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Recovery of Solvent and By-Products from Organosolv Black Liquor

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ABSTRACT

The recovery of alcohol and by-products from ethanol–water and methanol–water pulping liquors was studied. The recovery system proposed consists of three stages: black liquor flashing, lignin precipitation, and precipitation distillation of mother liquor. At the flash stage, 47 and 51% of the alcohol in the black liquor are recovered for ethanol and methanol processes, respectively. The lignin recovery yield at the precipitation stage is 67% for ethanol black liquor and 73% for methanol black liquor. The distillation of precipitation mother liquors enables recovery of 98% ethanol and 96% methanol from this stream as distillate, whereas the distillation residue contains significant amounts of sugars, furfural, and acetic acid that can be recovered. The study concludes with the overall mass balance for the recovery system proposed.

INTRODUCTION

In spite of being the most used pulping process, the kraft process suffers from several innate disadvantages. Thus, it generates emissions and effluents of a highly objectionable nature and the cost of a modern kraft mill is enormously high because of the nature of the chemical recovery process and the necessary environmental control measures. One answer to these concerns of the chemical pulping industry is the introduction of a radically new technology. In this way, organosolv pulping processes have been presented as a proven alternative to the kraft process (1). Organic solvents are used as pulp-

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ing agents in these processes (2, 3). Several factors are responsible for the interest in organosolv processes: the efficient recovery of solvent is feasible and practical (4), they have a substantial capital cost advantage over a comparably scaled kraft mill [which can be used to reduce the mill's size so they become attractive at 300 tons of pulp/day (against 1000 tons of pulp/day for a new kraft; see Ref. 4)], the process is environmentally benign and there is no air pollution by malodorous gases since the pulping is sulfur-free (5–7), and the pulps can be bleached easily without chlorine sequences (8).

Another important advantage of the organosolv processes is their ability to produce substantial quantities of useful by-products (lignin, sugars, furfural and acetic acid) in addition to pulp. Furthermore, the organosolv processes enables the recovery of by-products in easily handled forms. The development of markets for these by-products and their ultimate market value will eventually add significantly to the economics of the organosolv process. The variety of products from organosolv pulping by-products and their applications can be found elsewhere (9, 10). Lignin, for example, has been tested with positive results in numerous applications (11, 12).

Among the great variety of cooking solvents proposed in the literature, low molecular weight aliphatics alcohols, such as ethanol and methanol, are the most used due to their low cost and minimum environmental impact (1, 2). Besides, their high volatility in respect to water enables their easy recovery from black liquor by distillation.

This study is a contribution on the recovery of solvent and by-products from organosolv black liquors. A better understanding of this issue is required due to the great importance of the recovery system for the economy of the organosolv processes.

EXPERIMENTAL

The experimental study consists of four stages: wood cooking, black liquor flashing for partial recovery of the solvent, lignin precipitation by black liquor dilution with water at different pH values, and final solvent and by-products recovery by distillation. In addition, the pulp and the lignin recovered have been characterized. The work concludes with a proposal on the most suitable recovery system for the black liquors studied.

Two autocatalyzed cooks of *Eucalyptus globulus* were carried out, one in 50% ethanol–water (w/w) and another in 50% methanol–water (w/w). The liquor was exclusively composed of alcohol and water. The heating rate was 3°C/min. The cooking temperatures were 183 and 185°C for ethanol and methanol pulping, respectively, and the time at these temperatures was 100 minutes. These cooking conditions were found to be the most suitable for each alcohol in previous works (13, 14)

Equipment and Procedure

Industrial size chips (approximately 30 × 20 × 5 mm) were taken from a pulp mill. After air drying, the moisture content of the chips was 16.2% (TAPPI test method 264). The chemical composition of the wood was as follows: 21.9% lignin (TAPPI test method T 222), 47.2% cellulose (TAPPI test method T 203), 23.4% pentosans (TAPPI test method T 223), 2.5% extractives (TAPPI test method T 204), and 0.3% ash (TAPPI test method T 211). All values given above are on an oven dry wood basis.

The equipment used to carry out the cooking experiments has been previously described (15). It consists of a pressure vessel of 4 L (Zipper Clave, Autoclave Engineers, Erie, PA, USA) provided with an external heating system, forced liquor circulation, and measurement and control of both pressure and temperature. The autoclave was loaded with 429 g of dry wood and 3 L of liquor, and the system was purged with nitrogen; a slight overpressure of 0.2 MPa was maintained to avoid flashing and boiling of the liquor. At the end of the cook the system was cooled and the black liquor collected. The cooked chips were defiberized in 0.1 M sodium hydroxide (20 L/kg dry wood) and washed thoroughly with water.

