Effect of black liquor circulation on kraft and Soda (AQ) pulp quality

Aravamuthan Raja G.* Arasakesari Subramaniam** Sharma Arvind Kumar***

ABSTRACT

The research work studies the effect on delignification, and the bleachability and beatability of pulps as a result of increasing the amounts of black liquor recirculation in Kraft and Soda (AQ) cooking. The results are important, particularly in the case of extended delignification as well as in new methods of recovery system where the resultant white liquor can be manufactured in high concentrations, thereby necessitating high recirculation. The results of delignification show the effect of both dissolved hemicelluloses and dissolved lignin, besides the increase in effective alkali and sulfidity of the cooking liquor.

Key Words—Black Liquor, Effective Alkali, Kraft and Soda (AQ) Pulps, Hemicellulose Retention, Bleachability, Beatability, Strength Properties

1. Introduction :

The kraft pulping process involves regular usage of varying amounts of black liquor for maintaining the desired liquor-to-wood ratio. The volume of black liquor used depends on the percent active alkali, chip moisture content and liquor-to-wood ratio employed in the pulping process. Under normal operations, it can easily constitute a third of the total volume of circulation liquor. Since the recycling of black liquor even under normal circumstances can be thus high, it is evident that an appreciable quantity of organic materials dissolved in the previous cooks and some amount of residual chemicals are introduced at the beginning of each cook The effect of such recycled black liquor on pulp properties, mainly kappa number or permanganate number and bleachability, has been studied in the fifties without any conclusive results. While Mattson[1] concludes that there is an adverse effect on permanganate number and unbleached pulp brightness, Rothrock and Nolan[2] and May and Peckham[3] report that the recycling of black liquor does not appear to have any deleterious effect on the strength properties or the bleaching characteristics of the pulp.

Results of recent work in the Royal Institute of Technology, Stockholm, Sweden, indicate that an increase in the concentration of dissolved lignin in the cooking liquor results in a decrease in the delignification rate. The effective rate of delignification after 100 minutes of cooking time is twice in the absence of any dissolved lignin as that in the presence of 70 gpL of dissolved ligning at the start[4]. Further, from a comparison of the results of continuous flow process and a corresponding batch process cook, Sjoblom et al[5] observed that the selectivity of the cooking process can be affected substantially by the organic matter dissolved during the cook at normal liquor-to-wood ratios.

There are possibly two other effects which have not been studied in particular reference to black liquor recirculation. There have been suggestions that a high concentration of dissolved polysaccharides in the liquor would impede further dissolution of the same[6]. If this is so, some of the nonstabilized polysaccharides may also be retained in pulp due to their impeded dissolu-

*Western Michigan University, Kalamazoo, Michigan 49008.
**University of Washington, Seattle, Washington 98195
***Western Michigan University, Kalamazoo, Michigan 49008
Pulp & Paper Research Center
CP-500, Trois-Rivieres
QUEBEC, CANADA/GIA 5 H 7

tion. Hence, the effect of stabilizing agents such as AQ may be comparatively smaller in the presence of increasing amounts of black liquor. Secondly, the increased concentration of lignin and hemicelluloses increases the chance of enhanced redeposition. The reversal of such conditions, i e., the removal of black liquor rich in organic substances has been found to result in pulp with much lower content of lignin, higher brightness and lower pentosans than under normal conditions of kraft pulping[7]. Such readsorbed lignins have been reported to have a considerably higher absorption coefficient than the lignin that has never been dissolved in the first place[8]. In addition, with increased amounts of lignin being present, there is an added possibility of lignin condensation reactions leading to a loss in bleachability[9].

Further, the recirulation of increasing amounts of black liquor may change the sulfidity and/or effective alkali figures of the cooking liquor and these may affect the initial, bulk and residual delignification rates differently. The results obtained so far are not conclusive [10—12].

As is evident from the above, the effects of black liquor circulation have not been studied in a comprehensive manner, but the indications are that increasing amounts of spent liquor will be recycled in new recovery schemes such as Direct Alkali Recovery System (DARS) wherein the liquor is returned from the recovery section at a concentration of 350 gpL as compared with the 120-140 gpL in the conventional kraft system. To take complete advantage of this increase in concentration in terms of energy savings in the evaporator section, a greater amount of black liquor is returned to the digester[13]. The recirculation black liquor can constitute about 70% of the total liquor volume in such cases.

Hence, it is necessary to study the effects of such recycled black liquor on delignification of wood and also on the bleaching, beating and strength development characteristics of the resultant pulps.

2. Rationale And Significance :

The recycling of increasing amounts of spent liquor contributes to increasing amounts of dissolved lignin, hemicelluloses and inorganic chemicals like sodium sulfide and sodium hydroxide. In the case of kraft liquor, in the normal industrial process the effective alkali can be maintained constant by adjusting the white liquor to black liquor ratio within the limitations set by the liquor to wood ratio. But in most cases sulfidity becomes a dependent variable and varies along with the recycled liquor. Also, there is effectively some uncertainty in determining the effective alkali that the black liquor will contribute[14]. Such changes in effective alkali and/or sulfidity may even contribute to moving the transition point from bulk to residual delignification rates towards a different pulp lignin content[15].

Besides possible yield increase because of various redepositions and impedance to dissolution of cellulosic materials, one has to look for the mutually conflicting effects of lower delignification rates due to the dissolved lignin and higher rates of delignification due to the increased amount of cooking chemicals. There will be lower bleachability due to the redeposited lignin and the lignin condensations as well. Other effects like beatability will be again confounded by the presence of additional amounts of hemicellulose and the redeposited lignin.

Beatability and development of strength properties depend on how the paracrystalline regions in the original cellulose are modified during the process of pulping and the extent of such modification can be a function of temperature and ionic swelling characteristics of the cooking liquor and probably the cooking time[16,17]. Consequently, strength properties like tear and tensile indexes may depend on the H factor employed to obtain the desired delignification level in the various cooks.

Thus, it is important to determine the delignification rate, the transition point between different phases of delignification, the lignin free yield, the H factor, the pulp beatability and development of desirable paper-making properties in such pulps.

The detailed study in its entirety can hence lead to a fixed upper limit on recirculation of such spent liquor based on process parameters and pulp properties and it probably may lead to a more effective conversion process for pulp and paper from wood. Also, a more effective retention of hemicellulose, leading to a higher yield of pulp, implied that the forest raw material—wood—is more effectively utilized. Otherwise, the dissolved hemicelluloses are merely burnt up in the recovery furnace for their comparatively low fuel value.

3. Experimental Plan :

Concentrated kraft black liquor (approximately 18% solids) was obtained from S. D. Warren Company in Muskegon, Michigan. Black liquor for soda (AQ) cooking was prepared in the laboratory by making preliminary cooks with 0 5% anthraquinone, 18%, active alkali, 4 : 1 liquor to wood ratio and a cooking temperature of 170°C. These cooks were carried out with 1.5 h cooking time. Pulps produced from such cooks were discarded.

A mixture of hardwood chips procured from the S. D. Warren Company was the raw material for the whole study. The white liquor was made on site from sodium hydroxide and sodium sulfide. The experimental cooks were carried out in autoclaves heated in an oil bath. The experimental conditions are provided in Table 3.1.

TABLE 3.1 — COOKING CONDITIONS

Particulars	Kraft	Soda — AQ
Effective Alkali, %	18	18
Sulfidity in White Liquor, %	25	—
Anthraquinone	—	0.5%
Cooking Period, h	Variable	Variable
Cooking Temperature, °C	165	170°
Liquor to Wood Ratio	3 : 1	3 : 1

The bleaching experiments were done in a three-stage C-E D sequence with a limited charge of chlorine dioxide. The final bleached pulps were tested for reflectance at 457 nm. The bleaching conditions maintained in the three stages are presented in Table 3 2.

The pulp viscosity may be a misleading characteristic due to the varying amounts of retention of short chain hemicelluloses. Hence, not much emphasis was laid on pulp viscosity as an indicator of strength properties. Instead, the papermaking capabilities of the pulps produced were analyzed by refining in a PFI mill to 300—320 mL CSF, preparation of handsheets and determination of strength properties.

TABLE 3.2 — BLEACHING CONDITIONS

Particulars	Bleaching Stages C	E	D
%Chlorine	0.22 (Kappa)		
%NaOH		0.55 (%Cl_2)	
%Cholrinedioxide		—	1.0
Temperature, °C	ambient	70	70
Time, minutes	60	90	120
Consistency, %	3.5	10	10

4. Results and Discussion :

The results of pulp yield and kappa number obtained in kraft pulping for various recycle percentages of black liquor are presented in Table 4.1.

TABLE 4.1 —
YIELD AND KAPPA NUMBER KRAFT COOKS

Black Liquor Recycle %	Cooking Time 1.5 hour Yield, %	1.5 hour Kappa No.	2 hour Yield, %	2 hour KappaNo.
20	52.3	24.2	46.5	21.3
40	54.1	26.0	48.1	24.5
60	56.5	26.2	47.8	24.7
80	57.6	28.0	50.3	26.6

The results indicate that there is definite increase in yield with increased recycling of black liquor. However, there is decreased delignification as reflected by an increase in kappa numbers. Howevre, the extent of the observed increase in yield points definitely to better retention of carbohydrates. Additional experiments conducted in a related research work[18] indicate that the hemicellulose yields show an increase of about 3% (from 65 to 68%) when the liquor circulation rate is increased from 20 to 75%.

Similar yield and kappa number results for soda (AQ) pulps are presented in Table 4.2. The kappa number results obtained in soda (AQ) pulping are similar to those in kraft pulping. However, they are slightly lower for 2 h cooking time as compared with their kraft counterparts. This may be due to the fact that the black liquor solids in soda (AQ) black liquor was comparatively lower at 8% (as compared with 18% in kraft black liquor). The yield results for 2 h cooks show a steady increase with increased black liquor circulation. On the other hand, the results obtained with 1.5 h cooking time do not show a trend. However, it was expected that the increase in yield in soda (AQ) pulping would not be equal to the yield increase in kraft pulping due to the stabilizing effect of anthraquinone.

TABLE 4.2 —
Yield and Kappa Number — Soda (AQ) Cooks

Black Liquor Recycle %	Cooking Time			
	1.5 hour		2 hour	
	Yield, %	Kappa No.	Yield,%	Kappa No.
20	49.4	22.0	45.9	14.6
40	53.4	24.8	46.8	16.2
60	48 8	27.0	47.8	17.5
80	49.8	28.2	48 8	18.7

The greatest effect of black liquor circulation is felt in the bleachability of such pulps. The pulps, when bleached in a three stage C-E-D sequence under identical conditions, were found to attain significantly different levels of brightness values (see Table 4.3). The standard error for the brightness values varied between 0.5 to 1.2%. The fact that the pulp is rendered less bleachable may be due to the difference in the nature of redeposited and original lignins. However, it is interesting to note that a softer cooked pulp (2 h cooking time), yields a much higher final brightness value at all levels of black liquor recirculation. These results do have particular significance for extended delignification. The pulps thus obtabined do not show any significant difference in their beatability or strength properties.

All the pulps attained a freeness of 300-320 mL CSF after refining for 2500 revolutions in a PFI mill. The strength properties of these handsheets are presented in Table 4.4 Some marginal differences in the average strength properties are seen with the increase in recycle level of black liquor. However, they are not statistically significant

TABLE 4 3
BRIGHTNESS VALUES OF C-E-D BLEACHED PULPS (Kraft)

Black Liquor Recycle %	Cooking Time	
	1 5 hour	2.0 hour
	Brightness, %	Brightness, %
20	62.9	70.1
40	61.0	65.9
60	55.1	63.1
80	51.0	59.7

Corresponding results on bleachability, beatability and the strength properties are not currently available for the soda (AQ) pulps.

5. Conclusions :

It is seen that the increased black liquor recirculation essentially leads to higher residual lignin and slightly increased hemicellulose retention. It also affects the bleachability of the pulps adversely. However, the bleached pulps did not suffer any serious loss

TABLE – 4.4

STRENGTH PROPERTIES OF KRAFT HANDSHEETS

Strength Properties	Cooking Time h,	Levels of Black Liquor Recirculation			
		20%	40%	60%	80%
Burst Index	1.5	2.08	2.06	2.01	2.00
KPam²/g	2.0	2.12	2.12	2.10	2.08
Tensile Index	1.5	40.97	39.88	39.40	39.01
Nm/g	2.0	42.06	42.71	38.35	37.95
Tear Index	1.5	2.66	2.40	2,45	2.34
mNm²/g	2.0	2.67	2.56	2.56	2.45

in streugth properties. Hence, an increased level of black liquor circulation may easily be followed, in the case of unbleached grades, while additional modifications in bleaching may be needed for bleached pulps. A lot more remains to be studied, particularly the nature and molecular weight of retained lignin and hemicelluloses, color reversions characteristics of the bleached pulps and the actual delignification kinetics itself. It will be also worthwhile to determine all these effects in the case of soda (AQ) pulps.

Acknowledgements :

The work was supported in part by a Faculty Research and Creative Activities Fellowship award from Western Michigan University and by an assistantship from the College of Engineering and Applied Sciences at Western Michigan University.

References Cited :

1. Mattson, V., An Investigation of the Role of Recycled Black Liquor in Sulphate Pulping, Pulp Paper Int., 39 (2) : 77 (1956)
2. Rothrock, Jr., C. W. and Nolan, W. J., Further studies on the Alkaline Pulping of Scrub Oak, Tappi Journal, 35 (1) : 29 (1952).
3. May, M. N. and Peckham, J. R. Invetigation of the Reuse of Black Liquor in Kraft Pulping on Bleaching to High Brightness Levels, Tappi Journal, 41 (2) : 90 (1958).
4. Hartler, N., Extended Delignification in Kraft Cooking — A New Concept, Svensk Papperstid., 81 (15) : 483 (1978).
5. Sjoblom, K., Mjoberg, J. and Hartler, N , Extended Delignification in Kraft Cooking Through Improved Selectivity, Part I : The Effects of the Inorganic Composition of the Cooking Liquor, Paperi Puu, 65 (4) : 227 (1983).
6. Dillen, S. and Noreus, S , On the Influence of Sulphidity and Alkali Charge in Kraft and Polysulphide Pulping of Scotch Pine, Svensk Papperstid., 70 (4) : 122 (1967).
7. Surewicz, W., The Sorption of Organic Components from Cooking Liquor by Cellulose Fibers ; Its Relation to the "Dangerous Cooking Crest" in Alkaline Pulping (I), Tappi Journal, 45 (7) : 5 (1962).
8. Janson, J. and Palenius, I., Aspects of the Colour of Kraft Pulp and Kraft Lignin, Paperi Puu, 54 (6) : 343 (1972).
9. Gustafsson, C. and Soila, R., Condensation of Lignin and Carbohydrates when Heating Wood with Water at Various pH Values, Paper Puu, 38 9), (1956).
10. Gierer, J. Chemical Aspects of Kraft Pulping, Wood Science Technology, (NY) 14 : 241 (1980).
11. Lemon S , and Teder, A., Bulk Delignification of Pine, Svensk Papperstid., 76 (11) : 407 (1973).
12. Rekunen, S , Jutilla, E. Lahteenmaki, E., Lonnberg, B. and Virkola, N., