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Precipitation of Kraft Black Liquors by Alcohol–Calcium Solutions

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ABSTRACT

Industrial and laboratory kraft black liquors were precipitated with a) water-soluble solvents (alcohols and acetone), b) calcium and aluminum salts, and c) alcohol–calcium solutions. Volume of solvent and the amount of Ca (or Al) were varied over wide intervals, and their effect on the amount and composition of precipitate was studied. Alcohol–calcium solutions were the best precipitating agent (90% of the lignin was recovered with good filterability). The pollutant load of the resulting filtrate showed considerable reductions in some parameters. Precipitation of black liquors with alcohol–calcium solution instead of acid precipitation or ultrafiltration may be an alternative to combustion.

INTRODUCTION

Kraft pulping is the most important process of pulp production; an excellent pulp strength and the recovery of chemicals and power are its most noticeable advantages. At the end of the cooking, the noncellulosic fraction of wood is dissolved in a dark alkaline solution with chemicals that have not reacted. This black liquor (BL) is taken out of the digester

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and concentrated in multistep evaporators to elevate the solids concentration up to 60% (w/w). Finally, concentrated black liquor is burned in a furnace to produce energy and recover chemicals to reuse in further cooking. About half the solids in kraft black liquor are lignin degradation products. Carbohydrates from hemicellulose degradation and nonvolatile extractives are the other organic constituents.

Lignin derivatives have been employed in many applications, mainly as surface-active agents (kraft lignin and lignosulfonates are the derivatives most usually employed). Application as surface-active agents represents the main outlet for lignin derivatives. Other applications consist in transformation to chemicals: vanillin from lignosulfonates and dimethyl sulfide from lignin are the more interesting uses. Lignin is employed as a dispersant, emulsifier, stabilizer, binder, adhesive, and sequestering agent, and is used in industries such as cement and concrete, rubber, resins, ore flotation, and oil-well drilling (1). However, only a small fraction of the lignin produced can be utilized by the pulp industry. Recovery of kraft lignin permits its utilization as a raw material but also allows an increase in pulp production if recovery furnace capacity is the bottleneck in the process (2). Production of semichemical pulp gives a residual liquor with a moderate concentration of solids. In such situations recovery is not always possible and residual liquors are often sent to primary treatment.

Recovery of solids from black liquors is usually carried out by ultrafiltration (3–5) or acid precipitation (6–9). Ultrafiltration is a suitable method for separating lignin having a specific range of molecular weight. Forss and Furmann (10) employed this technique to obtain an adhesive from a high molecular weight lignin. Lin and Detroit (11) separated alkali–lignin by this method, and they proposed employing the fractionated lignin as a dispersant and as a viscosity reducer.

Acid Precipitation

In those cases where lignin is recovered from black liquors, the most frequently used method is precipitation with sulfuric acid or with carbon dioxide. About 70% of alkali lignin can be precipitated with carbon dioxide (7). Flue gases have been recommended for this purpose, although precipitation yield increases when pure CO_2 at elevated pressure is employed instead of flue gases. Moreover, acidification with CO_2 does not modify the sulfur balance in the recovery cycle. Acidification at pH 7–8 with CO_2 or sulfuric acid releases the sodium linked to the phenolic groups and forms sodium bicarbonate and a precipitate of lignin. If sulfuric acid is added at pH 2–3, lignin carboxylate groups liberate sodium and lignin precipitation increases. Some authors (5, 7, 8) have reported precipitation of 90% of the lignin at pH 2 to 3. However, the precipitate is difficult to filter and releases malodorous H_2S. Filtration is accelerated at 80°C by the coagulation of lignin particules; higher temperatures transform the lignin into a sticky form and filtration becomes difficult again.

Whalen (12) proposed a procedure to improve the filterability of lignin. The method consists in the addition of a water-insoluble organic solvent to the precipitated black liquor. An increase in filtration speed and a higher recovery of filtrate were observed when chloroform was added. Other solvents have shown similar effectiveness, and methylene chloride has yielded the best results. Whalen (12) proposed the creation of hydrogen bonds between lignin and solvent molecules as the cause of improvement in filterability; the lignin is thought to be surrounded by a sphere of solvent molecules that make the lignin heavier and hydrophobic, the result favoring agglomeration and precipitation. Although filtration is considerably accelerated, solvent requirements are elevated (0.9 mL of chloroform per gram of total solids).

Precipitation with CO_2 at pH 8 recovers about 70% of alkali lignin, although the percentage depends on solids content in black liquor and CO_2 pressure (7). Acidification with H_2SO_4 at pH 2 increases recovery of lignin, with 90% recovery and the above-mentioned difficulties with filtration.

