

Characterization of the Acidified Liquors from Bamboo (*Bambusa procera acher*) Black Liquors

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The sulphuric acid precipitation of lignin and silica was carried out with laboratory made black liquors from soda and kraft pulping of bamboo (*Bambusa procera acher*). The chemical composition of the acidified liquors was analyzed with respect to their main organic and inorganic constituents. It was found that 53-58 % of the original lignin and 77-82 % of the original silica were precipitated at pH 7, whereas the yield of precipitated lignin was 75-78 % at pH 2. Small differences in the yield of precipitated lignin between the various black liquors could be explained by the difference in Mw of the corresponding lignins: for soda lignin Mw was about 3300 Da (higher yield) and for kraft lignin about 2500 (lower yield). In pH range 2-11, the overall loss of volatile acids and non-volatile acids were 2-8 % and 1-13 %, respectively, and the corresponding loss of sodium was 2-6 %. In addition, the content of non-lignin contaminants in the lignin precipitates was evaluated with particular emphasis on carbohydrates, aliphatic carboxylic acids, and ash.

INTRODUCTION

The organic content of black liquors obtained from the alkaline cooking of wood and non wood materials represents 60-70% of the black liquor dry solids and consists mainly of lignin degradation products, polysaccharide-derived aliphatic carboxylic acids, and soluble polysaccharides (1), (2). The inorganic matter in the black liquor consists of sodium and sulfur together with smaller amounts of potassium and other metals. These elements are either bound to organics or are present in the form of various inorganic salts. In addition, in the case of non-wood black liquors a prominent amount of silicon (mainly as silica, i.e., silicon dioxide) may be present.

In modern mills black liquor is burned after evaporation to recover cooking chemicals and energy, while in many small, non-wood-utilizing mills it is often discharged into recipient waters after pretreatment to reduce the pollution load (3, 4). In the former case, many mills face the problem of overloading the recovery system because they operate at or above their designed recovery furnace capacity (5, 6). In the latter case, it is difficult to comply with environmental protection regulations, mainly because of the presence of

lignin-type materials in effluents. Lignin removal from black liquor prior to its further processing is a potential solution to both these problems. Removing some of the lignin from the black liquor reduces the amount of heat produced by the recovery boiler thereby allowing pulp production to be increased without exceeding the maximum load on the recovery furnace (5, 7-9). In the latter case, it should be pointed out that removal of lignin (especially its high-molecular-mass fraction) results in a significant decrease in COD and color, and renders the black liquor more amenable to biodegradation (10, 11). In addition, kraft and alkali lignins recovered can be considered valuable by-products of alkaline delignification.

The polymeric lignin fraction can be precipitated from black liquor more or less completely by acidification (12). Neutralization of phenolic hydroxyl groups in lignin occurs in the pH range 9-11, resulting in the highest proportion of lignin removal. A further lowering of the pH to about 2 additionally liberates the carboxylic groups (pK_a 3-5), allowing more lignin to be precipitated. The liquor is usually heated to overcome the filtration difficulties encountered at lower temperatures. The recovery of lignin from black liquor by acid

precipitation has been widely studied and nowadays, in kraft mills, precipitation of lignin by carbon dioxide and sulfuric acid are the most widely used methods (5, 13).

It is well known that problems in chemical recovery system are encountered in treating black liquors from silica-rich raw materials, such as straw, bamboo, bagasse, and other grasses (14, 15). In such cases, in addition to lignin, acidification simultaneously causes the effective precipitation of silica from these black liquors. This dual benefit would be of great interest for modern non-wood pulp mills that wish, for example, to unload their recovery units when expanding pulp production or producing a lower kappa number pulp and simultaneously to solve silica problems.

In spite of the long tradition of research dealing with the acid precipitation of alkaline lignin, the data available on the changes occurring in the chemical composition of the acidified black liquor remain limited, especially concerning to nonwood black liquors. Our previous study (2) focused on the detailed characterization of bamboo black liquors. The objective of this study was to investigate the changes in the chemical composition of bamboo soda and kraft black liquors that take place during acidification with sulfuric acid. Furthermore, the main constituents of the precipitates formed during acidification were also studied.

EXPERIMENTAL

Black Liquor samples

Black liquor samples were prepared by conventional soda and kraft pulping of air-dried bamboo

(*Bambusa procera acher*) chips in a laboratory-scale digester (16). The black liquors were separated from the pulps by pressing and were stored in a freezer prior to the acidification experiments. The cooking conditions and results are presented in Table 1. The composition and some properties of the black liquors are shown in Tables 2 and 3.

