moderate acid consumption (around 80% and 100 mEq/l, respectively). Because a fraction of the lignin is soluble in acid medium even at pH 1.5, lignin precipitation is not complete. When the pH value is lower than 3.5, the precipitation yield is only slightly increased, whereas acid consumption increases dramatically. The percentage of acid-soluble lignin is higher than in kraft black liquor precipitation, where around 95% of the initial lignin present in the black liquor can be precipitated at pH 4 (3, 7). Most of the added acid is consumed during the neutralization of dissolved sodium bicarbonate.

Figure 4 shows the relationship between color and COD of mother liquor and lignin precipitation yield. Because both color and COD are mainly due to dissolved lignin, the relationship is almost linear for these variables. The color and COD are reduced by 82 and 71%, respectively, when a 78% precipitation yield is reached (pH 3.5).

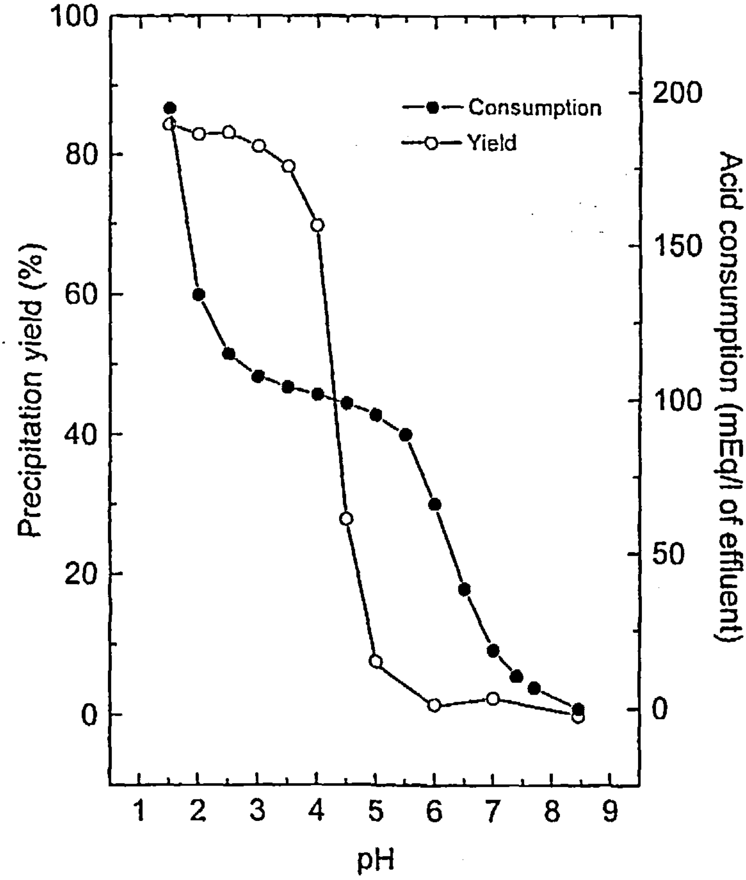

FIG. 3 Precipitation yield vs pH.