To carry out the lignin separation by precipitation at the conditions corresponding to a real process, the composition of the black liquor was adjusted to that corresponding to the concentrated black liquor leaving the flash, whose composition was determined by computer-assisted simulation (PROSIM, Logiciels de simulation de l’Ecole Nationale Supérieure d’Ingénieurs de Génie Chimique, Toulouse, France). To simplify, the flashing of black liquor was made from full pressure to atmospheric pressure. Thus, the black liquor was concentrated in a rotary evaporator and the concentrations of the volatile components were adjusted to their respective values.

The lignin was precipitated from the black liquor by dilution with water and acidulation with sulfuric acid. The precipitation was carried out at 25°C in a beaker provided with a magnetic stirrer. The lignin precipitated was separated by centrifugation at 3500 rpm for 10 minutes. Once the most suitable dilution ratio to achieve lignin precipitation was established the influence of pH was studied. Sulfuric acid was used to acidify the black liquor. The lignin precipitation yield was calculated from the difference between the lignin concentration in concentrated black liquor and the lignin concentration in precipitation mother liquor.

Pulp Characterization

Total Yield. After air drying of the pulp, it was weighted and the pulp moisture content was determined according to TAPPI T 210 test method.

Rejects Weight. The pulp was screened using a Somerville device after laboratory wet disintegration of 75,000 rotations (Büchel van der Korput B.V., Vendelier, The Netherlands). The rejects were collected and weighed after drying at 105°C.

Screened Yield. Screened yield was calculated from total yield and rejects weight.

Pulp Viscosity. The intrinsic viscosity of the pulp was determined according to SCANC15:62 test method.

Kappa Number. The kappa number was determined according to TAPPI 236 test method.

Acid-Insoluble Lignin in Pulp. The Klason lignin content of the pulp was established according to TAPPI T 222 test method.

Black Liquor Characterization

Lignin. UV spectrophotometry at 280 nm was used to determine the lignin concentration in both black liquors and precipitation mother liquors (16). The samples were diluted with pH 12 buffer solution (0.1 M boric acid adjusted to pH 12 with sodium hydroxide) to the proper concentration range. A purified lignin sample obtained from the black liquor by dilution with water (1:2) and acidulation to pH 2 with sulfuric acid was employed as standard.

Sugars. The sugars concentration in the black liquor was determined by HPLC using a Hi-Plex Pb column (Polymer Laboratories) and a refractive index detector (Waters 410 Differential Refractometer). To eliminate lignin interferences it was precipitated from black liquor samples by dilution with water (1:2). Prior to injection the sample was neutralized with PbO. The analysis conditions were: oven temperature, 85°C; detector temperature, 40°C; mobile phase, water; flow, 0.6 mL/min; injection volume, 25 μL.

Furfural. A black liquor distillate sample of 10 mL was mixed with 0.5 mL of aniline and 2 mL of acetic acid, and the mixture was stirred until the development of a pink coloration. After 15–20 minutes the absorbance of the sample was measured at 510 nm.

Acetic Acid. It was determined by titration: 50 mL of black liquor was titrated with 0.1 N sodium hydroxide until pH 6.5 was reached. This pH value corresponds to the titration end point for acetic acid in both ethanol 50% (w/w) and methanol 50% (w/w).

Lignin Characterization

Molecular Weight Distribution. Gel permeation chromatography (GPC) was used to determine the lignin molecular weight distribution. A series of three columns (Waters Ultrastyragel) with different pore sizes (100, 500, and 1000 Å) and a refractive index detector (Waters 410 Differential

Refractometer) were employed. Narrow calibration was carried out with polystyrene standards (162–38,000 daltons). The analysis conditions were oven temperature, 38°C; detector temperature, 40°C; mobile phase, tetrahydrofuran; flow, 1 mL/min; injection volume, 25 μL. The GPC parameters determined were: weight-average molecular weight (M_w), number-average molecular weight (M_n), polydispersity (M_w/M_n), and z-average molecular weight (M_z).

Phenolic Hydroxyl Groups. A spectrophotometric method based on the difference in absorption at 300 nm between phenolic units in neutral and in alkaline solutions was used to determine the phenolic hydroxyl groups content of lignin (17).

Carbonyl Groups. The lignin carbonyl groups content was calculated from UV spectroscopy measurements after lignin reduction with an excess of sodium borohydride in alkaline solution (18).