Acidification of black liquors

Acidification was carried out to the pH levels of 7-11 with 1 M H₂SO₄ and to pH 2 with 2 M H₂SO₄ at 80°C. In each case, the retention time was 10 min after the desired pH value was reached. The precipitate was separated from the liquid phase by centrifuging at 3000 rpm (30 min) and washed with dilute H₂SO₄ (pH 3). After washing, the precipitate was air-dried at 50°C and finally homogenized by grinding gently in a porcelain mortar before further analysis.

Analysis of liquors

The yield of precipitated lignin was calculated as the difference between the lignin concentration in the black liquor before and after precipitation, taking into account the change in liquor volume during precipitation (2-9 %). Lignin content was determined according to procedure described elsewhere 2 . The absorptivity values of 26.0 and 27.8 l/g.cm were obtained for the soda and kraft lignins, respectively.

The molecular-mass distribution of the dissolved lignin in the black liquor was determined by gel permeation chromatography using a photo diode array detector (GPC/PAD). A Superdex 75 gel column (470 mm x 10 mm I.D.) was used for separation of lignin fragments. The eluent was 0.1 M NaOH solution at a flow rate of 0.3 ml/min. The

Table 1 : Cooking data on soda and kraft pulping of bamboo

Parameter	Soda	Kraft 1	Kraft 2
Cooking conditions*			
EA, % on o.d. bamboo (as NaOH)	20	16	16
Sulfidity, %	0	25	45
H-factor	1640	930	930
Cooking results			
Yield, % on o.d. bamboo	49.2	51.7	51.9
Kappa number	28.2	21.0	18.1
Viscosity, ml/g	1030	1280	1330
* Liquor-to-bamboo ratio 4l/kg and time to maximum temperature (165°C) 85 min.			

Table 2 : Chemical composition and some characteristics of the black liquors

Parameter	Soda	Kraft 1	Kraft 2
Constituent (g/l)			
Organics			
Lignin	58.4	58.9	62.1
Hydroxy carboxylic acids	26.2	21.0	21.0
Formic acid	6.4	5.8	6.2
Acetic acid	5.8	5.6	5.8
Inorganics			
Sodium	25.7	25.3	27.2
Potassium	1.8	1.8	1.9
Sulfur	0.0	3.7	7.7
Silicon as silica (SiO ₂)	1.7	1.6	1.5
Property			
Dry solids, %	14.2	14.0	14.8
Density, g/dm ³	1.06	1.06	1.06
Residual alkali, g/l (as NaOH)	7.2	2.5	1.7
pH	13.3	12.6	12.5

Table 3 : Average molecular masses (Da) and polydispersity of the dissolved lignin in black liquors

Parameter*	Soda	Kraft 1	Kraft 2
M _w	3290	2680	2350
M _n	520	550	560
Polydispersity*	6.3	4.8	4.2
M _w weight average molecular mass, M _n number average molecular mass, and polydispersity M _w /M _n			

calculation of molecular masses was based on a calibration curve in which proteins were used as standards in the high-molecular-mass range and lignin-like mono- and oligomers in the low-molecular-mass range (17).

The aliphatic carboxylic acids (formic and acetic acids and hydroxy monocarboxylic and dicarboxylic acids) were determined according to procedures described elsewhere (18,19). The acidified liquors were neutralized with 0.1 M NaOH before analysis. The yield of precipitated silica was calculated from the silica concentration (based on the silicon measurement) in the black liquor and in the precipitates.

The silicon content of the black liquor was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For this analysis,

the black liquor was first dried at 105°C and then ground into fine powder, which finally (ca. 0.4 g) was digested in a closed polytetrafluoroethylene (PTFE) vessel in a CEM Mars-5 microwave oven in the presence of a mixture of concentrated acids HNO₃-HCl-HF (volumes 2.5, 7.5, and 1.0 ml, respectively) (20). The digested sample was diluted with ultrapure water for the ICP-AES analysis.

Sodium and potassium content were determined by a flame photometer (Radiometer Copenhagen FLM3).

Sulfur content was determined by an energy dispersive X-ray fluorescence analyzer (Metorex X-MET 920XRT) (21). Dry solids content and density were determined (according to the standard test methods TAPPI T 650 om-99 and TAPPI T 625 cm-85, respectively). Residual alkali was determined according to standard test method SCAN-N 33:94.