The elevated yields reported by some authors (5, 7, 8) have not always been reproduced (9, 13), and recoveries of lignin vary from 60 to 90% depending on the authors. Another disadvantage of acid precipitation is the consumption of acid, employed principally to neutralize salts from low molecular weight acids and only a minor quantity to neutralize lignin (3).

Ultrafiltration

Ultrafiltration differs from conventional filtration in the size of particles separated and in the characteristics of the material treated. In ultrafiltration, a solution instead of a solid–liquid mixture (used in filtration) is made to flow through a membrane. Particles smaller than the pore size will pass with the ultrafiltrate while larger particles will be retained on the membrane surface. The particle size in ultrafiltration ranges from 2 to 20 nm (14). The process is affected by fluid viscosity, pressure gradient, and membrane characteristics. Under certain conditions compactation of membranes may occur, which reduces flow. This situation happens when pores and particles have a similar size and is indicated by decreasing flow rates.

Sometimes this technique has been employed for lignin separation from residual liquors with diverse objectives. Forss and Fuhrmann (10) separated a highly polymerized lignin to develop an adhesive; Söderhjelm (4) removed the high molecular weight lignin from a black liquor and observed a drastic reduction in viscosity after this treatment; Hill and Fricke (3) fractionated a kraft black liquor with membranes of different pore sizes (500–300,000 Daltons); Uloth and Wearing (5) compared ultrafiltration and acid precipitation for lignin separation. Kirkman et al. (2) simulated the recovery of kraft lignin by ultrafiltration; they concluded that such a procedure is feasible and could avoid the bottleneck that limited recovery furnace capacity represents in increasing kraft pulp production. Lignin recovery is also affected by membrane pore size, and as can be seen in the above papers, the recoveries range vary from 54 to 80%. As a consequence, ultrafiltration is employed mainly to fractionate lignins rather than for recovery of total lignin.

Precipitation with Solvents

Black liquor precipitation with water-soluble solvents has received little attention. Among the possible solvents, alcohols have been employed to precipitate the carbohydrate fraction from residual liquors in bagasse pulping (6, 15). In previous work (13) an eucalyptus kraft black liquor was treated with ethanol at different ratios (0.2–12 L ethanol/L BL). About 40% of the pentosanes and 22% of the lignin could be recovered with this solvent. In another previous work (16) the effects of methanol, ethanol, and isopropanol on the amount of solids precipitated were determined at different alcohol/black liquor ratios. Only with a great excess of alcohol (10/1) is it possible to precipitate a considerable percentage of solids (60%).

The poor results obtained with alcohol precipitation made us consider the addition of polyvalent cations to black liquor. They are commonly used in sewage depuration, and their application to lignin precipitation has not yet been considered. Calcium(II) and aluminum(III) were selected as precipitants, and the inorganic salts were dissolved in alcohols to promote simultaneous precipitation of lignin and carbohydrates (16–20). The most significant result in cation–alcohol precipitation is the recovery of most of the lignin. Lignin recoveries of 90% or even higher were normal in cation–alcohol precipitation; consequently, a dramatic reduction in color was observed in the filtrates. Moreover, the precipitate showed good filterability at room temperature and filtrate retention was reduced.

After these encouraging previous results, the aim of this work is to study in depth the precipitation of kraft black liquors using solvents (alcohols such as methanol, ethanol, and isopropanol, and acetone) and polyvalent cations.

EXPERIMENTAL

Industrial kraft black liquors and other samples obtained in a 25-L pilot-plant digester were employed in the experimentation. Both types of samples were obtained from eucalyptus wood. Table 1 shows the characteristics of the black liquors employed.

Reagents

Methanol, ethanol, isopropanol, and acetone were of a minimum purity of 95%, calcium(II) was added in the form of anhydrous calcium chloride (purity 95%), and aluminum(III) as aluminum sulfate (purity 95%).

Procedure

Experimentation has been divided into three parts. The first set of runs was made to study the effect of solvents on black liquor precipitation; the

TABLE 1
Characteristics of Black Liquors

Key	Origin	Composition
BL1	Pilot plant (kappa = 29.1)	pH 12.5 Density = 1.06 Total solids = 131.4 g/L Ash = 48.9 g/L Lignin = 82.5 g/L Pentosanes = 10.21 g/L
BL2	Kraft mill	pH 12.56 Density = 1.10 Total solids = 199.34 g/L Ash = 98.70 g/L Lignin = 50.59 g/L Pentosanes = 4.90 g/L
BL3	Pilot plant	pH 12 Density = 1.06 Total solids = 146 g/L Ash = 62.4 g/L Lignin = 64.4 g/L
BL4	Kraft mill	pH 13.4 Density = 1.08 Total solids = 167.2 g/L Ash = 82.2 g/L Lignin = 78.3 g/L
BL5	Pilot plant	Density = 1.06 Total solids = 138.5 g/L Pentosanes = 9.4 g/L

second group of experiments explored the effect of calcium and aluminum salts addition; and the third group was carried out to study precipitation with cation–alcohol solutions.

