Effect of pH and Temperature on Lignin Precipitation During Kraft Pulping and Washing

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Abstract

Lignin precipitation during kraft pulping and pulp washing was evaluated by measuring kappa number gains and brightness losses in eucalypt kraft pulps treated with black liquor. Unbleached kraft pulp was mixed with black liquor and held for up to 180 min at pH between 5 and 11,5 and temperatures of 25, 60 and 90ºC. Significant pulp kappa number increases and brightness losses were only observed at pH ≤7.5 and temperatures ≥60ºC and were generally independent of reaction time. Thus, it is expected that lignin precipitation during the washing operation occurs only if mat pH is decreased to 7.5 or lower. Fully bleached kraft pulp was repulped at 90, 130 and 150ºC, and pH between 10 and 13. The results indicate that significant lignin precipitation during kraft pulping is quite unlikely, unless pH drops to 11 or lower. Xylan precipitation onto pulp fibres occur upon treatment with black liquor at pH 13. The impact of precipitated lignin and xylans on overall process yield, pulp bleachability and pulp quality is under evaluation.

INTRODUCTION

Lignin precipitation during pulping and washing has always been a major concern among bleached kraft pulp producers because it can lead to bleaching chemical waste and negatively affect pulp quality and bleachability. However, these are not concerns for unbleached pulp products, where precipitated lignin can result in yield gains, as first demonstrated by Hartler in his sorption cooking process (1). In this process, the pH of the black liquor is lowered to below 11,0 at the end of the cook, when lignin concentrations are high, in order to promote lignin precipitation on fibres. Lignin precipitation can also occur during pulp washing, when wash water pH is lowered below 10 (2,3), that is near or below the pKa of lignin free phenolic units (roughly 9-11, as cited in 4). Sundin and Hartler (4) demonstrated that lignin precipitation during pulp washing increases with increasing calcium ion concentration because ionized phenolic groups in lignin form complexes with calcium ions (or other multivalent ions), leading to coagulation and precipitation. The critical coagulation concentration of calcium was found to increase with increasing pH and decrease with increasing temperature (4).

A better understanding of conditions that promote or avoid lignin precipitation during pulping and washing will be useful to the kraft pulp industry. This study was undertaken to evaluate the impact of pH and temperature on lignin precipitation during kraft pulping and washing of eucalypt pulp.

Material and methods

Unbleached (kappa 17,2 and 36,7 % ISO brightness, 2109 ppm Ca) and bleached (90,7% ISO brightness, 168 ppm Ca) and black liquor samples were obtained from a Brazilian eucalypt kraft pulp mill. Black liquor samples had total solids contents of 15,2% (washing study) and 17,3% (pulping study).

Lignin precipitation during washing

The effects of reaction pH 5, 7, 5, 10 and 11, 5), time (15, 30, 60, 120 and 180 min) and temperature (25, 60 and 90ºC) on lignin precipitation during washing were simulated using bleached pulp samples. Black liquor (final concentration = 0,5 t total solids/t pulp), followed by sulfuric acid for pH adjustment (2%), were added to 10 g unbleached pulp samples in polyethylene bags. After manually mixing the samples, the temperature was adjusted by heating in a microwave oven, and the samples then maintained in a temperature controlled vapor bath, or at room temperature, for the desired reaction time. After completing the desired reaction time, the pulp samples were washed with excess distilled water and their pH adjusted to 5,5-6,0, before analysis of kappa number brightness.

Lignin precipitation during pulping

The effects of reaction pH (10, 11, 12 and 13) and temperature (90, 130 and 150°C) on lignin precipitation during pulping were evaluated by comparing results of reference cooks (without black liquor addition) to test cooks (with black liquor addition) of fully bleached kraft pulp (kappa number ~ 0). Black liquor, at a final concentration of 1,35 t total solids/t pulp, was added to bleached pulp samples followed by sodium hydroxide (reference cooks) or sulfuric acid (test cooks) for pH adjustment and distilled water for final consistency adjustment (7%). Samples were manually mixed and then transferred to an electrically heated, rotating autoclave, for pulping at a constant reaction time of 120 min. After completing the cooks, samples were exhaustively washed with tap water followed by distilled water, and their pH adjusted to 5,5-6 before analysis of kappa number and brightness.