RESULTS AND DISCUSSION

Pulp

The characteristics of the pulps obtained in the cooking runs are shown in Table 1. In both cases the lignin content of the pulp is high compared to the usual lignin content of kraft pulps. This fact does not affect significantly the quality of the pulp since the organoslv pulps can be bleached easily (8). The viscosity values are rather low for both pulps. However, the loss of viscosity of organosolv pulps during bleaching has been reported to be low (19). Therefore, the viscosity of the pulps obtained can be considered as acceptable. The screened yield were 55.8 and 54.3% for the ethanol and the methanol processes, respectively. This concordance between these values is due to the fact that the operating conditions used in each case are very similar.

TABLE 1
Pulp Characterization[a]

	Ethanol	Methanol
Kappa number	29	21.7
Klason lignin (%)	7.8	5.8
Viscosity (mL/g)	1039	1112
Total yield (%)	55.8	54.3
Screened yield (%)[b]	55.8	54.3

[a] Percentages on oven dry wood basis. Pulping conditions: 50% alcohol (w/w), 100 minutes, and 183 and 185°C for ethanol and methanol pulping, respectively.

[b] Weight of rejects was negligible in both cooks.

TABLE 2
Black Liquor Composition Before and After Flashing[a]

	Prior to flash		After flash[b]	
	Ethanol	Methanol	Ethanol	Methanol
Alcohol (g)	457.0	460.0	244.5 (53.5)	226.8 (49.3)
Water (g)	457.0	460.0	330.0 (72.2)	360.2 (78.3)
Furfural (g)	0.71	1.05	0.66 (93.5)	1.01 (96.4)
Acetic acid (g)	1.85	1.52	1.52 (82.0)	1.31 (86.2)
Lignin (g)	28.92	28.82	28.92 (100)	28.82 (100)
Xylose (g)	1.84	5.16	1.84 (100)	5.16 (100)
Glucose (g)	1.53	3.40	1.53 (100)	3.40 (100)
Galactose (g)	0.91	1.47	0.91 (100)	1.47 (100)
Arabinose (g)	1.47	2.32	1.47 (100)	2.32 (100)
Mannose (g)	1.03	0.67	1.03 (100)	0.67 (100)

[a] Referred to 1 L black liquor at the flash entrance.
[b] Figures in parentheses are the percentages remaining in the concentrated black liquor.

Black Liquor Flashing

The composition of the black liquors is shown in Table 2 for methanol and ethanol cooks. The amount of lignin extracted in both cases is practically the same. The generation of acetic acid in the ethanol cook is higher than in the methanol cook, whereas the methanol cook produces more furfural and much more sugars. The pH of the black pulping liquor is 3.99 and 4.02 for the ethanol and methanol pulping, respectively. The composition of the concentrated black liquor after flashing is also shown in Table 2. Alcohol, water, acetic acid, and furfural are the components recovered in the flash vapors. The nonvolatile substances are recovered quantitatively in the concentrated black liquor. The amount recovered for each component in the flash vapors can be calculated as the difference between inlet and outlet flash streams. The greater volatility of methanol and higher cooking temperature of the methanol cook determine a higher recovery for methanol (50.7%) than for ethanol (46.5%) as flash vapors. From these values it can be seen that a substantial amount of alcohol is recovered in both cases, which shows the importance of the flash stage in the economy of the recovery system. The high recovery is due to the fact that the black liquor enthalpy is used in the separation. Although the amount of water recovered is moderate, it also helps to reduce the water consumption. In spite of the fact that furfural and acetic acid have high boiling points, significant amounts of these substances can be found in the flash vapors. The occurrence of these substances might become a drawback because they can scale up due to solvent reuse.

Lignin Precipitation

The results in Table 3 indicate that the precipitation of the lignin contained in the concentrated black liquor leaving the flash can be accomplished successfully by dilution with water. The dilution of the concentrated black liquor does not imply a significant increase of the pH owing to the buffering effect of acetic acid and other organic acids released by wood during the cook. As can be seen in Table 3, the lignin precipitation yield for ethanol black liquor increases as the dilution ratio is raised. A substantial increment of the precipitation yield (from 59.9 to 67.0%) is attained when the dilution ratio changes from 1:0.79 to 1:1.68. However, the increase of the precipitation yield is low from a dilution ratio of 1:1.68. Therefore, a dilution ratio of 1:1.68 is the most appropriate ratio to use. The use of very high dilution ratios would lead to a great volume of mother liquors and a great consumption of energy at the distillation stage.

