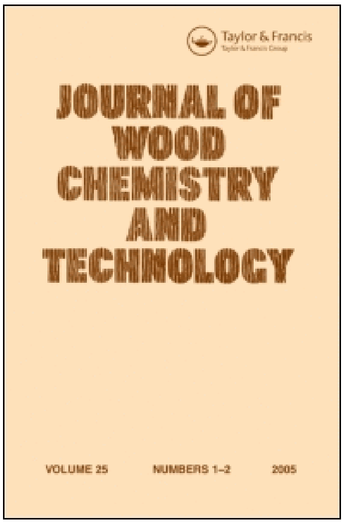

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Precipitation of Extractives onto Kraft Pulps during Black Liquor Recycling in Extended Delignification Process

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Abstract: Our objective was to study the extractives content and the bleachability of batch extended delignified kraft pulps during the black liquor recycling. Extractives accumulated in the black liquor during the black liquor recycling. Some of the extractives in the black liquor precipitated on the pulps in the pretreatment stage, which affected the bleachability of pulps. For softwood, after 5 stages of black liquor recycling, the extractive content of the kraft pulps increased by up to 4 times and the final brightness decreased up to 2.4% ISO. The amount of extractives precipitating on the pulps strongly depended on the final pH of the pretreatment black liquor, which was determined by the operating conditions such as sulfidity, alkali charge, and pretreatment temperature. High alkalinity and low pretreatment temperature was the most efficient combination to minimize extractives from precipitating, and to maintain high bleachability of the kraft pulps. For hardwood, large amounts of extractives precipitated onto fibers, and the extractive content, especially the neutral extractive content, of the hardwood kraft pulps was high. During the black liquor recycling, the drop of the final brightness of hardwood kraft pulps was larger than that of the softwood kraft pulps.

Keywords: Alkalinity, black liquor, bleachability, extended delignification, extractives, hardwood, kraft pulping, precipitation, pretreatment, recycling, softwood, sulfidity

This article is dedicated to the memory of our colleague and friend, Professor Josef S. Gratzl.

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INTRODUCTION

Due to the pressure of environmental regulations, many technologies have been developed to extend the delignification process in conventional kraft pulping to lower the residual lignin content without dramatically hurting the strength of the kraft pulps. These well-known extended delignification processes, including modified continuous cooking (MCC),[1] extended modified continuous cooking (EMCC),[2] isothermal cooking (ITC),[3] SuperBatch,[4] Lo-Solids,[5] and rapid displacement heating (RDH),[6] have been applied in the industry. Some of these processes include a black liquor impregnation stage. The black liquor pretreatment is used to neutralize the acidic groups in the wood,[7] save heat energy in warming the chips, and improve the selectivity of subsequent kraft cooking.[8]

Besides the residual lignin content, the extractives in kraft pulps also affect the bleachability. Extractives are minor natural components of the wood. Most of the extractives are removed during kraft pulping by saponification reactions and micelle formation.[9,10] During kraft pulping, about 80–85% of the extractives are dissolved in the black liquor.[11] However, at the end of the pretreatment or cooking stage, due to the negative effects of lignin repolymerization and/or condensation reactions, lignin fragments are more condensed and hydrophobic.[12] Therefore, they may precipitate from the black liquor and be adsorbed by the fiber surface. When the alkali concentration of the black liquor is low, it is easier for extractives and lignin fragments to precipitate onto the fiber surface. Using electron spectroscopy for chemical analysis (ESCA). it was found that the fiber surface of unbleached kraft pulps was covered with a higher concentration of extractives[13] and lignins[14] than that inside the fiber wall. This layer of organic compounds, either originating from wood fibers or forming during the kraft cooking, was more condensed and more inert toward bleaching chemicals. They retarded the bleachability of the pulp.[14]

Almost all batch-extended delignification systems, such as RDH, SuperBatch, and Enerbatch, involve at least one stage of black liquor impregnation.[15] The black liquor used in the pretreatment is recycled from the previous cooks. During the recycling, lignin fragments and extractives accumulate in the black liquor. Therefore, when the extractives content in the black liquor is very high and the pH of the black liquor is low, some of them may be adsorbed by the fiber surface. It was found that the contact time of the pulp with the black liquor during pulping was a factor influencing the bleachability of the pulp.[16] This may make the extended delignified kraft pulps harder to bleach than the conventional kraft pulps. A previous study has shown that hardwood pulps cooked by the RDH process were harder to bleach when compared with kraft-O_2 pulps.[17] Pulps produced from low-dissolved-solid liquors had an average brightness of 10 units higher than those produced from high-dissolved-solid liquors with the same kappa number.[18]

In this study, the behavior of the extractives precipitating on the fiber during black liquor recycling in batch extended-delignification kraft cooks was studied. A simplified extended delignification process, with one stage of black liquor pretreatment and no post treatment, was used in this study. The influence of the following factors on the extractives content and bleachability of softwood kraft pulps during five stages of black liquor recycling was studied: (1) sulfidity of the black liquor, (2) alkalinity, and (3) pretreatment temperature. For comparison, the effect of black liquor recycling in the hardwood extended delignification process was also described.