Precipitation with solvents was made with three alcohols (methanol, ethanol, and isopropanol) and acetone. For each one the volumetric ratio solvent/black liquor was changed over a large range. In precipitation with cations, calcium or aluminum salts were added directly to the black liquor. In precipitation with alcohol–cation solutions, cation concentration and volume of alcohol were varied to determine their effects on the yield and composition of precipitates. Moreover, filtration rate and volume of filtrate recovered were compared at different alcohol/black liquor ratios. Experiments with solvents (or salt–solvent solutions) were performed by the addition of a volume of solvent (or solvent solution) in a beaker. BL (100 mL) was then poured on the solvent and both were thoroughly mixed. The mixture was let to stand for 1 hour and filtered under vacuum. Solids retained were washed with three 5-mL portions of solvent, dried at room temperature, and stored for further analysis. Precipitation with salts was made by mixing solid salt and black liquor until complete dissolution of the salt. After 1 hour the precipitate was filtered and dried at room temperature before analysis. For each experiment, precipitated solids were determined by gravimetry, and samples were also analyzed for moisture, lignin, methoxyl groups, ash, sodium, and calcium (if calcium was added as a precipitant). Filtrates were distilled to recover alcohol; alcohol-free liquid was analyzed to determine pH, color, TOC, COD, and sodium and calcium content.

Analysis

Total solids. Determined by weighing and corrected for the value of the moisture content.

Moisture. Samples were dried in a furnace at 100–110°C for 24 hours, and moisture determined by difference of weight between solids dried at room temperature and after oven drying.

Lignin. 30–50 mg of sample was dissolved in 250 mL of 0.08 N NaOH, the alkaline solution was filtered, and its UV absorbancy measured at 280 nm. Lignin concentration can be calculated by the equation of a previous calibration (21), where L represents the lignin concentration in parts per million, and Ab is the absorbance at 280 nm:

$$L\ (\text{ppm}) = -0.34 + 53.37\text{Ab} \qquad (1)$$

Methoxyl groups. 100 mg of sample was treated with 2 mL of HI at 170°C for 30 minutes in a 30-mL glass reactor provided with a Teflon stopper. Reaction products were extracted with benzene (5 mL) and gas chromatographed under the following conditions:

Column: Carbowax; temperature of oven: 92°C; temperature of injector: 120°C
Detector: Flame ionization; temperature of detector: 130°C
Carrier gas: N_2; flow: 120 mL/min

A previous calibration with vanillic acid gave the following expression for the methoxyl groups content (M represents the milligrams of methoxyl groups in the sample and P_A the peak area in the chromatogram):

$$M\,(\text{mg}) = 0.503 + (1.64 \times 10^{-6})P_A \tag{2}$$

Ash. A tared crucible with 100 mg of sample was calcined at 600°C for 4 hours, transferred to a desiccator, and the ash content was determined gravimetrically.

Sodium and calcium. Samples were calcined and dissolved in a HCl solution. Sodium and calcium concentrations in the solution were measured by atomic absorption spectrometry.

Color. Measure of color in alcohol-free filtrate was performed on a Vitatron colorimeter. K_2PtCl_6 solutions were employed as standards in color calibration.

COD. The COD test were made on selected alcohol-free samples. The ASTM (D1252-88) standard was the procedure employed.

TOC. Alcohol-free samples were lyophilized to remove water and analyzed on a CHN analyzer (LECO, model CHN-600) to determine the carbon content.

RESULTS

Precipitation with Solvents

Four water-soluble solvents (methanol, ethanol, isopropanol, and acetone) were used as precipitants of black liquors (BL). Table 2 shows the experimental results achieved. Figure 1 shows the fraction of solids precipitated at different solvent/BL ratios with each solvent. As can be seen in Fig. 1, the yield of solid precipitated is substantial only at elevated solvent/BL ratios and with ethanol as solvent.

Although the fraction of solid precipitated is reduced, the components of black liquor are recovered in different proportions. Analysis of pentosanes and lignin in precipitates produced with methanol and ethanol shows that only a small proportion of lignin is recovered by solvent precipitation while pentosanes are completely precipitated when the solvent/black liquor ratio is greater than 1.

