Lignin removal from Alcell® pulp by washing with ethanol and water

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ABSTRACT

Washing of ethanol-based organosolv pulp (Alcell® process) in a solution of ethanol–water can reduce lignin content significantly. This study presents the results of a laboratory study designed to optimize the washing process for maximum lignin removal. Washing was carried out in a stirred batch reactor and in a displacement-washing cell. Lignin-removal efficiency was much higher in the displacement-washing cell. Key displacement-washing operating parameters (temperature, superficial velocity, ethanol concentration, and pulp consistency) were varied to determine their effects on lignin removal. The results are interpreted in terms of lignin solubility in the wash liquor and diffusion of dissolved lignin from the fiber wall. The results show that displacement washing can delignify the organosolv pulp from an initial kappa no. 54 to kappa no. 25.

Application

The results reported here suggest ways to improve lignin removal from ethanol-based organosolv pulp, particularly through displacement washing.

THE ALCELL® PROCESS IS AN ethanol-based, autocatalyzed solvent-pulping technology that is being implemented in a demonstration plant in Newcastle, NB (Repap Enterprises Inc.). The process typically yields a pulp of about kappa no. 50. Additional washing with a 50% (v/v) ethanol–water solution for 5 min at room temperature (1% pulp consistency) can further reduce lignin content to about kappa no. 32–33. Because the washing conditions are so mild, chemical reaction cannot be responsible for this large amount of lignin removal.

Economics and environmental concerns dictate that the kappa number of the pulp entering the bleach plant be as low as possible. Since a large fraction of the lignin in this solvent pulp can be washed out by an ethanol–water solution, it is very important to optimize this washing operation.

Washing is generally achieved by means of either dilution/thickening, displacement, or a combination of these two processes. Dilution and thickening requires a large amount of wash liquor. Moreover, washing efficiency is limited by the lignin content in the dilution liquor and the maximum consistency to which the pulp can be thickened after dilution. On the other hand, in displacement washing, wash liquor is forced to flow through a pulp pad, fibers are continuously contacted with the fresh wash liquor, and lignin is continuously removed with the spent wash liquor. Therefore, with the same amount of wash liquor, displacement washing is generally more efficient in removing lignin than dilution/thickening.

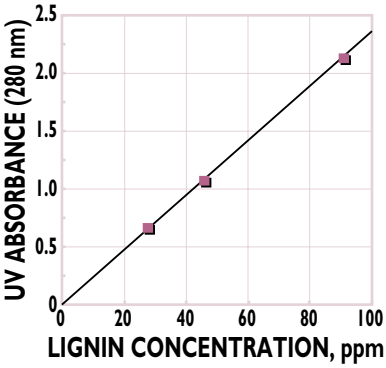
The factors affecting the displacement-washing efficiency of chemical pulp, such as kraft, have been examined in several studies *(1–4)*. However, there has been no systematic investigation of the washing of Alcell® pulp. In this paper, lignin removal from this ethanol-based solvent pulp is studied in a stirred batch reactor and then in a displacement setup. The objective was to optimize the washing operation by studying the effects of key operating variables on lignin removal.

EXPERIMENTAL

The pulp samples used in the experiments (Alcell Developments Inc., Newcastle, NB) were stored in a refrigerator. The brownstock pulp—produced from a mixture of birch, maple, and poplar—had a kappa number of 54.0. Pulp kappa number before and after washing was measured according to the appropriate CPPA standard.

The stirred batch reactor was a simple 2-L container. Equivalent to 10.0 g of moisture-free brownstock pulp was first mixed with about 400 g of water and disintegrated in a blender. Ethanol and water were then added so that the ethanol concentration was 50% (v/v) and the pulp consistency was 1.0%. Continuous mixing was provided by a mechanical stirrer. Timing was started immediately after ethanol addition. The experimental run was terminated by diluting the pulp slurry in a large amount of water after a specified amount of time (3 min, 5 min, 15 min, and 45 min). The pulp was then made into a handsheet and air-dried for kappa-number analysis.