EXPERIMENTAL

Raw Materials

A 30-year-old loblolly pine tree and a 30-year-old southern red oak tree grown in Raleigh, North Carolina, USA, were used in this study. The wood logs were debarked and chipped. The chips with around 50% moisture content (wet basis) were screened. The accepted fraction with the size between 1″ and 5/8″ and with the thickness under 8 mm was used. The chips were kept fresh in the refrigerator at 4°C to prevent the loss of extractives. The extractives contents of the wood are listed in Table 1.

Pulping

A simplified extended delignification process, with one stage of black liquor pretreatment and no post treatment, was used. The extended kraft cooks were done in two 7 L M&K digesters. One was used as the digester and the other was used as the liquor accumulator. Wet chips (1000 g, o.d. basis) were used in each cook. The temperature versus time profile of the cook is outlined in Figure 1. In the pretreatment stage, the wood chips were impregnated with black liquors. The temperature of the pretreatment stage was increased to a given temperature (160°C or 130°C) and kept for a period of time. The total time for the whole pretreatment stage was kept at 100 min. At the end of the pretreatment, the preheated cooking white liquor (2.5 L) was transferred to the digester to displace 2.5L of the pretreatment black liquor. Therefore, the liquor-to-wood ratio in the cooking stage was 4.5. The temperature of the system was then heated up to 170°C and kept at 170°C.

Table 1. Extractives content of the wood

Species	Southern pine	Southern red oak
Total extractives content, %	2.47	1.12
Neutral extractives content, %	0.17	0.19

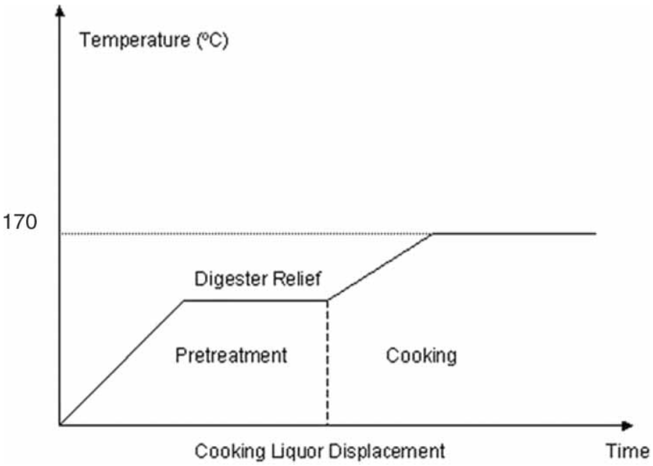

Figure 1. The profile of temperature versus time.

Due to the accumulation of organic solids in the black liquor after each stage of black liquor recycling, the delignification rate decreased. The H-factor was increased after each stage of the black liquor recycling in the same series so that pulps from each stage had approximately the same kappa number. The target kappa number for the softwood pulps was 24 and 9 for the hardwood pulps. The cooking conditions are described in Tables 2a and 2b.

Under each set of conditions, five stages of the black liquor recycling were conducted. In the first stage, white liquor was used in the pretreatment. In the following stages (2nd–5th), 3 L of the black liquor collected from the previous stage of cooking were used in the pretreatment. In each stage, the active alkali charge and sulfidity of the liquor at the very beginning of the pretreatment were kept exactly the same by adding the proper amount of concentrated NaOH and Na_2S solutions. The total volume of pretreatment liquor was at kept 4.5 L. White liquor (2.5 L) was used as the cooking liquor in all stages and it was preheated to 160°C before transferring. Each series of cook was done only once. The kappa numbers of pulps from the different series are listed in Table 3.

Table 2a. Conditions for extended kraft cooking of softwood

	Pretreatment stage	Cooking stage
Active Alkali, as Na_2O	7.5–12%	21%
Sulfidity	25–60%	25%
Liquor volume	4.5 L	2.5 L cooking WL
Temp. increasing rate	100°C/h	100°C/h
Maximum temperature	130–160°C	170°C
Time at maximum temp.	20–40 min	To target kappa number

Table 2b. Conditions for extended kraft cooking of hardwood

	Pretreatment stage	Cooking stage
Active Alkali, as Na_2O	11%	18%
Sulfidity	60%	25%
Liquor volume	4.5 L	2.5 L cooking WL
Temp. increasing rate	100°C/hr	100°C/h
Maximum temperature	160°C	170°C
Time at maximum temp.	20 min	To target kappa number

The dissolved solids content of the pretreatment black liquor was measured by drying the black liquor in an oven at 105°C. The organic solids content of the dissolved solids in the black liquor was measured by burning the organics in a muffle furnace at 500°C. Reported values are the average of three measurements.

Bleaching

Bleaching was conducted in high density polyethylene (HDPE) bags by mixing the pulps and bleaching chemicals together. The bags were sealed and put into a water bath at 70°C. The bleaching sequence D(E + P)D was used. The operating conditions used for bleaching are listed in Table 4. The final brightness of the pulp was measured according to the ISO standard. The pulp brightness was averaged over two bleaching experiments.