TABLE 2
Precipitation of BL1 with Solvents

Solvent/BL	ETH + BL1			MET + BL2			ISP + BL4	KET + BL2
(v/v)	P/BLS	LIG	PEN	P/BLS	LIG	PEN	P/BLS	P/BLS
0.10	—	—	—	—	—	—	0.02	—
0.20	0.05	—	1.56	—	—	—	—	—
0.25	—	—	—	—	—	—	0.02	—
0.4	0.13	—	3.39	—	—	—	—	—
0.5	—	—	—	0.09	1.83	1.42	0.04	0.10
0.6	0.20	—	5.99	—	—	—	—	—
0.8	0.27	—	7.94	—	—	—	—	—
1.0	0.29	6.43	11.72	0.13	1.46	2.76	0.04	0.16
1.5	—	—	—	—	—	—	0.06	—
2	0.43	11.14	9.79	0.20	2.55	3.51	—	0.18
4	0.57	19.50	10.58	0.37	6.55	3.83	—	0.17
6	—	—	—	0.38	4.69	3.93	—	—
8	0.77	26.90	8.46	0.36	4.63	4.36	—	—
10	0.78	27.28	9.15	0.28	3.10	—	—	—
12	0.86	30.29	10.37	—	—		—	—

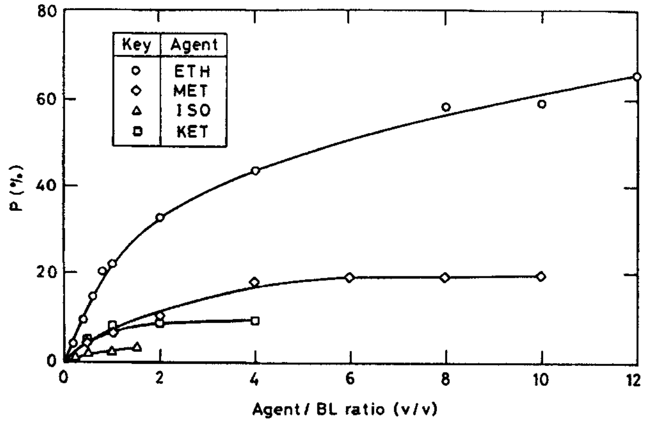

FIG. 1 Precipitation of black liquors with different agents.

Precipitation with Polyvalent Cations

The aim of this section is to select an agent that could increase the recovery of lignin. In the previous section, solvents showed little capacity to remove lignin from black liquors, so calcium and aluminum were added to promote lignin precipitation. Table 3 shows the solids and lignin recovered; percentage of solids precipitated were referred to initial solids (solids in black liquor and anhydrous salt). Most of the lignin is in the precipitate whatever the cation used; however, filtration is not rapid and the precipitate retains a large amount of water. The main difference between calcium and aluminum precipitation is the pH of the filtrate; calcium chloride does not modify the pH significantly, while aluminum chloride reduces the pH to 3.5. The explanation of this reduction is the formation of insoluble aluminum hydroxide at elevated pH, which removes hydroxide ions from black liquor and produces a solid that coprecipitates with lignin. In addition, pH reduction favors the precipitation of lignin by acidification.

Calcium and alcohols have been selected as components in the solutions employed to precipitate solids from black liquors. Calcium salts are more soluble than aluminum salts in methanol and ethanol, remove more lignin, and do not yield an acid filtrate. Among the solvents used in the first section, acetone was rejected as a solvent for use with calcium(II) because the lignin precipitate is difficult to filter.

Table 4 shows the results of precipitation with the systems methanol–calcium(II), ethanol–calcium(II) and isopropanol–calcium(II). The effectiveness of precipitation is expressed by the percentage of total solids precipitated (P_{TS}) (the solids precipitated, P refers to the sum of solids in black liquor, BLS, plus the added calcium salt). However, calcium salts and other inorganic constituents are present in the precipitate and must be considered to evaluate the effectiveness of the precipitation, so the

TABLE 3
Black Liquor Precipitation with Polyvalent Cations

Precipitant	Salt (g/L BL)	Cation (mol/L BL)	BLS (g/L BL)	P (g/L BL)	P_{TS} (%)	Lignin in precipitate (g/L BL)
$CaCl_2$	107.3	0.92	146 (BL3)	182.1	71.89	66.4
	210.6	1.81	146 (BL3)	251.6	70.56	52.3
$Al_2(SO_4)_3$	103.3	0.60	199 (BL2)	191.2	63.25	36.2
	100.0	0.58	199 (BL2)	221.3	74.01	54.1
$AlCl_3 \cdot 6H_2O$	77.6	0.58	167 (BL4)	145.8	59.61	—

TABLE 4
Precipitation of BL5 with Alcohol–Calcium(II)