A different behavior can be observed for methanol black liquor precipitation. Thus, the lignin precipitation yield is higher for methanol black liquor (65.1% for 1:0.63) than for ethanol black liquor at low dilution ratios (59.9% for 1:0.79). The precipitation yield increases slightly when the dilution ratio rises from 1:0.63 to 1:1.45, and it decreases significantly from 1:1.45. In this case a dilution ratio of 1:0.63 has been chosen as the most suitable ratio since it enables a precipitation yield very close to the maximum and does not involve a high volume of precipitation mother liquors. The difference in behavior observed between the ethanol and methanol lignin in the precipitation study may be caused by the different molecular weight distributions and functional groups contents. Thus, the methanol lignin is more soluble, due to its higher functional groups content and lower molecular weight. This leads to a lower precipitation yield.

The results of lignin precipitation for different pH values at the dilution ratios selected above are contained in Table 4. In the case of ethanol, the effect of pH on the increment of the precipitation yield is very low. This yield varies

TABLE 3
Lignin Precipitation Yield vs Black Liquor Dilution

Ethanol		Methanol	
Dilution	Precipitation yield (%)	Dilution	Precipitation yield (%)
1 : 0.79	59.9	1 : 0.63	65.1
1 : 1.68	67.0	1 : 1.45	67.6
1 : 2.58	67.1	1 : 2.27	63.3
1 : 3.48	68.3	1 : 3.09	60.8
1 : 4.38	67.5	1 : 3.90	58.6

TABLE 4
Lignin Precipitation Yield vs pH

	Precipitation yield (%)	
pH	Ethanol, dilution 1 : 1.68	Methanol, dilution 1 : 0.63
3	67.1	67.6
2	67.6	70.3
1	68.5	72.1

between 67.1 and 68.5%. Therefore, the use of acid to improve lignin precipitation is not recommended. For the methanol black liquor a substantial increase of the precipitation yield can be attained by the addition of acid. A pH value of 2 is the most suitable because it allows a good precipitation yield (70.3%) for moderate acid consumption. The acidulation to pH 1 can be rejected since the incremental increase of precipitation yield does not justify the great increase of acid consumption. The lignin precipitation yields obtained are similar to the lignin precipitation yield for wheat straw soda black liquors (20) and lower than that for the kraft black liquors (21).

The properties of the lignin isolated at the precipitation conditions selected are shown in Table 5. Both lignins have similar properties. However, some differences can be observed. The molecular weight of the methanol lignin is lower than the molecular weight of ethanol lignin, as shown by the M_w value. The higher fraction of high molecular weight in the ethanol lignin can also be seen from the higher value of M_z. Likewise, this fact determines a wider molecular weight distribution, which is reflected in the higher polidispersity value (M_w/M_n). The functional groups content is slightly lower for ethanol lignin. The lignins isolated have a functional groups content and a molecular

TABLE 5
Lignin Characterization

	Ethanol	Methanol
M_w	3020	2778
M_n	1053	1197
M_w/M_n	2.87	2.32
M_z	9081	6135
Phenolic hydroxyl (%, w/w)	1.83	1.94
Carbonyl (mol/C_9)	10.7×10^{-4}	11.2×10^{-4}

weight distribution similar to those of other organosolv lignins that have been successfully employed as components of ligno-phenol-formaldehyde resins (22).

Solvent and By-Products Recovery System

The usual recovery system for organosolv black liquors includes flashing of the black liquor, lignin precipitation, and distillation of precipitation mother liquor, as shown by others (4, 6, 23). The recovery system proposed for the continuous process, illustrated in Fig. 1, can be simulated from the experimental results, which have been obtained in batch runs.

The lower heat of evaporation and higher volatility of the alcohol compared to water enables its partial recovery at the flash stage. The overhead vapor, which contains alcohol, water, acetic acid, and furfural, is condensed and sent to the cooking stage. As was mentioned above, the concentration of furfural and acetic acid in the condensate is significant. The rise in black liquor concentration for these substances due to solvent reuse is described by the following expression:

$$C = C_i \left(1 + \frac{100 - x}{x}\right) \sum_{j=1}^{n} \left(\frac{y}{100}\right)^j \tag{1}$$

where C is the concentration in the black liquor after j alcohol reuse cycles, C_i is the concentration in the black liquor for a batch cook, y is the percentage of black liquor by-passed around the flash stage, and x is the percentage of the substance evaporated at the flash stage. The accumulation of acetic acid will be higher than that of furfural since its volatility is also higher. The effect of