Pulp and liquor analyses

Pulp kappa number and brightness and black liquor total, organic and inorganic solids were analyzed according to Tappi standard methods. Pulp xylan analysis was performed by HPLC using a refractive index detector, after acid hydrolysis of the pulp according to Klason method.

Percent lignin (and yield gain) was estimated from pulp kappa number using the formula (5):

Kappa number *0,15 = % lignin.

RESULTS AND DISCUSSION

Lignin precipitation during washing

The possibility of lignin precipitation on pulp was evaluated by reacting unbleached pulp with black liquor. The reaction time had little effect on pulp kappa number (Fig. 1 A-D), with the greatest kappa number changes observed at low pH (pH 5 and 7,5) and high temperature (60 and 90°C). The relatively lower kappa number observed at 90°C as compared to 60°C at pH 5 (Fig. 1A) is probably due to alkaline leaching, during the extended reaction period (180 min).

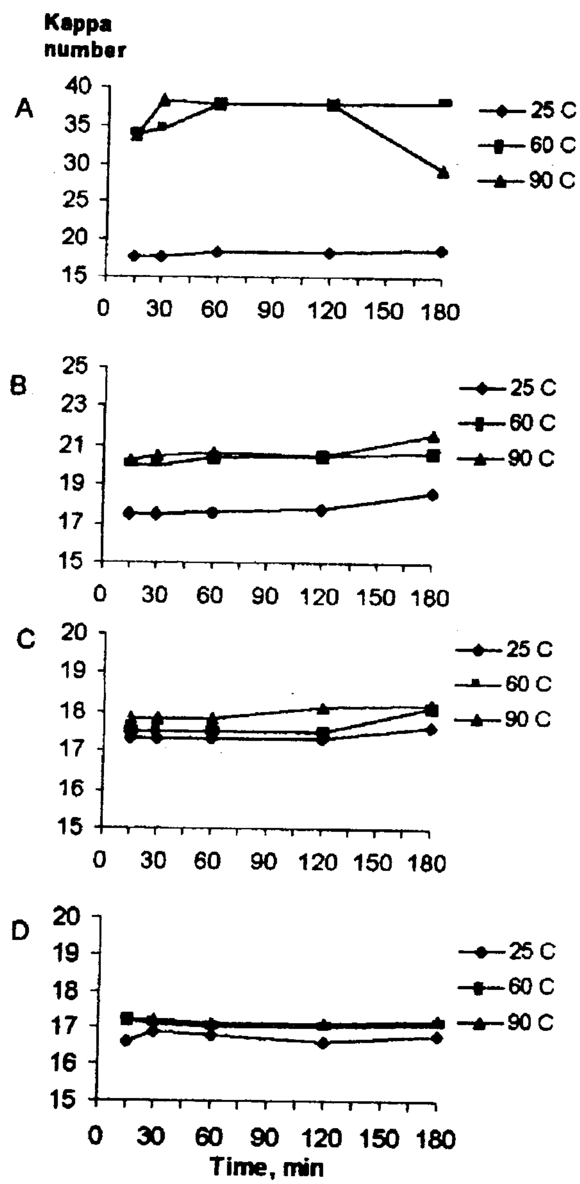

Fig. 1 Kappa number of unbleached eucalypt kraft pulp (original kappa 17,2) after mixing with black liquor (0,5 t solids/t pulp) for reactions carried out at (A) pH5, (B) pH 7,5, (C) pH 10 and (D) pH 11,5 at 3 different temperatures for up to 180 min.

It is apparent that the only significant kappa number increases over the original unbleached pulp occur at pH 5 (12-18 kappa units) and to a much lesser extent at pH 7,5 (3 units) when the temperature is raised to 60°C or higher. This can be seen clearly in Fig. 2, where kappa numbers differences are plotted against reaction pH for a 15-min reaction time. If the kappa gain is assumed to be derived solely from lignin precipitation, the kappa gains observed would represent a yield gain of 1,8-2,7% at pH 5. Given that the kappa number gain is due to lignin on the fibre surface, and not in the bulk fibre (6), even a small increase in kappa, could significantly affect pulp properties.