		MET		ETH		ISO	
Alc/BL	Ca (g)	P_{TS}	F	P_{TS}	F	P_{TS}	F
0.10	0.34	18.98	—	27.81	64	11.14	110
0.25		34.71	68	36.58	—	13.35	116
0.50		28.07	100	21.61	113	19.03	136
1.00		20.05	128	21.36	166	13.03	171
1.50		20.63	220	28.03	224	13.26	236
0.10	1.03	60.41	50	66.29	48	62.35	55
0.25		62.65	53	61.71	66	54.89	74
0.50		60.78	77	54.36	90	54.69	108
1.00		55.26	126	54.15	160	56.92	160
1.50		55.41	—	57.13	152	68.25	195
0.10	1.38	65.92	38	71.38	28	68.54	35
0.25		73.86	48	70.68	50	65.19	53
0.50		66.28	60	64.24	80	60.65	90
1.00		64.93	97	59.01	110	57.56	150
1.50		62.11	130	63.63	150	63.62	198
0.10	1.72	73.94	36	72.68	30	74.67	28
0.25		72.80	43	69.54	44	70.97	41
0.50		63.74	94	65.70	—	70.81	55
1.00		62.84	120	62.24	112	64.38	114
1.50		65.03	150	61.21	156	63.19	190
0.10	3.44	79.45	26	77.38	29	76.12	28
0.25		63.75	—	79.73	31	68.70	36
0.50		73.78	47	74.52	58	68.94	64
1.00		65.97	187	62.60	114	64.92	116
1.50		56.09	231	55.77	188	59.71	165
0.10	6.88	82.10	25	71.55	39	50.26	82
0.25		68.38	46	70.80	—	52.71	83
0.50		69.67	62	64.67	64	57.71	69
1.00		51.97	106	50.57	143	54.06	125
1.50		55.53	129	51.95	172	65.14	184
0.10	10.32	87.76	24	65.24	45	—	—
0.25		55.68	70	73.10	47	—	—
0.50		70.54	53	62.39	58	—	—
1.00		44.17	117	45.37	149	—	—
1.50		51.17	138	47.08	182	—	—
0.10	13.76	66.90	35	51.46	67	—	—
0.25		59.95	—	68.07	—	—	—
0.50		81.49	—	63.86	71	—	—
1.00		40.41	128	42.97	153	—	—
1.50		51.66	136	47.02	182	—	—

composition of the precipitate (ash, lignin, methoxyl groups, calcium, and sodium) was also calculated.

$$P_{\mathrm{TS}} = \frac{\mathrm{P}}{\mathrm{BLS} + \mathrm{CaCl_2}} \tag{3}$$

Measurement of Pollutant Load in Filtrates

Precipitation with alcohol–calcium(II) solutions removes a considerable amount of organic compounds from black liquor, most of them responsible for the pollutant load of the liquor. The resulting filtrate consists of a clear liquid with low solids content. Analysis of the pollutant load will determine the final disposal of the filtrate.

Previous to this analysis, the filtrate is distilled to recover alcohol and to refer the results to the volume of alcohol-free liquid. pH, color, lignin, COD, and TOC were determined on the residue of the distillation; the values of these analyses are given in Table 5.

TABLE 5

Pollutant Load in Filtrates (alcohol-free)

Ethanol–Ca Precipitation

ETH/BL	Ca (g/L BL)	pH	Color (cu)	LIG (g/L)	COD (mg/L)	TOC (mg/L)
1	17.4	12.4	2,900	3.6	228,000	13,600
1	10.3	12.5	21,200	7.9	288,000	15,400
1.5	3.4	11.3	210,900	33.8	129,000	41,800
1	13.9	12.4	17,000	8.3	178,000	18,500

Methanol–Ca Precipitation

MET/BL	Ca (g/L BL)	pH	Color (cu)	LIG (g/L)	COD (mg/L)	TOC (mg/L)
1	17.1	12.2	2,100	1.6	379,000	9,000
1.5	3.4	12.8	210,900	38.5	437,000	34,400
1	10.5	12.7	23,400	7.6	447,000	14,700
1	13.8	12.4	4,100	2.8	511,000	11,700

Isopropanol–Ca Precipitation

ISO/BL	Ca (g/L BL)	pH	Color (cu)	LIG (g/L)	COD (mg/L)	TOC (mg/L)
0.1	3.4	10.6	290,900	47.6	379,000	47,400
1.5	3.5	10.1	84,300	17.7	156,000	—
1	13.7	12.8	11,700	5.6	298,000	15,400
1.5	73.8	12.2	2,300	3.5	79,480	—
BL 5		13.4	530,700	78.3	710,000	54,200

Alcohol–calcium(II) treatment produces a filtrate with a spectacular reduction in color. The main cause of this is the precipitation of most of the lignin, the principal component of black liquor and one of those responsible for color. Reduction of these parameters (color and lignin content) depends on calcium added more than alcohol volume. Proportions in the range of 1.03–1.72 g Ca/100 mL BL cause a drastic reduction in color and lignin; at lower values the precipitation of lignin is not complete, while calcium addition above this range has no effect because the lignin has already been removed.