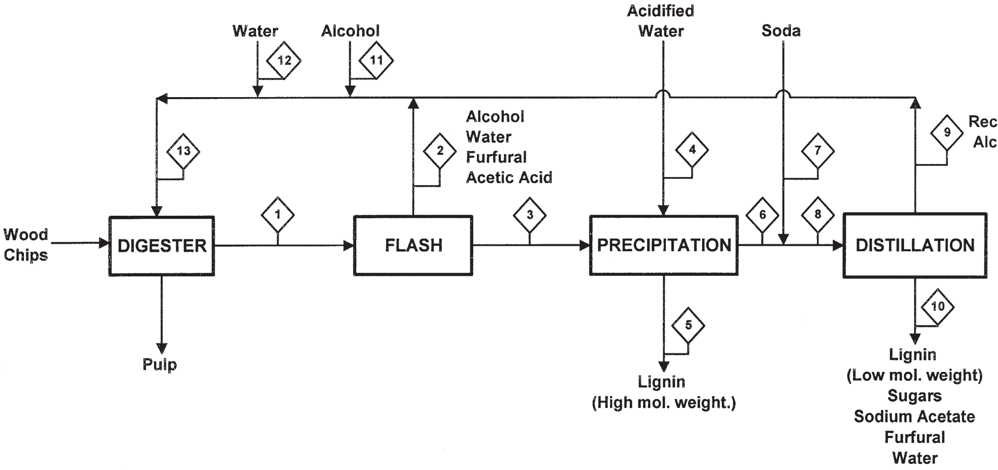

FIG. 1 Pulping and recovery system studied.

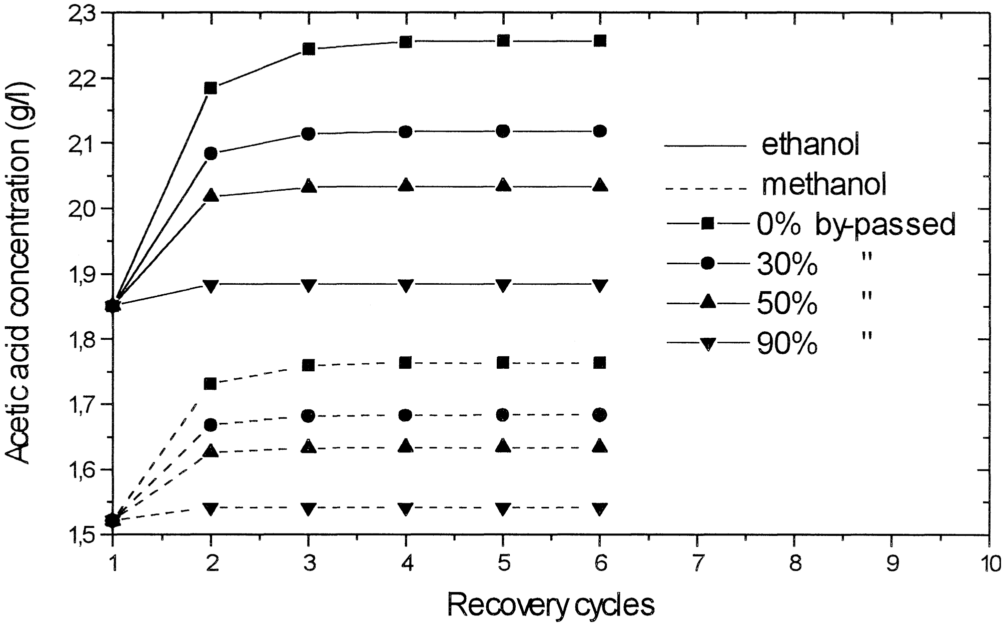

FIG. 2 Acetic acid concentration in black liquor vs alcohol reuse cycles.

alcohol reuse on the acetic acid concentration as a function of the percentage of black liquor by-passed around the flash stage is shown in Fig. 2. In this figure the effect of black liquor by-passing on acetic acid accumulation is also shown. A flash stage without black liquor by-pass would result in a rise in the acetic acid concentration of the black liquor. This rise would have values of 22 and 16% for the ethanol pulping and methanol pulping, respectively. In both cases it would not lead to a significant change in the acidity of the pulping medium since the acids released by the wood are weak and the cooking medium is buffered. In the case of furfural, the rise in the concentration has a value of 6.9 and 4.0% for the ethanol and methanol pulping, respectively. Therefore, the accumulation of volatile species can be considered as acceptable. If part of the black liquor were by-passed around the flash stage, the accumulation would be lower. For instance, in the ethanol pulping when 30% of the black liquor is by-passed, the rise in the acetic acid concentration has a value of 13%. However, the enthalpy of the black liquor by-passed cannot be used in the flash stage. To summarize, the black liquor by-pass around the flash stage is not necessary.