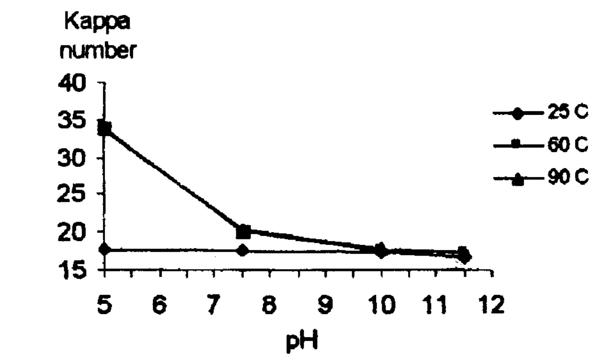

Fig. 2 Effect of reaction pH and temperature on kappa number of unbleached eucalypt kraft pulp (original kappa = 17, 2) after mixing with black liquor (0,5 t solids/t pulp) for 15 min.

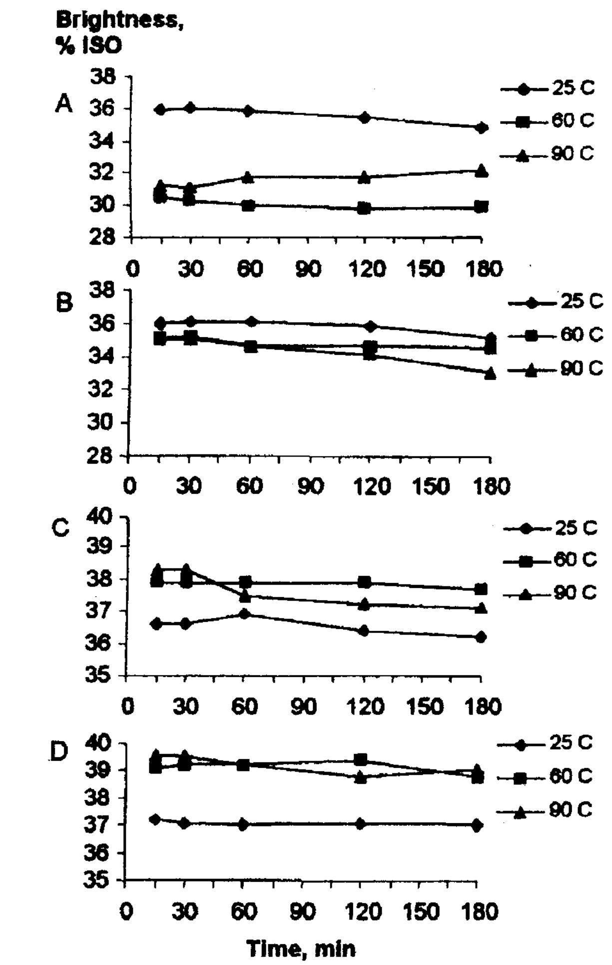

Fig. 3 Brightness of unbleached eucalypt kraft pulp (original brightness = 36,7% ISO) after mixing with black liquor (0,5 t solids/t pulp) for reactions carried out at (A) pH5, (B) pH 7,5, (C) pH 10 and (D) pH 11,5 at 3 different temperatures for up to 180 min.

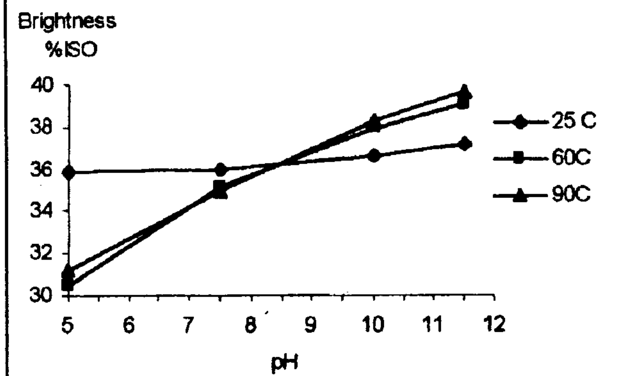

Fig. 4 Effect of reaction pH and temperature on brightness of unbleached eucalyptus kraft pulp (original brightness = 36,7% ISO) after mixing with black liquor (0,5 t solids/t pulp) for 15 min.