COD is also considerably reduced with respect to its original value; however, the COD level in the filtrate is still high, perhaps due in part to the salt employed in precipitation. If calcium is added as calcium chloride, chloride anions will appear in the filtrate and elevate the COD. A careful selection of calcium salt, e.g., calcium nitrate, could reduce the COD. In this case the nonoxidizable nitrate anion does not contribute to COD, while chloride anion will increase the consumption of dichromate in the COD test. Although COD is still high in the filtrate, the elimination of most of the lignin must constitute an important advantage because a difficultly biodegradable material has been removed.

DISCUSSION

Black liquors with different solid contents cause differences in the amount of precipitate obtained. Thus, in the precipitation, the expression of yield must be carefully chosen to take this fact into account. The ratio "solids precipitated/solids in black liquor (total initial value)" was the measurement adopted in this work for showing effectiveness in precipitation when no salt is added to the solvent. Figure 1 represents the behavior of four solvents in precipitation of black liquors. Ethanol showed the highest yields in precipitated solids while the other solvents had similar responses. Besides the low results, a large volume of solvent is necessary to obtain a moderate yield (e.g., ethanol at a ratio of 12 L/L BL removes 65% of solids).

Calcium(II) and aluminum(III) increase the recovery of solids spectacularly as expressed by the data in Table 3. Calcium chloride in alcoholic solutions was the precipitant used in the third set of experiments. Figure 2 shows the effect of calcium(II) addition on the percentage of solids precipitated; in this figure the ratio alcohol/BL is the parameter varied for the different curves. Several conclusions can be drawn from Fig. 2:

Precipitation increases with calcium addition up to a ratio of 1.72 g Ca/100 mL BL. Above this ratio, the percentage of precipitation stabilizes and even goes down as calcium addition continues.

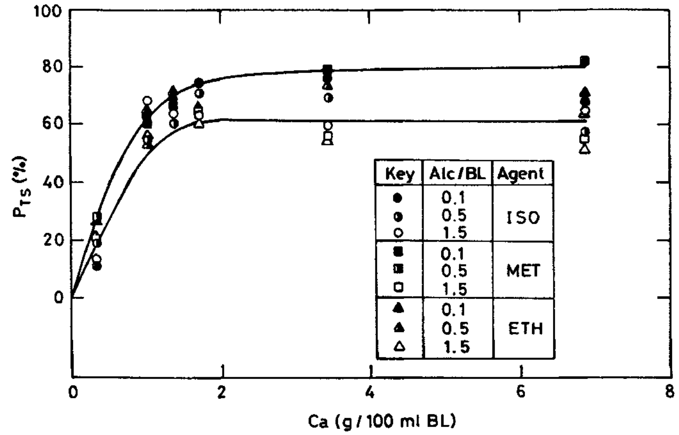

FIG. 2 Total solids precipitated with alcohol–calcium(II) mixtures.

Increasing the concentration of alcohol in the range 0.1–1.5 Alc/BL causes a modest decrease in the precipitation of BL solids.

The behaviors of the three alcohol–calcium systems are similar, with no difference among them caused by the nature of the alcohol.

The volume of alcohol causes few variations in precipitated solids in the isopropanol–calcium system; there is only a minimum difference between the extremes of the range.

The first observation is explained if we consider the phenomena involved and the expression chosen to represent the yield of precipitation. At the beginning of calcium(II) addition, calcium(II) reacts completely with the lignin and other black liquor solids. If addition goes on, the yield increases until precipitation is completed. Figure 2 shows that this situation occurs at a ratio of 1.72 g Ca/100 mL BL. At higher ratios the additional calcium(II) does not find more solids to precipitate and remains in solution, so the yield (expressed by Eq. 3) decreases because more salt is employed to precipitate the same amount of solids. A slight decrease in precipitation is observed when the alcohol/BL ratio increases, which means that some components are more soluble if the volume of solution increases. Precipitation trials made with solvent have shown an increase in precipitation of solids with increasing solvent volume (see Fig. 1), so it is reasonable to suppose that, in the system alcohol–calcium(II), the increase in alcohol concentration does not redissolve the black liquor solids, but a fraction of the calcium salt precipitates (or perhaps there is an insoluble compound formed with salt and solids).