At the precipitation stage the lignin fraction with a higher molecular weight is separated as a precipitate whereas the low molecular weight lignin remains dissolved in the precipitation mother liquors. These mother liquors also contains sugars, acetic acid, and furfural. Prior to the distillation tower, soda is added to the mother liquors (6). The addition of soda avoids lignin precipitation in the stripping section of the distillation tower, where the alcohol concentration drops dramatically. It also neutralize organic acids (i.e., acetic acid) which are recovered in the distillation residue as sodium organic salts and prevents their recovery in the distillate.

The simulation of the distillation showed that the distillate contains only traces of furfural due to its high boiling point (162°C). The first plate of the rectification section of the distillation tower does not contain nonvolatile substances, such as sugars, lignin, and organic acids salts, but contains a significant amount of furfural. A side draw from this plate could be sent to another distillation tower where furfural would be obtained as a distillation residue and the distillate would contain the alcohol and the water (4). This alternative would also increase water recovery. The recovery of furfural as a chemical commodity could improve the economics of an acidic organosolv process. However, the recovery of furfural could be difficult due to its low concentration in the black liquor. The solvent recovered at the distillation stage is sent to the cooking stage after mixing with the flash condensate and with make-up streams of water and alcohol. The distillation residue can be concentrated and marketed as a syrup or it can be spray dried.

The simulation of the distillation allowed us to determine the number of plates of the distillation tower needed for different alcohol recovery yields. The results are plotted in Fig. 3. The number of plates needed for the distillation column is moderate up to an alcohol recovery yield of about 96–98%.

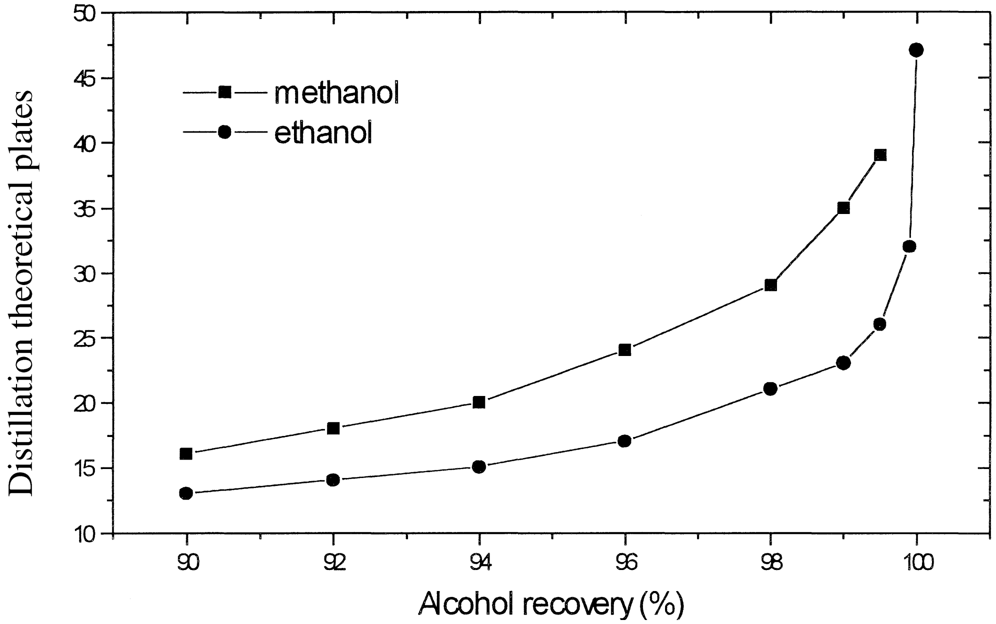

FIG. 3 Distillation plates vs alcohol recovery.