Analysis of precipitates

Carbohydrate content was determined after their total acid hydrolysis with sulfuric acid (TAPPI 249 cm-00) and the resulting monosaccharides were analyzed as their per (trimethylsilyl)ated derivatives by gas chromatography/flame-ionisation detection (GC/FID) (22).

Silicon content was determined by ICP-AES. The dried powdered precipitate was treated and analyzed in a way identical to that of the dried powdered black liquor. Ash content was determined

Table 4 : Lignin content in the acidified liquors at different pHs (g/l)*

pH	Soda	Kraft 1	Kraft 2
11	57.2	10	42.4
10	42.4	44.7	47.4
9	32.1	34.0	36.6
8	27.5	29.4	31.7
7	24.4	26.9	29.1
2	12.7	13.7	15.8

* For the initial values, see Table 2.

at 700°C.

RESULTS AND DISCUSSION

Lignin

Fig. 1 illustrates the yield of precipitated lignin when the bamboo soda and kraft black liquors were acidified to pH 7. Lignin yield increased with the decrease in pH. This result resembles earlier findings about wood, bagasse, and wheat straw black liquors (5, 6), (23-25). At pH (8), (49-53)% of the original lignin was precipitated and further acidification to pH 2 increased the yield to 75-78 %. However, these yields were relatively low compared to those of earlier studies on softwood and hardwood black liquors (5, 6), (8), (23, 26) but were at the same level as those obtained with bagasse black liquor (24). One of the possible reasons for the low yield was the low dry solids content (14-15 %) before acidification of the black liquors in our experiments. Another possible reason was the lower molecular mass of the dissolved lignin in the bamboo black liquors (M_w 2300-3300 Da, Table 3) compared to that in wood black liquors (M_w 3500-3600 Da for softwood and 3300-3400 Da for hardwood) separately measured in our laboratory.

The yield of precipitated lignin was decreased in the following order (Fig. 1) soda black liquor-kraft black liquor (25 % sulfidity, kraft I)-kraft black liquor (45 % sulfidity, kraft 2). The main reason for these mutual differences was considered to be the differences in lignin molecular masses (Table 3) caused by the degrading influence of hydrogen sulfide ions (HS^-) on native lignin (12). Thus, it was concluded that lignin with higher molecular mass is more easily precipitated compared to lignin with lower molecular mass.

The lignin content of the acidified liquors is shown in Table 4.

Silica

Fig. 2 shows the yield of precipitated silica when black liquors were acidified to pH 7. Within this pH range silica yield increased as the pH of the black liquor decreased and this finding is also consistent with the precipitation mechanism described elsewhere (27). The silica concentration in the original black liquors was quite low (1.5-1.7 g/l, Table 2) compared to that (3.0-12.3 g/l) in black liquors obtained from other bamboo species as well as other non-wood materials (14), (28, 29). This probably explained the low silica yield (61-70 % at pH 9) in our experiments compared to the yields (85-95 %) obtained in pilot and commercial scale studies using the carbonation technique for different non-wood silica-rich black liquors (29). Iler (27) has pointed out that the rate of aggregation of silica particles, which indicates the rate of deposition of silica from aqueous solution increases rapidly along with silica concentration. The carbonation technique used in black liquor desilication has also shown a very high removal of silica in liquors with a high concentration of silica (29).

It was observed that at pH 2 almost all the silica remained in the filtrate. This phenomenon occurred due to the polymerization of silicic acid and the formation of silica gel was very slow at pH 2 (27). For these reasons, the precipitation of silica from aqueous solution proceeded very slowly at this pH compared to that at a pH above 7. Clearly, therefore the acidification time in our experiments was too short to precipitate any silica at this pH. However, it could not be observed from the results precisely at what pH value silica ceases to precipitate from