Lignin recovery is shown in Fig. 3. The behavior observed can be summed up as follows:

Lignin precipitation increases rapidly with added calcium up to 1.72 g Ca/100 mL BL (30 g $CaCl_2$/100 g_{TS}). At this value lignin precipitation is complete and consequently further addition of calcium(II) has no effect.

The volume of alcohol has less influence on lignin recovery than does the calcium concentration. The effect is only evident at elevated calcium concentration. Under these conditions, recovered lignin increases slightly with alcohol/BL ratios.

Addition of calcium(II) to black liquor displaces sodium(I) from lignin molecules (dissolved as sodium phenolate and carboxylate), and then the repulsive forces, those maintaining the lignin molecules in a dispersed state, are reduced and the lignin particles agglomerate and precipitate. The beginning of precipitation by cation addition also depends on the solution. Electrophoresis studies have related the electrolyte addition to the falling of the zeta potential of the particles. Moreover, each solution has a characteristic zeta potential at which precipitation begins. The progressive addition of alcohol will modify this value. If the effect of alcohol is to promote precipitation, this would explain the slight increase of precipitated lignin when the alcohol/BL ratio increases.

Because lignin recovery does not decrease with the volume of alcohol, the reduction in solids observed (Fig. 2) must be caused by the dissolution of the calcium salt (or any other black liquor component other than lignin) as previously mentioned.

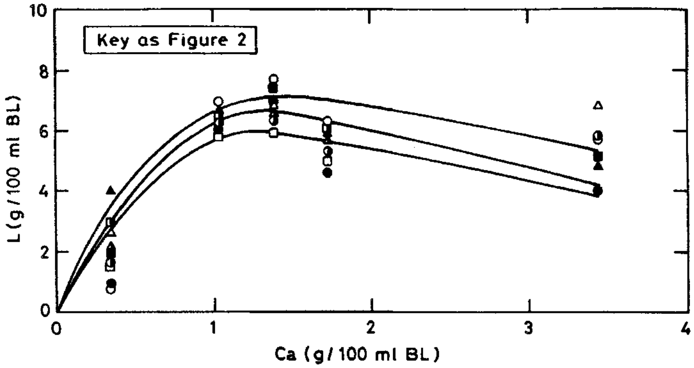

FIG. 3 Lignin precipitated with alcohol–calcium(II) mixtures.

Purity and Filterability of Precipitates

The evaluation of the precipitation method has only considered percentages of recovery for total solids and lignin. However, other aspects, such as precipitate purity, filtrate recovery, and filterability, must be considered to evaluate the feasibility of this method.

In acid precipitation the filtration is very slow at pH 2–3. In this case, filtration is performed at 80°C to improve lignin filterability. In alcohol–calcium precipitation, differences in filterability were observed when the volume of alcohol changed. A set of experiments was designed to study this behavior and to quantify the effects. These experiments consisted of precipitations made with 5 g $CaCl_2$/100 mL BL (1.72 g Ca/100 mL BL) and different alcohol/BL ratios; the precipitated solids were separated by vacuum filtration (the vacuum was maintained constant at 600 mmHg) and the volumes of filtrate at different times were measured.

In Figs. 4, 5, and 6 the fraction of filtrate recovered at different times is presented; the fraction of filtrate is expressed as the filtrate volume divided by the total volume [alcohol calcium(II) solution plus black liquor]. This parameter has been selected as a measure of filterability and varies with the volume ratio of alcohol. Figures 4 to 6 show the velocity of filtration and the filtrate volume recovered, both increasing when the volume ratio of alcohol increases in the range studied. Only isopropanol has a different behavior; it presents a maximum filterability for an alcohol/BL ratio of 1. A reduced volume of alcohol (0.1 and 0.25 L/L BL) causes

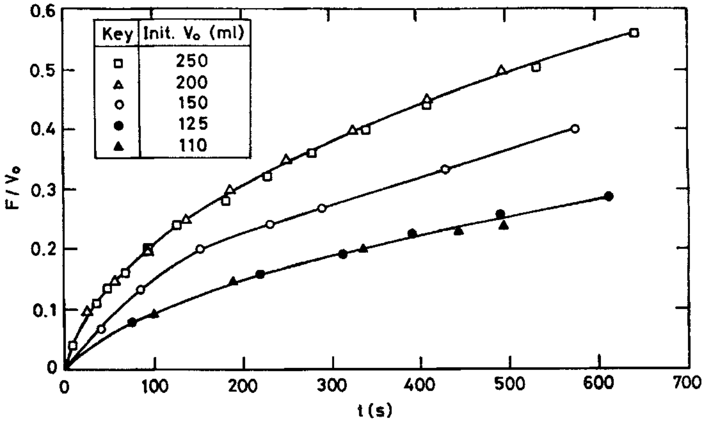

FIG. 4 Filterability after precipitation with ethanol–calcium(II) mixtures.