TABLE 6
Mass Balance for the Ethanol Process[a]

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
Alcohol	47.98	22.31	25.67			25.67		25.67	25.16	0.51	0.51		47.98
Water	47.98	13.34	34.64	109.5		144.14		144.14	1.05	143.09		33.59	47.98
Furfural	0.080	0.0052	0.075			0.075		0.075	Traces	0.075			0.0052
Acetic acid	0.24	0.043	0.20			0.20						0.043	
Lignin	3.04		3.04		2.04	1.00		1.00		1.00			
Xylose	0.19		0.19			0.19		0.19		0.19			
Glucose	0.16		0.16			0.16		0.16		0.16			
Galactose	0.095		0.095			0.095		0.095		0.095			
Arabinose	0.15		0.15			0.15		0.15		0.15			
Mannose	0.11		0.11			0.11		0.11		0.11			
Soda							0.13						
Sodium acetate								0.27		0.27			

[a] Basis: 100 weight units of black liquor at the digester outlet.

From this yield range the number of plates of the column increases remarkably as the alcohol recovery is raised, which means higher investment and operating costs. According to Fig. 3, the most suitable recovery yield for the distillation stage is 98% for ethanol and 96% for methanol, which can be accomplished with 21 and 24 plates towers, respectively. The feed plate of the towers calculated are the 10th for ethanol and the 14th for methanol.

TABLE 7
Mass Balance for the Methanol Process[a]

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
Alcohol	47.68	24.17	23.51			23.51		23.51	22.57	0.94	0.94		47.68
Water	47.68	10.35	37.33	40.94		78.27		78.27	Traces	78.27		37.33	47.68
Furfural	0.11	0.0039	0.10			0.10		0.10	Traces	0.10			0.0039
Acetic acid	0.15	0.021	0.13			0.13							0.021
Lignin	2.90		2.90		2.04	0.86		0.86		0.86			
Xylose	0.52		0.52			0.52		0.52		0.52			
Glucose	0.34		0.34			0.34		0.34		0.34			
Galactose	0.15		0.15			0.15		0.15		0.15			
Arabinose	0.23		0.23			0.23		0.23		0.23			
Mannose	0.067		0.067			0.067		0.067		0.067			
Soda							0.088						
Sodium acetate								0.18		0.18			
Sulfuric acid				0.052		0.052							

[a] Basis: 100 weight units of black liquor at the digester outlet.

Recovery System Mass Balance

The recovery system mass balance for a continuous process is shown in Tables 6 and 7, where the number of the streams correspond to those indicated in Fig. 1. The mass balance was established from the separation yield for the different species at each stage and was calculated on the basis of 100 weight units of black liquor leaving the digester. It is an approximate balance since it does not take into account minor constituents such as tars, extractives, lipids, and carbohydrate degradation products. The results obtained in this study are in general in good agreement with those reported by others (24, 25). In these works it has also been shown that cellulose accounts for 50–55% of the initial dry wood weight, and the main by-products (high molecular weight lignin, sugars, furfural, and acetic acid) for 25–30%; the rest, about 20%, are tars, extractives, lipids, and other wood degradation products.

The main characteristics of methanol and ethanol processes are summarized in Table 8. The dilution factor needed for ethanol black liquor precipitation is higher than for methanol, so a higher amount of precipitation mother liquor is fed to the distillation tower. This means greater energy consumption at this stage. On the other hand, sulfuric acid is not needed to precipitate ethanol black liquor, which reduces the cost of chemicals. The consumption of soda is similar in both processes. Alcohol consumption is higher for the methanol process than for the ethanol process (2.0 vs 1.1%); however, this is not a seri-

TABLE 8
Comparative Study between Ethanol and Methanol Processes

	Ethanol	Methanol
Dilution ratio at precipitation stage	1:1.68	1 : 0.63
pH at precipitation stage	3.4	2
Dilution water at precipitation stage (L/kg wood)	7.27	2.75
H_2SO_4 consumption (g/kg wood)	—	3.49
NaOH consumption (g/kg wood)	8.62	5.9
Distillation tower feed (l/kg wood)	11.6	7.11
Distillation plates	21	24
Make-up alcohol (%)	1.06	1.97
Make-up water (%)	70.0	78.3
Pulp (g/kg wood)	558	543
High molecular weight lignin (g/kg wood)	135.4	137
Low molecular weight lignin (g/kg wood)	66.4	57.8
Sugars production (g/kg wood)	46.8	87.8
Sodium acetate (g/kg wood)	17.9	12.1
Furfural production (g/kg wood)	4.98	6.72

ous disadvantage for the methanol process since methanol is cheaper than ethanol. The amount of by-products obtained in both processes is similar. The main difference is the higher amount of sugars produced in the case of methanol.