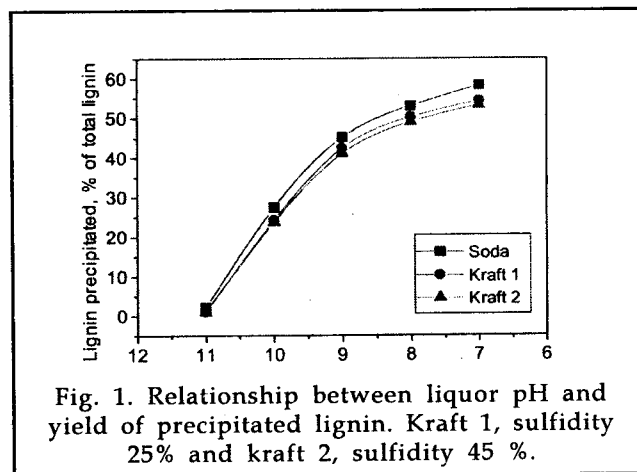
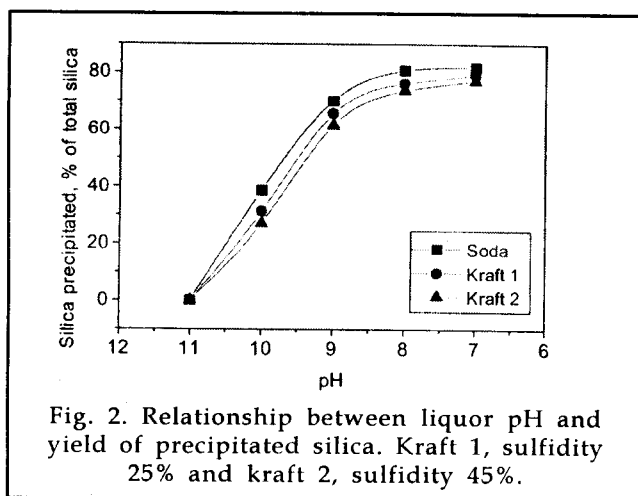


Fig. 1. Relationship between liquor pH and yield of precipitated lignin. Kraft 1, sulfidity 25% and kraft 2, sulfidity 45 %.



black liquor.

The yield of precipitated silica was slightly decreased in the black liquors in the order (Fig. 2): soda black liquor - kraft black liquor (25% sulfidity, kraft 1) - kraft black liquor (45% sulfidity, kraft 2). The silica content of the original black liquors decreased in the same order (Table 2), which might be the main reason for the differences in precipitation yield; the higher the silica content in the black liquor, the higher the precipitation yield of silica. The silica content in the acidified liquors is shown in Table 5.

Aliphatic Carboxylic acids

The determination of aliphatic carboxylic acids (formic and acetic acids and hydroxy acids) was done only for acidified liquors originating from kraft black liquor with 25% sulfidity (Kraft 1). The results are presented in Table 6. The concentration of these acids in the acidified liquors slightly decreased as the pH of the black liquor decreased. The overall loss of volatile acids (formic and acetic acids) was 2-3 % and the loss of non-volatile acids (hydroxy acids) was 1-11 % when the black liquor was acidified to pH 7. Further acidification to pH 2 resulted in the liberation of acids, and the loss of volatile and non volatile acids was 8 % and 13 %, respectively. These losses were caused by the retention of acids in the precipitates. Acid washing of the precipitates (pH 3) resulted in the release of 45-80% of non-volatile carboxylic acids into the washing liquor.

Sodium and potassium

Analysis of the sodium and potassium contents was performed on the acidified liquors obtained from kraft black liquor with 25% sulfidity (kraft 1).

Table 5. Silica content in acidified liquors at different pHs (g/l)*

pH	Soda	Kraft 1	Kraft 2
11	1.7	1.6	1.5
10	1.0	1.1	1.1
9	0.5	0.6	0.6
8	0.3	0.4	0.4
7	0.3	0.3	0.3
2	1.6	1.5	1.4

* For the initial values, see Table-2

The sodium content in these liquors is presented in Table 7. The concentration of sodium slightly decreased as the pH of the black liquor decreased to 7, almost returning to its original value at pH 2. The loss of sodium, caused by its retention in the precipitates, was insignificant (2-6%). When the pH was lowered to 7, sodium loss increased due to the increasing amount of precipitate which contains mainly sodium-containing lignin (i.e., only phenolic groups were liberated) and also sodium sulfate and aliphatic acids as their sodium salts were partly entrained. Sodium loss at pH 2 was decreased because the precipitate mainly contained sodium-free lignin (i.e., carboxylic groups were also liberated). The liberated sodium was converted into sodium sulfate. Acid washing of the precipitates (pH 3) removed the entrained sodium sulfate and some of the sodium, which was chemically bound to the lignin as well as to the aliphatic acids /5, 8/. The changes in the potassium content were similar to those in the sodium content.