The displacement-washing experiments were performed in a stainless-steel displacement cell constructed by Ali *(5)*. The cylindrical cell is 200mm high and has an inside diameter of 75 mm. The pulp was disintegrated in a stainless-steel blender in deionized water for about 20 s at a consistency of 0.05% and then poured into the cell while draining. The packed beds were then formed by draining the pulp suspension. After drainage, the



I. Calibration of lignin concentration vs. UV absorption at 280 nm

Time, min	Kappa number
0	54.0
3	33.0
5	31.2
15	30.6
45	30.7

* Ethanol water solution 50% (v/v), temperature 23°C, pulp consistency 1%

*I. Effect of mixing time on kappa-number reduction in a continuously stirred tank **

Wash Stage	Kappa number
...	54.0
1	31.6
2	26.1
3	23.9
4	21.1

* Pulp at 1% consistency washed in four consecutive stages with fresh 50% (v/v) ethanol water solution for 5 min at 23°C

*II. Effect of multiple-stage washing on kappa-number reduction in a continuously stirred tank **

packed beds were compacted to the desired bed height so that the specified pulp consistency could be achieved.

Displacement washing was simulated by pumping an ethanol–water mixture through the pulp bed with a peristaltic pump. Mixing-cup samples collected at the exit of the displacement reactor were analyzed for lignin concentration with an ultraviolet (UV) spectrometer (at a wavelength of 280 nm). A typical calibration curve for the lignin concentration (mg/L, termed as ppm) and UV absorption is presented in **Fig. 1**, which shows that the straight-line relationship between the two was excellent. The experimental variables were temperature, ethanol concentration in the wash liquor, superficial velocity, and pulp consistency.

The mean residence time of the fiber bed was characterized by tracer test with a 30-g/L glucose solution. The glucose concentration in the samples collected during the tracer test was measured with a polarimeter (Rudolph Research model no. Autopol 111-589-10).

	Temperature, °C	Superficial velocity, mL/min	Ethanol concentration, % (v/v)	Pulp consistency, %
Fig. 2	23, 52, 63	108	50	9.7
Fig. 3	63	43, 108, 237	50	9.7
Fig. 4	52	108	50, 70, 90	9.7
Fig. 5	63	108	50	9.7, 14.7

* Bed height = 4 cm

*III. Experimental variables for displacement-washing results illustrated in Figs. 2–5**