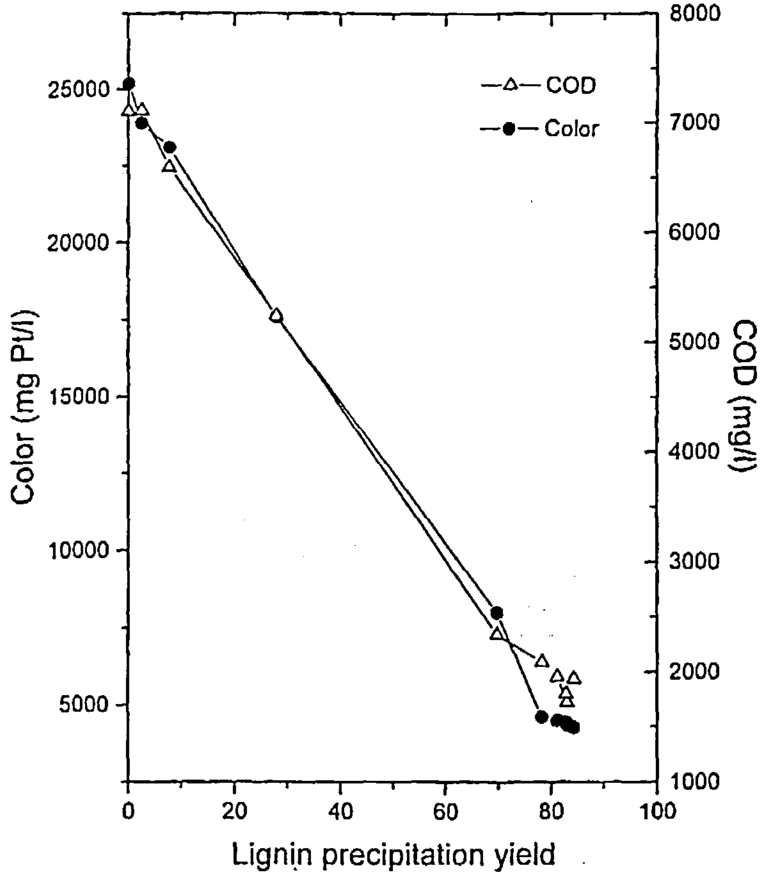

FIG. 4 Color and COD of mother liquor vs lignin precipitation yield.

Lignin Washing

Design of Experiments

Experimental results for fractional factorial design are shown in Table 3. Table 5 summarizes the analysis of variance for the experiments. The model sum of squares is 2.8971, and this accounts for over 99% of the total variability in ash content. F_0 distribution for effects indicates that the significant effects are: C, D, AE + BC + DF, and BF + CD. Therefore, only the main effects of rate and time of agitation have a significant influence on the ash content of washed lignin. Both variables have an unfavorable effect. An increase of

15 minutes in the agitation time or 130 rpm in the agitation rate produces an increase in ash content of 69 and 36% (based on average lignin ash content), respectively.

The operating levels for the remaining variables were chosen depending on economic and operating factors. Thus, the selected acid, H_2SO_4, is less expensive and corrosive than HCl. A wash solution/lignin ratio of 200 mL/g and an acid concentration of 0.001 N were established in order to reduce the consumption of chemicals. The process can be carried out at room temperature. Once the variables that have the greatest influence on the washing process (time and agitation rate) were established, a set of runs was carried out in order to study their respective effects.

Experimental Study of Variables Effect

The effect of time and agitation rate on the ash content of the washed lignin is shown in Fig. 5. The ash content increases as the sludge disintegration increases, which is proportional to time and agitation rate. The agitation time has only a slight influence on the response when the agitation rate is 25 rpm. The consistency of the filter cake is also affected by the time and agitation rate as shown in Fig. 6; the less intensive the disintegration, the lower the

TABLE 5
Effects and Analysis of Variance for Washing Results

Effect	Effect value[a]	Sum of squares	Degrees of freedom	Mean square	F_0
A	0.110	0.04840	1	0.04840	6.20
B	0.063	0.01563	1	0.01563	2.00
C	0.660	1.74240	1	1.74240	223.03
D	0.345	0.47610	1	0.47610	60.94
E	−0.073	0.02103	1	0.02103	2.69
F	0.068	0.01823	1	0.01823	2.33
AB + CE	−0.083	0.02723	1	0.02723	3.48
AC + BE	−0.010	0.00040	1	0.00040	0.05
AD + EF	−0.130	0.06760	1	0.06760	8.65
AE + BC + DF	0.248	0.24503	1	0.24503	31.36
AF + DE	−0.043	0.00723	1	0.00723	0.92
BD + CF	0.093	0.03423	1	0.03423	4.38
BF + CD	0.220	0.19360	1	0.19360	24.78
Total error		0.01563	2	0.00781	
Total		2.91270	15		

[a] 95% confidence level: ±0.044 (basis on % ash content); average ash content value for experimental runs: 0.96% ash content.