As expected from the kappa number results, pulp brightness values were also relatively independent of reaction time (Fig. 3 A-D). For pH values < 7, 5 brightness was higher brightness were achieved at the temperatures of 60 and 90°C. In general the higher pulp brightnesses were obtained at conditions that caused minimum lignin precipitation.

Significant brightness loss (up to 5% ISO) compared to the original unbleached pulp (36, 7% ISO) was only observed for high temperature treatments at pH 5 (Fig. 4), in agreement with the kappa number gains noted previously.

The results obtained are in accordance with the concept of critical coagulation concentration of calcium ions in the black liquor necessary for lignin precipitation (4). It has been shown previously that the critical coagulation concentration decreases with increasing temperature and decreasing pH (4). Given the constant calcium ion concentration in the black liquor used in this study, the amount of lignin precipitation (as measured by kappa gain) would be expected to increase with increasing temperature and decrease with increasing pH, as was observed (Fig. 2).

The relationship between kappa gain and brightness loss after washing varied non-linearly with reaction temperature and pH. At pH 5 and 60 or 90°C, the 12-18 unit kappa gain observed (Fig. 2) corresponded to a 5-6% brightness loss over the original pulp (Fig. 4), whereas at pH 5 and 25°C (Fig. 2), the kappa gain 1, 5 units) over the original pulp corresponded to a proportionally much greater

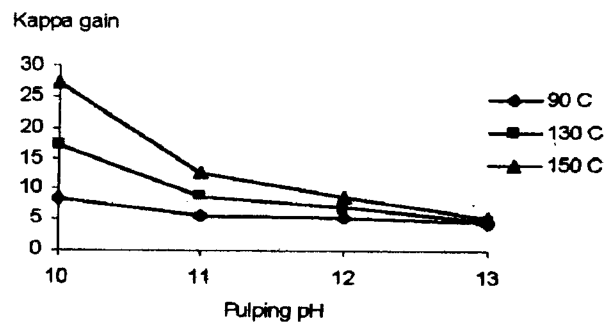

Fig. 5 Kappa number gain of bleached eucalypt kraft pulp upon addition of black liquor (1,35 t solids/t pulp) during pulping at different pH's and temperatures.

brightness loss of 1,8% (Fig. 4). At pH 11,5 and 60 or 90°C, there was no kappa change as compared to the original pulp (Fig. 2), but a brightness gain of 2-3% ISO was observed (Fig. 4), whereas at 25°C a kappa loss of 0,3 units (Fig. 2) actually corresponded to a brightness gain of 0,3% ISO (Fig. 4).

Lignin precipitation during pulping

The kappa number gain during pulping of bleached kraft pulp observed upon addition of black liquor to the cook was greatest at low pH and high temperature (Fig. 5), condition known to favor lignin precipitation (1). At pH 13, the kappa gain was equivalent for all reaction temperatures tested (about 5 kappa units), whereas at pH 10, the kappa gain for the cook at 150°C (27,3 units) was over 3-fold that obtained at 90°C (8,5 units). This corresponds to yield gains of 4,3% at 150°C and 1,3% at 90°C, assuming that kappa gain was due solely to lignin precipitation. As in the washing study, the results confirm that at a constant calcium ion concentration in the black liquor, lignin precipitation increases with decreasing pH and increasing temperature.

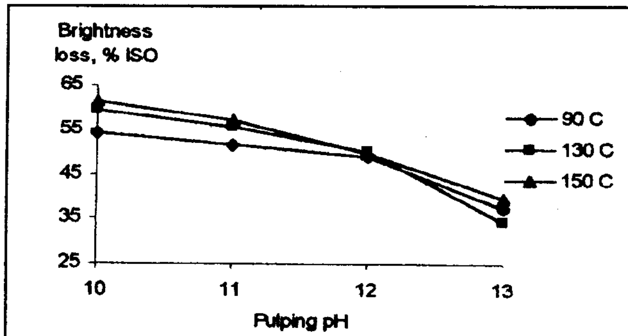

Fig. 6 Brightness loss of blached eucalypt kraft pulp addition of black liquor (1,35 t solids/t pulp) during pulping at different pH's and temperatures.