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REFERENCES

1. P. Stockburger, "An Overview of Near-Commercial and Commercial Solvent-Based Pulping Processes," *Tappi J.*, *76*(6), 71–74 (1993).
2. S. Aziz and K. Sarkanen, "Organosolv Pulping—A Review," *Ibid.*, *72*(3), 169–175 (1989).
3. A. Jöhansson, O. Aaltonen, and P. Ylinen, "Organosolv Pulping–Methods and Pulp Properties," *Biomass*, *13*(1), 45–65 (1987).
4. E. K. Pye and J. H. Lora, "The Alcell Process," *Tappi J.*, *74*(3), 113–118 (1991).
5. T. Laxen, "The Characteristics of Organosolv Pulping Discharges," *Pap. Puu*, *69*(5), 417–421 (1987).
6. P. N. Williamson, "Repap's Alcell Process: How It Works and What It Offers," *Pulp Pap. Can.*, *88*(12), 47–49 (1987).
7. G. Dahlmann and C. Schroeter, "The Organocell Process—Pulping with the Environment in Mind," *Tappi J.*, *73*(4), 237–240 (1990).
8. Y. Ni, C. Dixon, and T. Ooi, "Kinetics of Hydrogen Peroxide Bleaching of Alcell Derived Pulp," *Can. J. Chem. Eng.*, *75*(1), 48–52 (1997).
9. R. A. Northey, "Low-Cost Uses of Lignin," *ACS Symp. Ser.*, *476*, 146–175 (1992).
10. O. Bobleter, "Hydrothermal Degradation of Polymers Derived from Plants," *Prog. Polym. Sci.*, *19*, 797–841 (1994).
11. J. J. Lindberg, K. Levon, and T. Kuusela, "Modification of Lignin," *Acta Polym.*, *39*(1/2), 47–50 (1988).
12. O. Faix, "New Aspects of Lignin Utilization in Large Amounts," *Papier*, *12*, 733–739 (1992).
13. M. A. Gilarranz, M. Oliet, F. Rodriguez, and J. Tijero, "Ethanol–Water Pulping: Cooking Variables Optimization," *Can. J. Chem. Eng.*, *76*(2), 253–260 (1998).
14. M. A. Gilarranz, M. Oliet, F. Rodríguez, and J. Tijero, "Methanol-Based Pulping of *Eucalyptus globulus*," *Ibid.*, *77*(3) (1999).
15. F. Santos, F. Rodríguez, M. A. Gilarranz, D. Moreno, and F. García-Ochoa, "Kinetic Modelling of Kraft Delignification of *Eucalyptus globulus*," *Ind. Eng. Chem. Res.*, *36*(10), 4114–4125 (1997).
16. D. T. Thrin, "The Measurement of Lignin in Kraft Pulping Liquors Using an Automatic Colorimetric Method," *J. Pulp Pap. Sci.*, *14*(1), 19–22 (1988).
17. Y. Z. Lai, "Determination of Phenolic Hydroxyl Groups," in *Methods in Lignin Chemistry*, Springer-Verlag, New York, NY, 1992, pp. 423–434.
18. C. L. Chen, "Determination of Carbonyl Groups," in *Methods in Lignin Chemistry*. Springer-Verlag, New York, NY, 1992. pp. 446–457.
19. M. Cronlund and J. Powers, "Bleaching of Alcell Organosolv Pulps Using Conventional and Nonchlorine Bleaching Sequences," *Tappi J.*, *75*(6), 189–194 (1992).

20. M. A. Gilarranz, F. Rodríguez, M. Oliet, and J. A. Revenga, "Acid Precipitation and Purification of Wheat Straw Lignin," *Sep. Sci. Technol*., *33*(9), 1359–1377 (1998).
21. V. C. Uloth and J. T. Wearing, "Kraft Lignin Recovery: Acid Precipitation Versus Ultrafiltration," *Pulp Pap. Can*., *90*(9), 67–71 (1989).
22. T. Sellers Jr., J. H. Lora, and M. Okuma, "Organosolv-Lignin-Modified Phenolics as Strandboard Binder. I. Organosolv Lignin and Modified Phenolic Resin," *Mokuzai Gakkaishi*, *40*(10), 1073–1078 (1994).
23. G. Petty, "Canadians Pioneer a Small-Scale Pulp Mill," *Pap. Technol*., *30*(2), 10–13 (1989).
24. R. C. Myerly, M. D. Nicholson, R. Katzen, J. M. Taylor, "The Forest Refinery," *Chemtech*, pp. 186–192 (March 1981).
25. J. H. Lora, E. K. Pye, S. R. Winner, "Industrial Scale Alcohol Pulping," *AIChE Proc*., *For. Prod. Symp. 1989–90*, pp. 35–39 (1992).

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