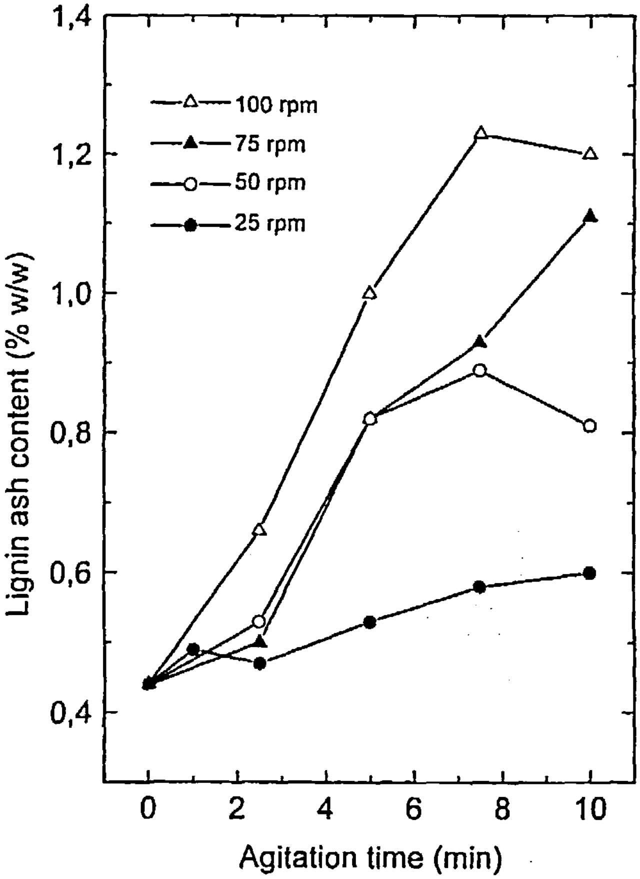

FIG. 5 Ash content of washed lignin vs agitation time at different agitation rates.

cake consistency. The amount of wash solution retained in the filter cake is large for sludge samples washed at poor disintegration conditions. However, the ash content of these samples is very low. From these results it can be deduced that the salt concentration of the wash solution remaining in the filter cake is lower. At these moderate disintegration conditions the amount of salts passing from the sludge to the wash solution is low. In the subsequent filtration the less concentrated wash solution elutes salts from the cake. The ash content of lignin cake is then determined by the low salts concentration of retained wash solution.

To sum up, the washing procedure takes place in two ways: by dilution during sludge resuspension and by elution during the lignin recovery stage by filtration. When the disintegration is very low ($t < 5$ minutes, $\omega = 25$ rpm) the washing process takes place mainly by elution, so the ash content of the washed sample is low and nearly identical to the value for samples washed without agitation (no sludge disintegration), which can only be washed by elution.

As shown in Fig. 7, the filtration time of washed lignin drops as the time and agitation rate are reduced (low sludge disintegration). This is a result of the higher sludge particle size (26). For samples washed at 25 rpm for 1–3 minutes, a minimum value of filtration time is reached (35 minutes).

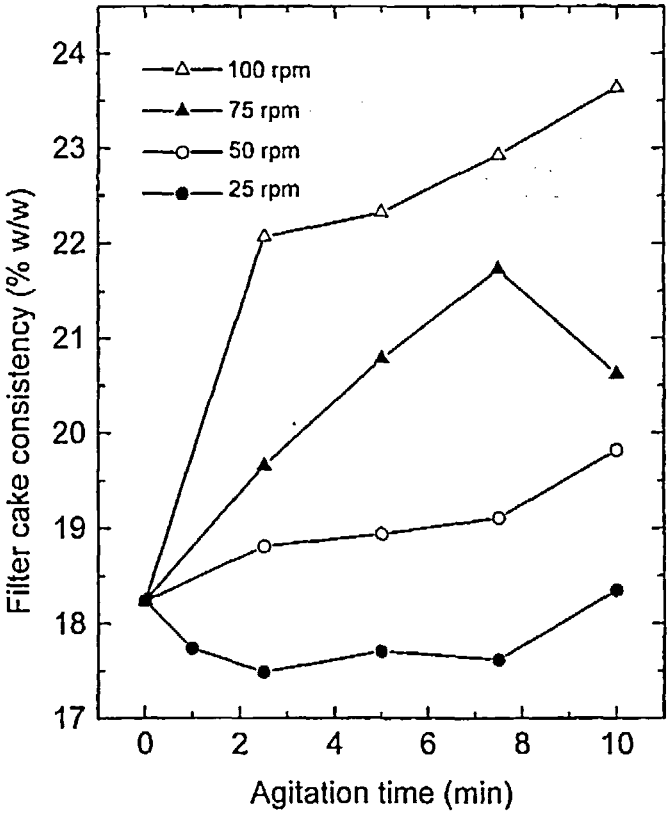

FIG. 6 Filter cake consistency vs agitation time at different agitation rates.

Table 6 shows the salts content of unwashed and washed lignin. A single washing stage carried out at optimum conditions (25 rpm and 2.5 minutes) reduces the ash content from 14.1 to 0.47% and the sodium content from 9.23 to 0.06%. Uloth and Wearing (7) and Loufti et al. (10) reported a reduction of sodium content from 10.5 to 3.7% after one wash with 1 N H_2SO_4, and to 1.35% after two washes with 1 N H_2SO_4, using 4.5 L of wash solution per kg of lignin. Kim et al. (12) obtained lignin with a sodium content of 0.03% using 30 mL of 0.01 N H_2SO_4 wash solution per g of lignin, but they needed a reprecipitation stage and 4 washes. The current work shows that to attain a high purity lignin in a single washing stage, both high volumes of wash solution (200 mL/g) and optimization of the variables are required. The divalent cation/monovalent cation ratio in the solid lignin sample is higher than