RESULTS AND DISCUSSION

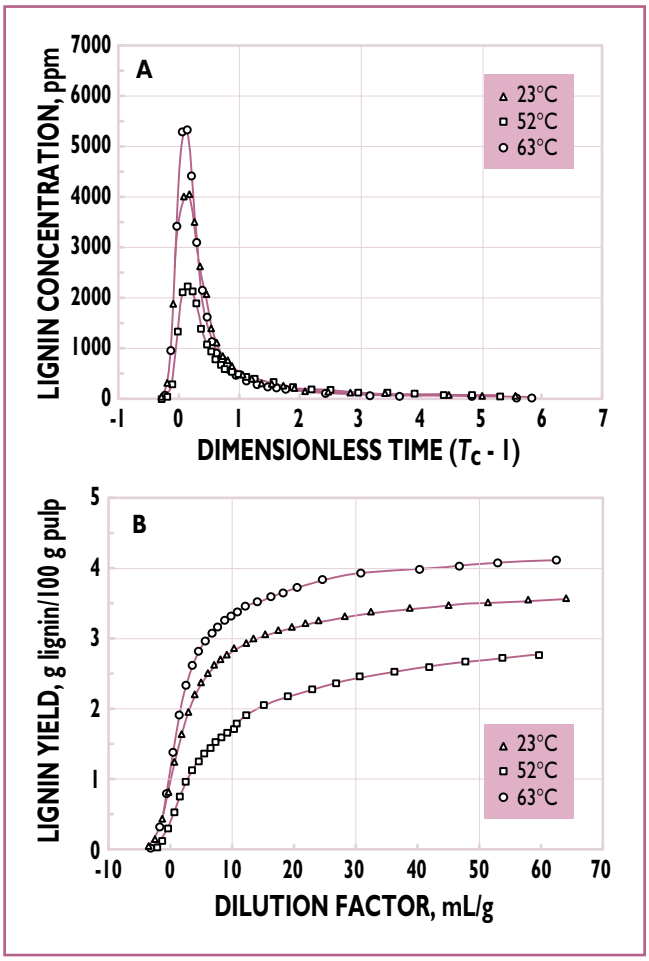
Washing in a stirred batch reactor

Lignin diffusion from the pulp fibers during washing affects the efficiency of the washing process. The impact of lignin diffusion was evaluated by investigating the effect of mixing time on lignin removal. **Table I** shows the decrease in kappa number as a function of mixing time for pulp washed in 50% (v/v) ethanol–water at 23°C and 1% consistency. While the initial decrease in kappa number is very rapid, it reaches a constant value after about 5 min.

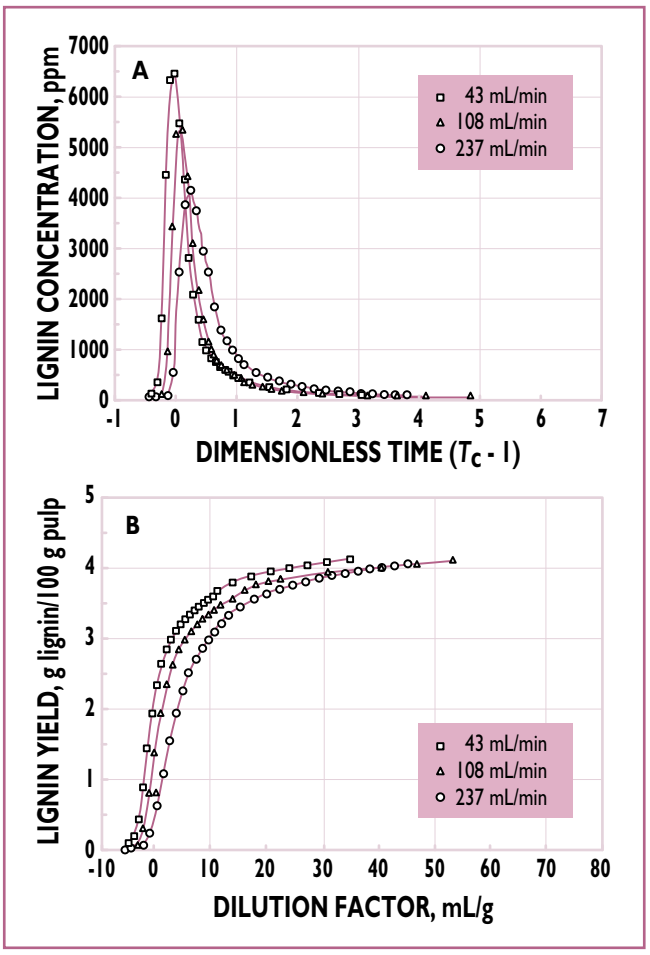
In the next set of experiments, the same pulp sample was subjected to multiple washings with fresh 50% (v/v) ethanol–water at 23°C and 1% consistency. A mixing time of 5 min was chosen for each washing stage. **Table II** presents the data for four consecutive washing stages. These results show that the kappa number can be reduced by an additional 10 units during the last three wash stages. It is also apparent that lignin removal stops after about 5 min of washing, a consequence of the increased lignin concentration in the wash liquor. This implies that maximum lignin removal can be achieved with displacement washing, since this would place the fibers in continuous contact with fresh wash liquor.