Extraction and Fractionation

To determine the extractives content of the wood meal and the pulp, samples of wood chips and pulps were dried overnight in a vacuum oven at 45°C. The wood meals were prepared by grinding the wood chips in a Willey mill and sieving through a 40-mesh screen. Wood meal (20 g, o.d. basis) or 15 g of pulp (o.d. basis) was extracted for at least 10 h in a soxhlet with acetone

Table 3. Pulp kappa number in different series

Kappa number	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Series I	23.2	24.0	24.8	23.8	25.2
Series II	25.0	23.4	24.2	25.2	24.8
Series III	23.3	24.4	23.6	23.1	22.9
Series IV	23.7	23.3	22.9	24.8	24.7
Series V	22.5	24.3	24.8	24.5	24.5
Series VI	8.9	9.2	9.0	9.1	9.2

Table 4. Process conditions for bleaching

Stage	Time (min)	Temp (°C)	Consistency	Chemical charge	Final pH
D_0(SW)	60	70	10%	K.F. = 0.25	
D_0(HW)	60	70	10%	K.F. = 0.20	
E + P	60	70	10%	NaOH = 1.5% H_2O_2 = 0.5%	10.3–10.9
D_1	180	70	10%	ClO_2 = 1.0%	3.5–4.0

and then 95% ethanol. The extraction solutions were combined and evaporated *in vacuo* at 45°C.

The extracts were hydrolyzed at 70°C in a 500 mL flask for 4 h with 80 mL of 0.5 M KOH in 95% ethanol. Then the solution was diluted with 80 mL water and the pH was adjusted to 13.2 ± 0.2 by adding KOH. The diluted solution was extracted in a separatory funnel with hexane 3 times, each with 50 mL of hexane. The extractives in the hexane phase were labeled as the neutral fraction. The water phase was acidified to *ca.* pH 2.5 by adding 1 M HCl and extracted with chloroform (3 × 50 mL) in a separatory funnel. The chloroform extractives were labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractives content of the sample. The reported extractives content was the average of three measurements.

Repeatability of the Extraction and Bleaching Processes

The differences in the bleachabilities and extractives contents of the pulps were rather small in some cases. The repeatability of the extraction and bleaching data was evaluated in a similar previous study.[19] In that study, the 95% confident interval deduced from 6 replicates of the measurements was ±0.4% ISO for bleachability and ±0.02% for pulp extractives content. Some of the bleaching results after different stages were marginally different. Experiments from this study showed that the properties of the black liquors, such as dissolved solids content, were significantly different in different recycling stages in most cases.

RESULTS AND DISCUSSION

Series I: High Alkali and High Sulfidity Pretreatment of Softwood

In this series, softwood chips were used. In the pretreatment, the initial active alkali charge was 11% and the sulfidity was 60%. Figure 2 shows the dissolved

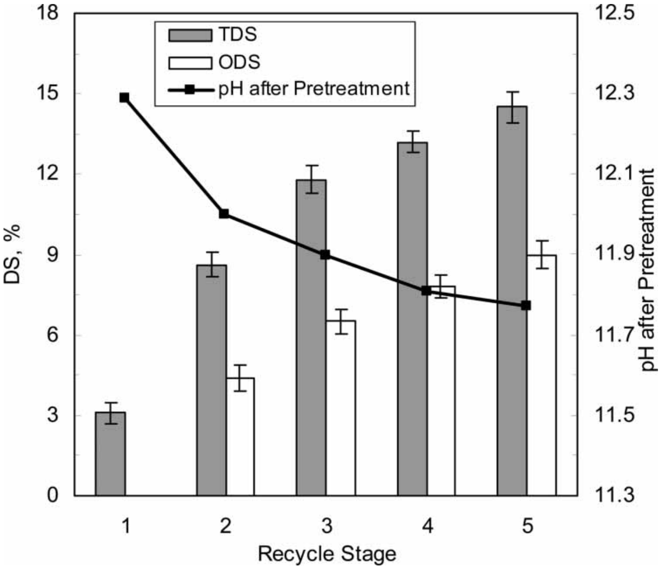

Figure 2. Properties of the black liquor (Series I).

solid content of the pretreatment black liquor before the pretreatment and the pH value of the black liquor after the pretreatment. After five stages of black liquor recycling, the total dissolved solid (TDS) content and the organic dissolved solids (ODS) content in the pretreatment black liquor increased very quickly. The pH of the black liquor after the pretreatment decreased after each stage of black liquor recycling. The OH^- concentration in the fifth stage was decreased to as much as 30% of that in the first stage.

The properties of the kraft pulps are shown in Figure 3. The extractives content in the pulps built up very quickly. After 5 stages of black liquor recycling, the total extractives content in the pulp was almost 5 times as much as that in the first stage. The neutral extractives content was also increased by almost 4 times. The final brightness of the bleached pulps dropped by 2% ISO after 5 stages of recycling. During the black liquor recycling, more and more extractives accumulated in the black liquor. When the pH of the black liquor dropped, it was easier for the extractives to precipitate onto the fiber surface.

Series II: High Alkali and Low Sulfidity Pretreatment of Softwood

In the pretreatment, the active alkali charge was 11% and the sulfidity was decreased to 25% at the beginning of the pretreatment in each stage. The properties of the black liquor and kraft pulps are shown in Figures 4 and 5, respectively. Although the TDS and ODS in the black liquor increased

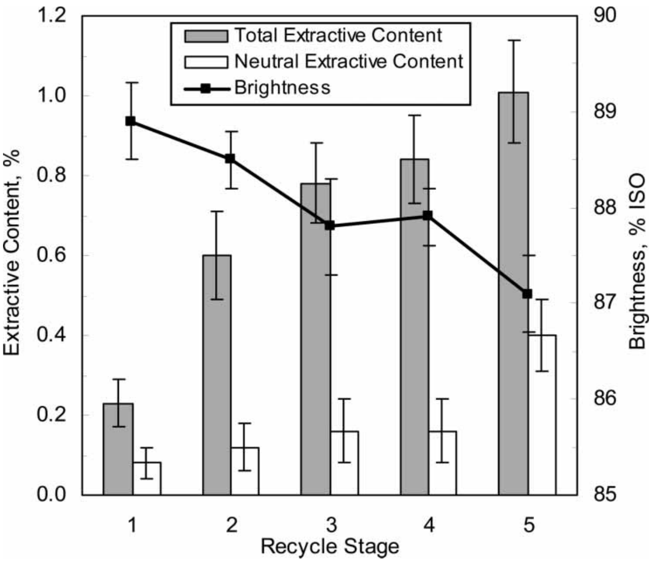

Figure 3. Extractives content and final brightness of kraft pulps (Series I).

rapidly after 5 stages of black liquor recycling, the extractives content of the kraft pulps had only a small increase, 40% for the total extractives content and 70% for the neutral extractives content. The final pH of the black liquor remained almost constant at 12.4 during the black liquor recycling. The tendency for extractives to precipitate during the black liquor recycling had only a small change. Due to extractives built up in the black liquor during recycling, the extractives content of the kraft pulps increased. The final brightness was only decreased by about 1% ISO after 5 stages of black liquor recycling. The final brightness of kraft pulps in series II was lower than that in series I because of the lower pretreatment sulfidity. This confirmed the result obtained from an early study.[20]

Series III: Constant pH of Black Liquor after Pretreatment

The purpose of performing the cooks in Series I and Series II was to study the effect of sulfidity during the black liquor recycling. However, from Series I it seemed that the final pH of the black liquor after the pretreatment influenced the extractives content and bleachability of the kraft pulp to a large extent. It is hard to evaluate whether the drop in the final brightness of the kraft pulps was mainly due to the black liquor recycling or to the drop in the final pH of the pretreatment black liquor. In this series, the effect of the final pH was eliminated. Softwood chips were used and the sulfidity of the pretreatment was

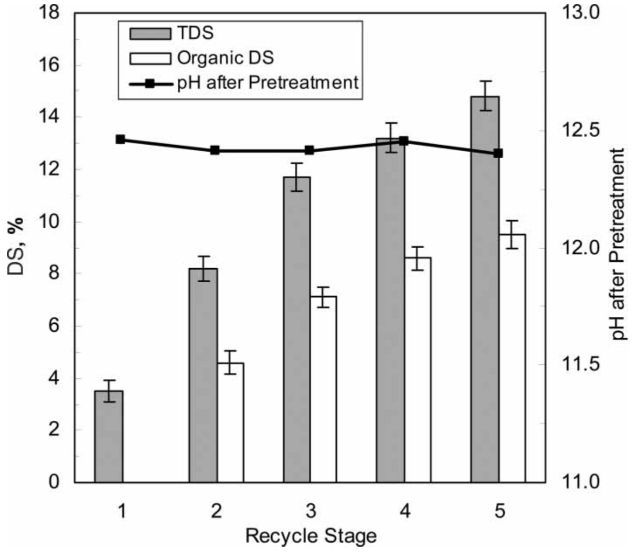

Figure 4. Properties of the black liquor (Series II).

kept at 60%. However, the starting active alkali charge of the black liquor was adjusted accordingly so that the final pH of the black liquor was around 12. The properties of the black liquor and kraft pulps after each stage are shown in Figures 6 and 7.

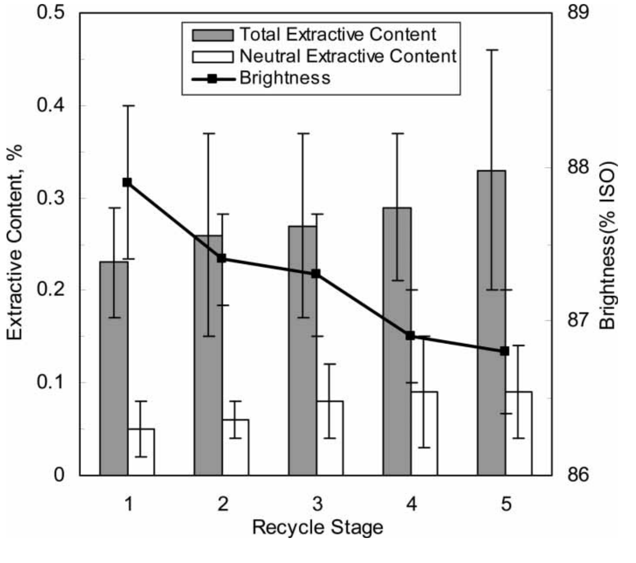

Figure 5. Extractive content and final brightness of kraft pulps (Series II).

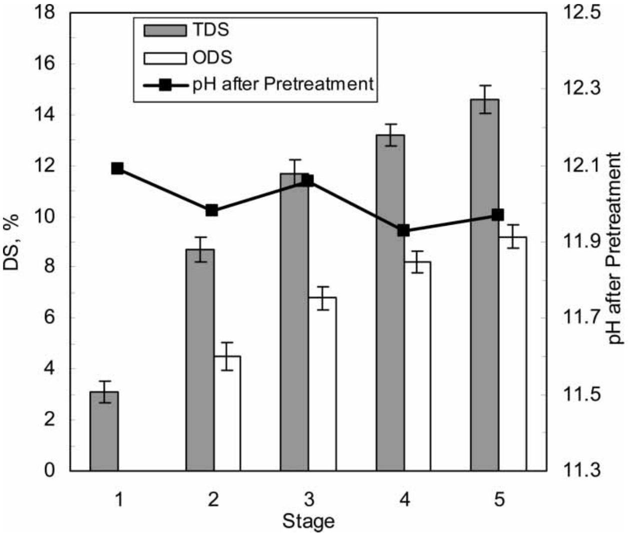

Figure 6. Properties of the black liquor (Series III).

Due to the accumulation of organics in the black liquor, after 5 stages of black liquor recycling, the total extractives content and neutral extractives content of the kraft pulps were both increased by 2 times, which was much less than in series I. The final brightness of the kraft pulp in the 5th stage was about 1.2% ISO, lower than that in the 1st stage. In series I, the difference

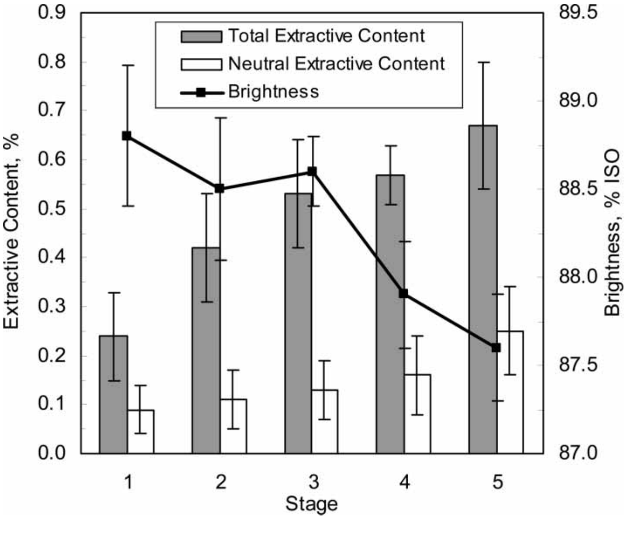

Figure 7. Extractive content and final brightness of kraft pulps (Series III).

was about 2%. Therefore, to avoid the further build up of extractives in pulps, extra alkali should be added to the pretreatment stage after each stage of black liquor recycling to keep the final pH of the black liquor high. White liquor profiling is an efficient way to increase the pH value of the pretreatment liquor and prevent the precipitation of extractives.[20]

Series IV: Low Alkali-High Sulfidity Pretreatment of Softwood

From series I and series III it is easy to understand that if the active alkali charge in the pretreatment stage is lowered, it is easy for the extractives to build up on the surface of the pulps. In this series with softwood chips the sulfidity in the pretreatment was 60% and the initial active alkali charge was decreased to 7.5%. The properties of the black liquor and kraft pulps are shown in Figures 8 and 9, respectively.

The final pH of the pretreatment black liquor was about 1.0 unit lower than that in series I. After 5 stages of black liquor recycling, the final pH of the pretreatment black liquor decreased by around 1.0. Therefore, during the black liquor recycling, it was easier for the extractives to precipitate. The total extractives content and neutral extractives content were higher than in the corresponding stages in series I. After 5 stages of black liquor recycling, the total extractives content and neutral extractives content was increased by 2 and 3 times. The final brightness of the kraft pulps was decreased by 2.4% ISO. Obviously, the lower final bleachability of the pulps in this series than in

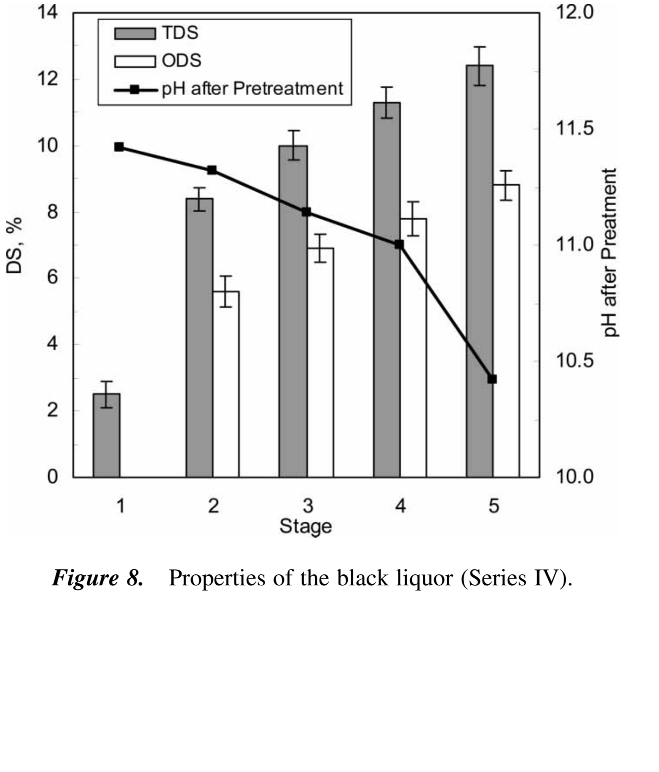

Figure 8. Properties of the black liquor (Series IV).

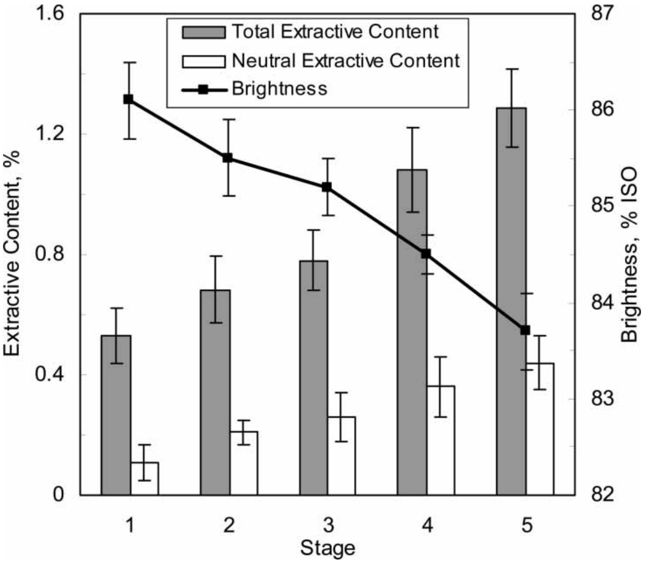

Figure 9. Extractives content and final brightness of kraft pulps (Series IV).

series I was also due to the lower active alkali charge in the pretreatment. This was confirmed by an early study.[20]

Series V: Low Temperature Pretreatment

The previous series were all done at a pretreatment temperature of 160°C. At a high pretreatment temperature, the pH of the black liquor dropped drastically at the end of the pretreatment. This may cause the precipitation of lignin fragments and extractives during the pretreatment.[8] The high temperature pretreatment would have an adverse effect on the bleachability of kraft pulps during black liquor recycling. In this series, the maximum temperature in the pretreatment stage was kept at 130°C. Softwood chips were used. The AA charge was 11% and the sulfidity was 60% at the beginning of the pretreatment. The properties of the black liquor and kraft pulps are shown in Figures 10 and 11, respectively.

After the low temperature pretreatment, the final pH of the pretreatment black liquor in each stage was at least 0.5 higher than that in the corresponding stage in the high temperature pretreatment cases (Series I). The extractives content of the kraft pulps, especially the neutral extractives content, was much lower than that in the high temperature pretreatment cases. Due to the slow rate of the extractives buildup, the bleachability of the kraft pulp after 5 stages of black liquor recycling was decreased by less than 1% ISO.

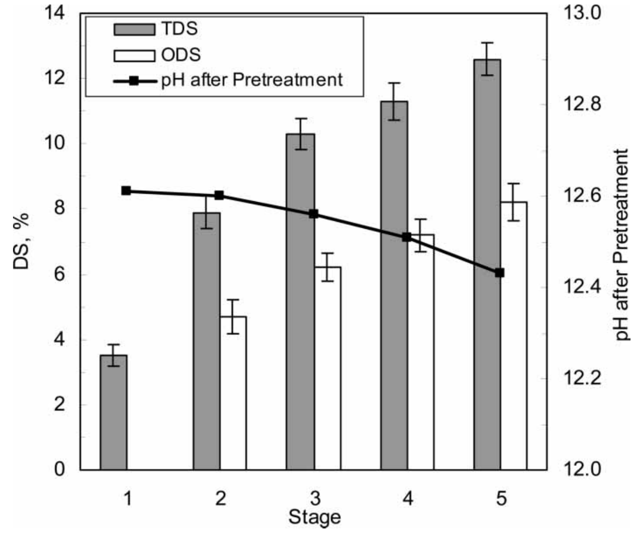

Figure 10. Properties of the black liquor (Series V).

Series VI: Hardwood

As a comparison, the precipitation of extractives of hardwood chips during the black liquor recycling was also studied. Usually the neutral extractives content

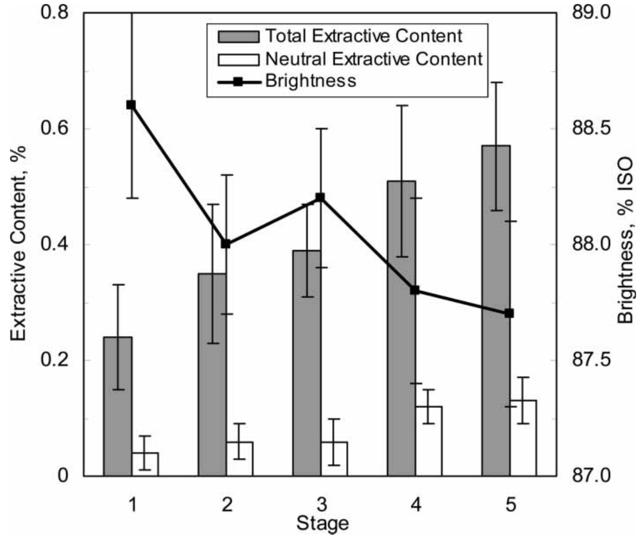

Figure 11. Extractives content and final brightness of kraft pulps (Series V).

in hardwoods is higher than that in softwoods. The fatty acid and resin acid content in hardwoods is much lower than that in softwoods. The removal efficiency of neutral compounds in hardwood by the micelle formation mechanism during the kraft pulping is expected to be low.[21] Therefore, during black liquor recycling, more and more neutral compounds accumulate in the black liquor. They tend to stay with the pulps and finally affect the pulp properties. On the other hand, the kappa number of hardwood kraft pulps is usually much lower than that of the softwood kraft pulps. The charge of bleaching chemicals is generally based on the kappa number of the pulps. Therefore, the extractives content per kappa number for hardwood kraft pulps is much higher than that of the softwood kraft pulps. The black liquor recycling thus will have a more pronounced influence on the bleachability of hardwood kraft pulps than on softwood kraft pulps.

In this series, hardwood chips were used. The active alkali charge was 11% and the sulfidity was 60% at the beginning of the pretreatment. The properties of the pretreatment black liquors and the hardwood kraft pulps are shown in Figures 12 and 13.

Due to the higher acidity of oak chips,[22] even with the same alkali charge and sulfidity, the final pH of the pretreatment black liquor was a little lower than the corresponding softwood cases. The extractives content of hardwood kraft pulps, especially the neutral extractives content, was much higher than that of softwood pulps. After 5 stages of black liquor recycling, the total extractives content and neutral extractives content was increased by one and three times, respectively. The final brightness of the hardwood kraft pulps was decreased by 2.2% ISO after 5 stages of black liquor recycling.

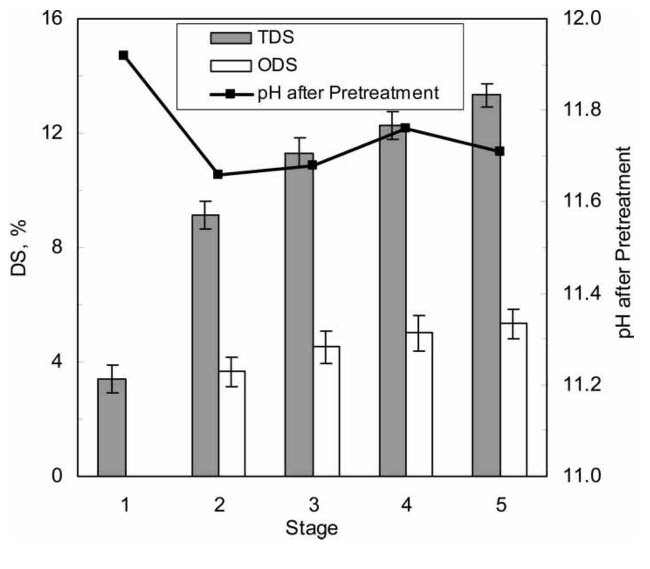

Figure 12. Properties of the black liquor (Series VI).

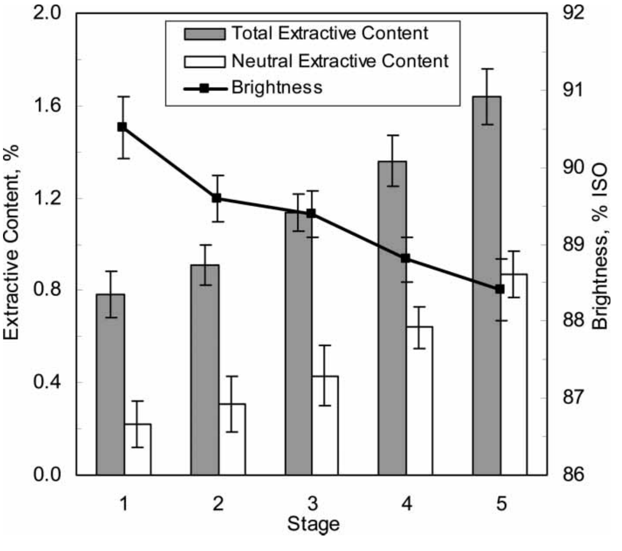

Figure 13. Extractives content and final brightness of kraft pulps (Series VI).

CONCLUSIONS

In a batch-extended delignification process, extractives accumulate in the pulps during black liquor recycling, which affects the bleachability of pulps. The amount of extractives precipitating onto the pulps depends on the final pH of the pretreatment black liquor. In different series of black liquor recycling, the effects of final pH, sulfidity, sulfidity excluding final pH, alkalinity, pretreatment temperature, and wood species were studied. The influence of sulfidity, alkali charge, pretreatment temperature, and wood species is summarized as follows:

- With a lower sulfidity in the pretreatment, the final pH of the black liquor is higher. A lower amount of extractives precipitates on the fiber surface and the decease in final brightness of the bleached pulp is smaller than with a higher sulfidity in the pretreatment. The overall final brightness of the pulps with a lower sulfidity pretreatment is lower than those with a higher sulfidity pretreatment.
- With a lower alkali charge in the pretreatment, the final pH of the black liquor is lower. A larger amount of extractives precipitates onto the fiber surface and the decrease in final brightness of the bleached pulp is higher than with a higher alkali charge in the pretreatment. The overall final brightness of pulps with a lower alkali charged pretreatment is lower.
- With a lower pretreatment temperature, the final pH of the black liquor is higher. Fewer extractives precipitate onto the fibers and the final brightness

drop of the pulp is smaller than with a higher pretreatment temperature. The final brightness of bleached pulps with a higher pretreatment temperature is comparable to that with a lower pretreatment temperature.

- For the hardwood, a large amount of extractives precipitate on fibers and the extractive content, especially the neutral extractive content of the hardwood kraft pulps s high. During the black liquor recycling, the decrease in final brightness of bleached hardwood kraft pulps is larger than that of softwood kraft pulps.

REFERENCES

1. Dillner, B. Modified continuous cooking. Japan Pulp Paper **1989**, *26* (4), 49–55.
2. Macleod, J.M. Extended delignification: Status report. Appita J. **1993**, *46* (6), 445–452.
3. Hoglund, O. Effects on pulp properties of black-liquor pretreatment and isothermal cooking (ITC). In *3rd European Workshop on Lignocellulosics and Pulp*; 1994; 37–53.
4. McDonald, S.; Uusitalo, P.; Hiljanen, S. Performance of mill-scale superbatch displacement batch cooking systems. *1993 Tappi Pulping Conference*, Nov. 1–3; Atlanta, GA, 1993; 415–422.
5. Kawakami, C.; Wiley, E.; Stromberg, B. Lo-solids cooking update—yield improvement, AQ effect and application to overload digester. Kami Pa Gikyoshi. **2000**, *54* (9), 39 (PaperChem Abstract).
6. Andrews, E.K. RDH kraft pulping to extend delignification, decrease effluent, and improve productivity and pulp properties. Tappi J. **1989**, *72* (11), 55–61.
7. Lonnberg, B.; Qing, S. The effect of kraft liquor lignin on delignification. *9th International Synposium on Wood and Paper Chemistry*; 1997; 92–1–2–4.
8. Engstrom, J.; Lonnberg, B.; Pekkala, O. Black liquor pretreatment in kraft cooking. Paperi Ja Puu—Paper and Timber **1994**, *76* (1–2), 59–66.
9. Gellerstedt, G. In *Pulping Bleaching: Principles and Practice*; Tappi Press: Atlanta, 1996; Sect III, Chap. 1.
10. Odberg, L.; Forsberg, S.; McBride, G.; Persson, M.; Stenius, P.; Strom, G. Surfactant behavior of wood rosin components. (2) Solubilization in micelles of rosin and fatty acid. Svensk Papperstid **1985**, *88* (12), R118–R125.
11. Bilyuba, T.S.; Bogdanova, E.V. Balance and dynamics of extractive resinous substances during the kraft pulping process. Gidroliz. Lesokhim. Prom. **1975**, *1* (14), (PaperChem Abstract).
12. Pekkala, O. Effect of prolonged cooking on delignification and pulp properties studied by flow-through kraft cooking and its modifications. In *5th Intermational Symposium on Wood and Pulping Chemistry*, May 22–25; Raleigh, NC, 1989, 255–261.
13. Ohno, N.; Sawatari, A.; Yoshimoto, I. Studies on distribution of extractives in pulp fibers by means of ESCA. Jpn. Tappi J. **1992**, *46* (10), 1295 (PaperChem Abstract).
14. Laine, J.; Stenius, P.; Carlsson, G.; Strom, G. Effect of ECF and TCF bleaching on the surface chemical composition of kraft pulp as determined by ESCA. Nord. Pulp Pap. Res. J. **1996**, *11* (3), 201–210.
15. Headley, R.L. Pulp cooking developments focus on fiber yield, lower chemical use. Pulp & Paper **1996**, *70* (10), 49–57.

16. Hillis, W.E.; Sumimoto, M. Effect of extractives on pulping. In *Natural Products of Wood Plants II Chemicals Extraneous to the Lignocellulosic Cell Wall*; Rowe, J.W., Ed.; Springer-Verlag, 1989; 897.
17. Jacobs, C.J. The bleachability of rapid displacement heating softwood and hardwood pulps compared to conventional kraft pulps. M.S. Thesis, North Carolina State University: Raleigh, NC.
18. Lloyd, J.; Allison, R.; Horne, C. Laboratory kraft pulping with low dissolved solids concentrations. *51st Appita Annual General Conference, 2: Proceedings*; 1997; 565–571.
19. Dai, Q.; Chang, H.M.; Jameel, H. Effect of digester relief on the bleachability of softwood kraft pulps from batch extended delignification. *2001 Pulping Conference: Proceedings (Tappi)*, November 4–7; 2001; 767–777.
20. Kumar, K.R.; Chang, H.M.; Jameel, H. Effect of pulping conditions on bleachability of hardwoods. *1995 Pulping Conference: Proceedings (Tappi)*, October 1–4; 1995; 539–552.
21. Odberg, L.; Forsberg, S.; McBride, G.; Persson, M.; Stenius, P.; Strom, G. Surfactant behavior of wood rosin components. (2). Solubilization in micelles of rosin and fatty acids. Svensk Papperstid. **1985**, *88* (12), R118–R125.
22. Roffael, E. Release of volatile organic acids from wood chips and wood-particle boards. Holz Roh-Werkstoff. **1989**, *47* (11), 447–452.