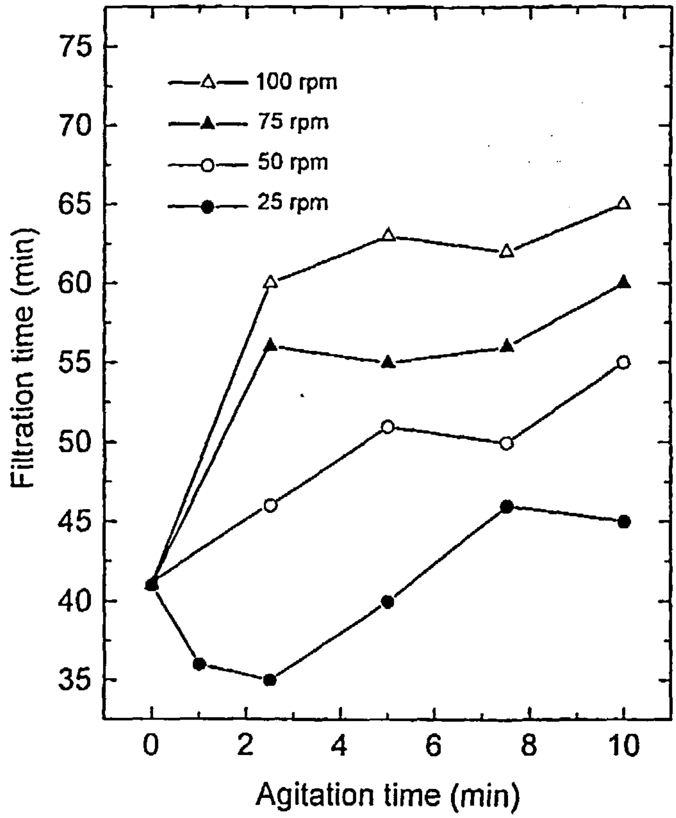

FIG. 7 Filtration time vs agitation time at different agitation rates.

TABLE 6
Comparison of Unwashed Lignin vs Washed Lignin

Species (% w/w)	Unwashed lignin	Washed lignin
Ash content	14.1	0.47
Silica	0.28	0.18
Sodium	9.23	0.057
Potassium	2.05	0.018
Calcium	0.39	0.011
Magnesium	0.09	0.007

in the effluent. This fact is due to the above-mentioned capacity of lignin to retain polyvalent cations (24, 25).

CONCLUSIONS

To improve the purity of lignin recovered from wheat straw soda pulping effluent, a pretreatment of the effluent for removal of both suspended solids and dissolved silica is proposed. Results show that centrifugation is the best way to eliminate suspended solids. An 87% reduction on the silica content of the lignin is attained when this technique is used. Dissolved silica is removed by precipitation at pH 5.0 prior to lignin precipitation, which allows a reduction up to 58% of the dissolved silica that coprecipitates with the lignin. Therefore, if suspended solids and dissolved silica are removed, the total reduction of lignin silica content is around 95%. Up to 80% of the total lignin can be precipitated in acid media in a single stage at pH 3.5 with a low consumption of acid (around 100 mEq/L). Under these conditions, 82% of color and 71% of COD are also removed.

Statistical design of experiments applied to lignin purification shows that only agitation rate and agitation time have a significant influence on the washing process. The ash content is remarkably reduced during washing when the above-mentioned variables are at low values. Under these conditions the lignin washing process takes place mainly by salt elution during the filtration stage. When the operating conditions are 25 rpm and 2–3 minutes, the ash content is very low (0.47%) and a minimum filtration time is achieved (35 minutes). Using the proposed method, lignin with a purity up to 99.5% can be obtained.

REFERENCES

1. S. B. Deshmukh and C. V. Deshponde, "Alkali Lignin Removal by Unconventional Method," *Indian J. Environ. Health*, *28*(4), 342–344 (1986).