Table 1 Yield gain and xylan precipitation on bleached eucalypt kraft pulp upon addition of black liquor 1.35 t solids/t pulp) during pulping at 150°C and pH 10 and 13.

Yield parameter, % on pulp weight	Bleached pulp cooked at 150°C without black liquor		Bleached pulp cooked at 150°C with black liquor	
Treatment pH	10	13	10	13
Gravimetric-yield Gain, %	ref.	ref.	4,40	3,18
Kappa-yield Gain, %	ref.	ref.	4,49	1,11
Xylans, %	14,4	12,5	14,3	14,4

The brightness loss of bleached pulp during pulping upon addition of black liquor to the pulping liquor was also greater at low pH, but was relatively independent of reaction temperature (Fig. 6). Pulping at pH 10 led to brightness losses (54, 1 to 61,3% ISO) one and a half times greater than at pH 13 (37,3 to 39,6% ISO).

There was a relatively much smaller effect of pH on kappa gain than on brightness loss during pulping at 90°C than at higher temperatures (Fig. 5 and 6). At pH 10, the 61,3% brightness loss observed at 150°C a brightness loss of 54,1% corresponded to a kappa gain of only 8,5 units. However, at pH 13, a brightness loss of 39,6% at 150°C corresponded to a kappa gain of only 8,5 units. However, at pH 13, a brightness loss of 39,6% at 150°C corresponded to a kappa gain of 5,2 units; a ratio similar to the 37,4% brightness loss and 4,4 unit kappa gain observed at 90°C.

Although results from the washing and pulping studies are not directly comparable, since the former was carried out with unbleached pulp and the latter with bleached pulp, it can be noted that at the same pH (10). Temperature (90°C) and reaction time (120 min), addition of black liquor at 1,35 t solids/t pulp (pulping study, Fig. 5), resulted in a kappa gain of 8,5 units whereas addition of black liquor at 0,5 t solids/t pulp (washing study, Fig 1C) resulted in a kappa gain of 0,9 units. At the higher black liquor solids concentration, the corresponding brightness loss was 54,1% ISO (Fig. 6), whereas at the lower concentration, there was a 0,5% brightness gain (Fig 3C). These differences may reflect the fact that at the lower solids concentration, the lignin and calcium ion concentrations were below the critical concentration necessary for lignin precipitation (4).

It is well known that xylans can also precipitate during pulping, and the yield gains observed may have been due to a combination of lignin and xylan precipitation. Preliminary analyses of the pulps indicated that some xylan (~2%) precipitation did occur during treatment of bleached eucalyptus pulp with black liquor at pH 13 (Table 1). No xylan precipitation due to black liquor addition was observed at pH 10. This is in agreement with the literature, which claim the absence of xylans in solution for precipitation at pH 10 (7). The relative contributions of lignin and xylan to kappa gain during pulping is currently being investigated.

CONCLUSION

Lignin precipitation during pulp washing, as measured by kappa gain, only occurred at pH below 7,5 and temperatures of 60°C or higher and was independent of reaction time. At ambient temperature, lignin precipitation during washing was negligible, regardless of pH. Lignin precipitation during pulping, as measured by kappa gain, was relatively low (5-8 units) at 90°C, but increased up to 3 fold at temperatures of 130 and 150°C, when the pH was 11 or lower. Kappa number gains in both washing and pulping were accompanied by brightness losses, but the relationship between these two variables was highly dependent on pH and temperature. The occurrence of xylan precipitation from black liquor onto bleached eucalyptus fibres is significant at pH 13 but absent at pH 10.

ACKNOWLEDGEMENT

This work was partially supported by "Conselho Nacional de Desenvolvimento Cientifico e Technologico-CNPq", through a research scholarship granted to one of the authors. The authors would like to thank Celulose Nipo-Brasileira for supplying pulp and black liquor samples.

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