Displacement washing

The efficiency of lignin removal during displacement washing was evaluated for a range of operating conditions. Four variables were investigated—temperature, superficial velocity, ethanol concentration, and pulp consistency. The experimental design was to vary a single parame-



2. Effect of temperature on lignin removal. (Other experimental conditions are listed in Table III.)



3. Effect of superficial velocity on lignin removal. (Other experimental conditions are listed in Table III.)

ter while holding the other three constant. **Table III** shows the operating conditions for the laboratory experiments.

Temperature. The effect of temperature on displacement washing was the first variable investigated. The results are shown in **Fig. 2**. Washing was carried out at three temperatures: 23°C, 52°C, and 63°C. The other experimental conditions were held at the constant values shown in Table III. The corresponding mean residence time of the fiber bed was about 2.6 min.

Figure 2A shows the lignin concentration, *[L],* as a function of (T_c – 1), where T_c is the dimensionless time defined as

$$T_c = (t - \bar{t}_d)/(\bar{t}_r - \bar{t}_d) \quad (1)$$

where

t = average sample time

$\bar{t}_d$ = mean residence time resulting from the dead volume

$\bar{t}_r$ = mean residence time in the actual pulp bed.

Both $\bar{t}_r$ and $\bar{t}_d$ are determined from the corresponding glucose step-change response curve by the following relationship

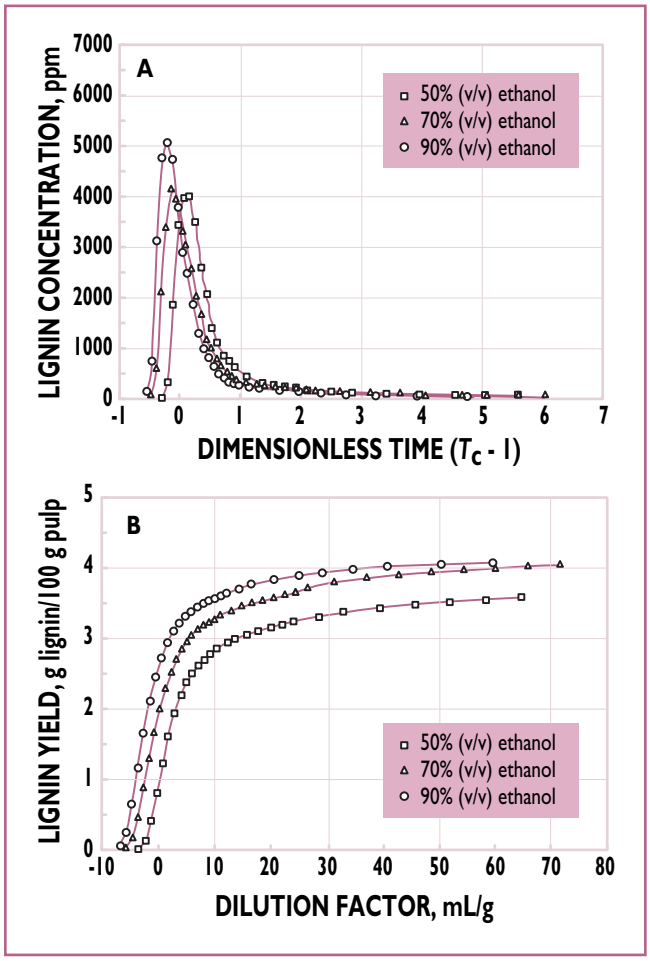
$$\bar{t}_r \text{ or } \bar{t}_d = \int_o^\infty \left(1 - C/C_o\right) dt \quad (2)$$