2. J. S. M. Venter and G. H. Van der Klashorst, "The Recovery of By-products and Pulping Chemicals from Industrial Soda Bagasse Spent Liquors," in *Tappi Environmental Conference*, Portland, 1987.
3. Z. Zhiliang, Y. Jinquan, Z. Xiangji, and M. Qiang, "A Study of Chemical Treatment of Straw Pulp Effluent Black Liquor," *Water Treat.*, *7*(3), 347–354 (1992).
4. R. A. Northey, "Low-Cost Uses of Lignin," *ACS Symp. Ser.*, *476*, 146–175 (1992).
5. J. H. Lora, C. F. Wu, E. K. Pye, and J. J. Balatinecz, Lignin Properties and Methods, *American Chemical Society*, 1989, pp. 312–323.
6. A. G. Kirkman, J. S. Gratzl, and L. L. Edwards, "Kraft Lignin Recovery by Ultrafiltration: Economic Feasibility and Impact on the Kraft Recovery System," *Tappi J.*, *69*(4), 110–114 (1986).
7. V. C. Uloth and J. T. Wearing, "Kraft Lignin Recovery: Acid Precipitation Versus Ultrafiltration," *Pulp Paper Can.*, *90*(9), 67–71 (1989).
8. D. L. Woerner and J. L. McCarthy, "Ultrafiltration of Kraft Black Liquor," *AIChE Symp. Ser.*, *80*(232), 25–33 (1984).
9. S. S. Kulkarni, E. W. Funk, and N. N. Li, *Membrane Handbook*, Van Nostrand Reinhold, New York, NY, 1992.
10. H. Loufti, B. Blackwell, and V. Uloth, "Lignin Recovery from Kraft Black Liquor: Preliminary Process Design," *Tappi J.*, *74*(1), 203–210 (1991).
11. R. Alen, P. Patja, and E. Sjöstrom, "Carbon Dioxide Precipitation of Lignin from Pine Kraft Black Liquor," *Tappi*, *62*(11), 108–110 (1979).
12. H. Kim, M. K. Hill, and A. L. Fricke, "Preparation of Kraft Lignin from Black Liquor," *Tappi J.*, *70*(12), 112–116 (1987).
13. M. Neyman, W. R. Brown, K. R. Kurple, and E. J. Fritz, "Antisolvent Extraction of Lignin," *AIChE Symp. Ser.*, *246*, 20–31 (1985).
14. D. M. Whalen, "A Simple Method for Precipitating Easily Filterable Acid Lignin from Kraft Black Liquor," *Tappi*, *58*(5), 110–112 (1975).
15. K. R. Kurple, *Separation of Kraft Lignin from Kraft Black Liquor*, Report to the US Department of Energy, DOE/CE/15193-T1, 1988.
16. S. B. Deshmukh and C. V. Deshpande, "Alkali Lignin Removal by Unconventional Method," *Indian J. Environ. Health*, *28*(4), 342–344 (1986).
17. Z. Xiaohua, T. Huiling, and H. Qionghua, "Treating Alkaline Straw Pulp Black Liquor by Coagulation and Adsorption," *Water Treat.*, *6*(4), 461–464 (1991).
18. J. C. Villar, A. Caperos, and F. García-Ochoa, "Precipitation of Kraft Black Liquors by Alcohol-Calcium Solutions," *Sep. Sci. Technol.*, *31*(12), 1721–1739 (1996).
19. K. H. Ekman, "Retention by Lignins of Sulphur from Sulfate Liquors," *Pap. Timber*, *48*(6), 575–578 (1966).
20. R. F. Buchholz, J. A. Neal, and J. L. McCarthy, "Some Properties of Paucidisperse Gymnosperm Lignin Sulfonates of Different Molecular Weights," *J. Wood Chem. Technol.*, *12*(4), 447–469 (1992).
21. J. Marton and T. Marton, "Molecular Weight of Kraft Lignin," *Tappi*, *47*(8), 471–476 (1964).
22. R. D. McElroy and K. Lai, "Fractionation, Purification, IR, ^{1}H NMR, ^{13}C NMR Spectra and Property Studies of an Industrial Based Sludge Lignin," *J. Wood Chem. Technol.* *8*(3), 361–378 (1988).
23. G. Almendros, A. T. Martínez, A. E. González, F. J. González-Vila, R. Fründ, and H. D. Lüdemann, "CPMAS ^{13}C NMR Study of Lignin Preparations from Wheat Straw Transformed by Five Lignocellulose-Degrading Fungi," *J. Agric. Food Chem.*, *40*, 1297–1302 (1992).

24. F. Kulik, J. Wieber, B. Pethica, and P. Zuman, "Binding of Copper(II) and Zinc(II) Ions on Various Lignins," *J. Electroanal. Chem.*, *214*, 331–342 (1986).
25. M. K. Hill, *Ultrafiltration of Kraft Black Liquor. Phase I*, Report to the US Department of Energy, US Department of Energy Contract DE-ACO2-82CE40606, 1985.
26. O. Söhnel and J. Garside, *Precipitation*, Butterworth-Heinemann, Oxford, 1992.

Received by editor May 15, 1997
Revision received August 1997