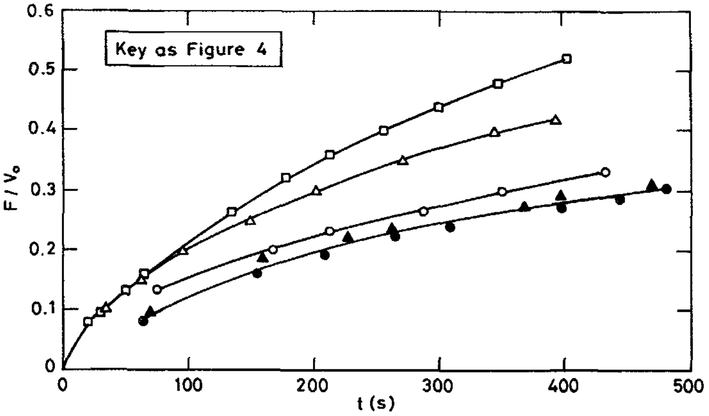

FIG. 5 Filterability after precipitation with methanol–calcium(II) mixtures.

a slow filtration rate; on increasing the alcohol ratio, filtration is accelerated and the volume of filtrate also increases. For methanol and ethanol, maximum velocity of filtration is obtained at the maximum alcohol ratio (1.5 L/L BL), while for isopropanol, the maximum is obtained at 1 L/L BL. The volume ratio of alcohol causes a similar variation in the volume of filtrate that is recovered; higher volume ratios remove a higher percentage of filtrate.

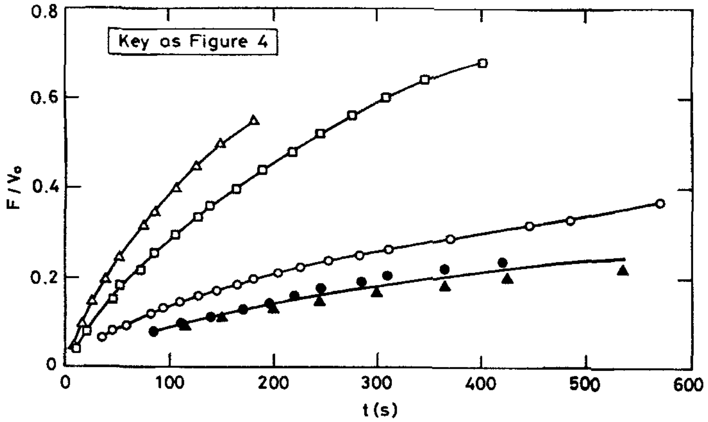

FIG. 6 Filterability after precipitation with isopropanol–calcium(II) mixtures.

Consequently, precipitation with alcohol–calcium(II) solutions removes most of the black liquor solids and gives better filterability than does acid precipitation. Calcium(II) and alcohol have different effects in the process; calcium(II) acts as the precipitant, while alcohol improves filtration of precipitate and reduces liquid retention by the precipitate.

CONCLUSIONS

Recovery of lignin from kraft black liquors gives a raw material suitable for use in many fields. The treatment of a fraction of black liquors would permit an increase in pulp production if this is limited by recovery furnace capacity. In semichemical pulp production, precipitation of spent liquors with alcohol–calcium solutions could be an alternative if recovery is not possible.

In black liquor precipitation, calcium salts cause the lignin (and other organic constituents) to precipitate. If addition of calcium(II) is adjusted, lignin precipitation is almost complete and the filtrate obtained shows a spectacular reduction in color; other parameters such as lignin, COD, and COT experience parallel diminutions. Addition of calcium(II) in alcoholic solution improves filterability, increases the volume of filtrate, and gives a precipitate with a higher lignin content.

NOMENCLATURE

Ab	absorbance at 280 nm
Alc	alcohol
BL	black liquor
BLS	black liquor solids (g/L BL)
Ca	calcium concentration (g of Ca/100 mL BL)
COD	chemical demand of oxygen (mg/L)
ETH	ethanol
F	filtrate (mL/100 mL BL)
ISO	isopropanol
KET	acetone, propanone
L	lignin concentration (g/100 mL BL) (ppm)
LIG	percentage of lignin in precipitate (g lignin/100 g precipitate)
M	methoxyl groups in samples (mg)
MET	methanol
P	precipitate (g/L BL) (%)
P_A	peak area of methyl iodide
PEN	percentage of pentosanes in precipitate (g pentosanes/100 g precipitate)

P_{TS}	percentage of total solids, defined in Eq. (3) (g precipitate/100 g of total solids)
t	time (s)
TOC	total organic carbon (mg/L)
V_0	initial volume (alcohol + BL) (mL)

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