Sulphur

The sulfur content in the acidified liquors (i.e., the formation of sodium sulfate) increased significantly during acidification with sulfuric acid, as can be seen from Table 8. Such an increase in sulfur content may disturb the balance of the chemical recovery system (8). In certain situations, the maximum lignin recovery possible without adversely affecting the sulfur balance of the mill was reported to be 10-15 % of the total lignin, using H₂SO₄ for precipitation at pH (8, 5). In general, the addition of a surplus of sulfate ions into the liquor would lead to a complex recovery of sodium as sodium hydroxide and the effect on the balance of the chemical recovery system would greatly depend on the overall situation in the mill. However, in practical applications, it is advantageous to perform partial

Table 6 : Change in the content of hydroxy and volatile acids during acidification of kraft black liquor (kraft 1)*

pH	Formic acid g/l	Loss of formic acid %	Acetic acid g/l	Loss of acetic acid %	Hydroxy acids g/l	Loss of hydroxy acids %
11	5.7	1.7	5.5	1.8	20.7	1.4
10	5.7	1.7	5.5	1.8	19.1	8.9
9	5.7	1.7	5.5	1.8	18.9	10.2
8	5.7	1.7	5.5	1.8	18.8	10.7
7	5.6	3.4	5.5	1.8	18.8	10.7
2	5.3	8.6	5.2	7.1	18.4	12.6

* For the initial values, see Table 2.

precipitation (i.e., to pH 8-9) of lignin by carbon dioxide originating mainly, for example, in the mill's flue gases.

The composition of precipitates

The main components in the precipitates obtained at different pHs are presented in Table 9. Lignin content increased while carbohydrate content fell as the pH of the acidified black liquor decreased. At pH 11 the precipitate contained a large proportion of carbohydrates. However, the amount of precipitate at this pH level was very low, less than 1 % of the black liquor dry solids. When the pH was lowered to 7, the precipitates contained a large proportion of lignin and had a high ash content; the ash mainly comprised sodium compounds and silica. At pH 2 the precipitate mainly contained lignin and only small amounts of carbohydrates and hydroxy carboxylic acids were present.

CONCLUSION

The main purpose of this study was to investigate the possibility to remove lignin together with silica from bamboo alkaline black liquors. The chemical composition of the acidified liquors at pH range 7-10 was the main interest, since these partly acidified black liquors are normally returned to the chemical recovery system. In addition, complete acidification at pH 2 was studied to investigate whether it would be possible to separate a lignin product of high purity with a high precipitation yield. The most important findings are summarized below: The lignin and silica content in the black liquors were significantly changed during acidification. When the pH was lowered to 7, the

Table 7 : Change in the sodium content during acidification of kraft black liquor (kraft 1)*

pH	Sodium content g/l	Loss of Sodium %
11	24.6	2.7
10	24.1	4.7
9	24.0	5.2
8	23.9	5.4
7	23.7	6.4
2	24.9	1.5

For the initial value, see Table 2.

lignin and silica contents were rapidly reduced by 53-58% and 77-82%, respectively. In contrast, when the pH was further lowered to 2, the lignin content continued to decrease while almost all the silica was retained in the acidified liquors. The maximum precipitation yield of lignin was 75-78% of the initial lignin at pH 2 when the black liquor dry solids content were 14-15%. The aliphatic carboxylic acid and sodium content in the black liquor were changed during acidification. In pH range 2-11, the overall loss of volatile acids and non-volatile acids were 2-8% and 1-13%, respectively, and the corresponding loss of sodium was 2-6%. With respect to the yields of precipitated lignin and silica only small differences between the soda (one black liquor was studied) and kraft (two black liquors made with different sulfidity levels were studied) black liquors were found.

Table 8 : Change in the sulfur content during acidification of the black liquors (g/l)*

pH	Soda	Kraft 1	Kraft 2
11	3.0	10	5.0
10	5.0	6.5	10.3
9	6.5	7.8	10.6
8	7.2	8.2	10.7
7	7.8	9.1	11.7
2	17.2	18.3	24.0

* For the initial values, see Table 2.

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Table 9 : Composition of the precipitates at different pHs (kraft 1, % of o.d. precipitate)

pH	Lignin*	Carbohydrates	Hydroxy carboxylic acid	Ash**	Silica
11	2.7	84.2	7.0	6.1	0.0
10	76.7	9.2	6.1	8.0	2.4
9	81.6	5.1	4.5	8.8	4.8
8	82.5	4.7	3.9	9.0	4.8
7	83.8	4.5	3.7	8.0	4.7
2	92.3	3.8	3.5	0.3	0.2

* Calculated by difference.
** Contains silica.

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