where

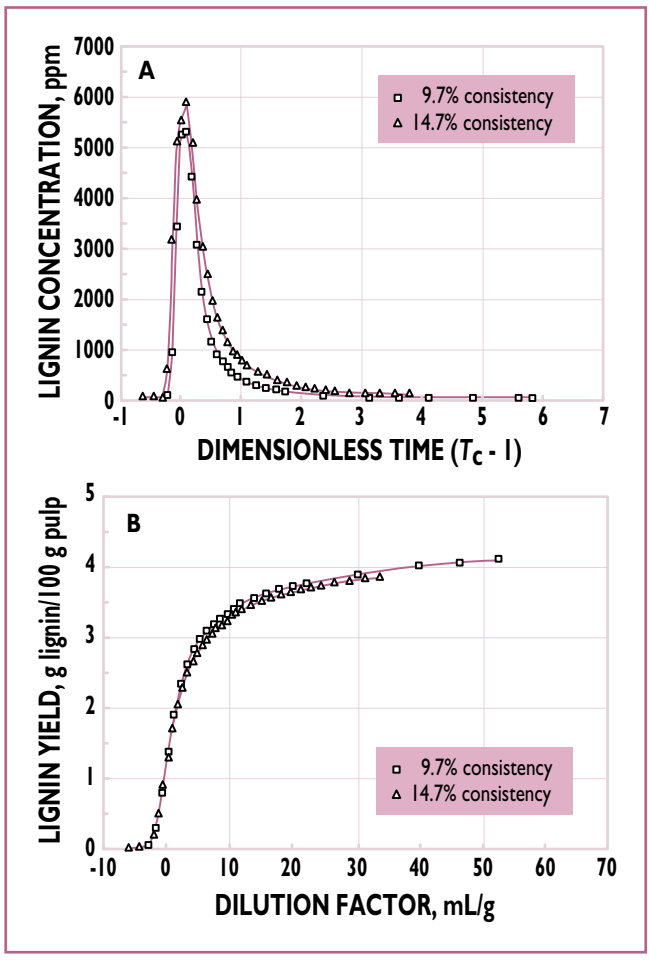
C = glucose concentration.

Figure 2A shows that the lignin concentration at the exit increases rapidly to a maximum, decreases sharply, and finally reaches an asymptotical concentration. The lignin concentration curve can be characterized by the maximum lignin concentration, $[L]_{max}$, and the total amount of lignin, L_t, removed during washing. L_t is calculated as shown in Eq. 3.

$$L_t = \int_0^t [L]\, Q_v\, dt \quad (3)$$



4. Effect of ethanol concentration on lignin removal. (Other experimental conditions are listed in Table III.)



5. Effect of fiber consistency on lignin removal. (Other experimental conditions are listed in Table III.)

where

Q_v = wash-liquor flow rate.

Lignin yield—depicted in Fig. 2B—is the value of L_t per 100 g of pulp.

Figure 2A also shows that $[L]_{max}$ increases dramatically with increasing temperature. This suggests that the solubility of lignin in 50% (v/v) ethanol–water increases strongly as the washing temperature increases. The lignin breakthrough at 23°C also appears to be slightly later. This is probably because the diffusion of lignin is slower at lower temperature.

The lignin yield is plotted against the dilution factor in Fig. 2B. The dilution factor is defined as the volume of wash liquor minus the volume of liquor originally in the fiber bed, divided by the weight of the dry fibers. Figure 2B shows that the lignin yields after washing at 23°C, 52°C, and 63°C were, respectively, 2.86, 3.61, and 4.13 g/100 g pulp. Clearly, much more lignin can be washed out at higher temperature. As explained earlier, this is probably because of the higher solubility of lignin in ethanol–water at higher temperature.

The kappa numbers of the final washed pulps at 23°C, 52°C, and 63°C in Fig. 2 were determined as 33.5, 29.4, and 25.6, respectively. Lignin removal during washing can also be calculated from the difference in kappa number before washing (kappa no. 54.0) and after washing at each temperature level. With a factor of 0.145 (determined experimentally) to convert kappa number into lignin content based on percentage on pulp, the calculated lignin yields were 2.97, 3.57, and 4.12 g/100 g pulp at 23°C, 52°C, and 63°C, respectively. Comparison of these calculated values with the final lignin yields depicted in Fig. 2B shows a closed lignin mass balance, lending confidence to the accuracy of the lignin-breakthrough curves.

Superficial velocity. The effect of superficial velocity on lignin removal during displacement washing is illustrated in **Fig. 3**. The

KEYWORDS
Alcohols, chemical reactions, delignification, diffusion washing, ethanol, mixtures, organosolv pulps, process variables, pulps, variables, washing, water.

superficial velocities were 43 mL/min, 108 mL/min, and 237 mL/min. The corresponding mean residence times (t_r) were 6.17 min, 2.68 min, and 1.16 min, respectively. The other experimental conditions were held at the constant values listed in Table III. Since the superficial velocity is inversely proportional to the mean residence time, Fig. 3 can also be interpreted in terms of residence time.

Figure 3A shows that the maximum lignin concentration, $[L]_{max}$, increases with increasing residence time, while the tailing of the lignin breakthrough curve increases with decreasing residence time. This implies that lignin diffusion must be rate-limiting in the experiment with the shortest mean residence time.

The lignin yield vs. dilution factor in Fig. 3B shows that the final lignin yield is independent of the residence time. However, at a more practical dilution factor of 3.0 mL/g, the lignin yields are 3.1, 2.7, and 1.8 g/100 g pulp at a t_r of 6.17 min, 2.68 min, and 1.16 min, respectively. This shows that, in practice, sufficient residence time must be provided to achieve efficient displacement washing for this solvent pulp.

Ethanol concentration. The effect of ethanol concentration on lignin removal during displacement washing is shown in **Fig. 4.** Ethanol concentrations were 50%, 70%, and 90%. The other experimental conditions were held at the constant values listed in Table III.

Figure 4A shows that the maximum lignin concentration, $[L]_{max}$, is slightly higher and occurs at smaller values of (T_c – 1) with increasing ethanol concentration. Since the mean residence time is the same in the three experiments, these results suggest that the diffusion coefficient of lignin is higher at higher ethanol concentrations.

Figure 4B shows that the final lignin yield at 50%, 70%, and 90% ethanol concentrations were 3.61, 4.08, and 4.14 g/100 g pulp, respectively. The kappa numbers of these washed pulps were 29.4, 26.4, and 25.5, respectively. The corresponding calculated final lignin yields were, respectively, 3.57, 4.0, and 4.13 g/100 g pulp, in good agreement with the experimental values. At a more practical dilution factor of 3.0 mL/g, the lignin yields are 2.0, 2.7, and 3.1 g/100 g pulp at ethanol concentrations of 50%, 70%, and 90%, respectively. These results also show that the final lignin yield at 70% ethanol concentration is slightly lower than that at 90% ethanol concentration, while lignin removal at 50% ethanol concentration is almost four kappa-number units less than that at 90% ethanol.

Pulp consistency. The effect of pulp consistency in the fiber bed is shown in **Fig. 5**. Pulp consistencies were 9.7% and 14.7%. The other experimental conditions were held at the constant values listed in Table III. Figure 5 shows that consistency has no effect on displacement washing of the ethanol-based organosolv pulp.

CONCLUSION

A substantial amount of lignin can be removed from Alcell pulp (an ethanol-based organosolv pulp) by washing with an ethanol–water solution. Displacement washing offers much better results than a stirred batch operation. Experimental results show that a brownstock pulp at an initial kappa no. 54 can be delignified to about kappa no. 25 by an extended displacement washing. At a more practical dilution factor of 3.0 mL/g (while washing with a 50% ethanol concentration at 63°C for a mean residence time of 6.17 min), 3.1 g lignin/100 g pulp—corresponding to kappa units of 21.4—can be removed.

Lignin removal during displacement washing can be increased by increasing the temperature and ethanol concentration. The increase in lignin removal is probably because of the higher lignin solubility under these conditions. A contact time of about 10 min is required to achieve maximum lignin removal and avoid diffusion limitations for lignin during displacement washing. The consistency of the fiber bed does not affect the washing results.

The results presented in this report were obtained under laboratory conditions, which are closer to ideal than those of an industrial washing operation. Nevertheless, we believe that the conclusions drawn from this study can be applied to an industrial setting. **TJ**

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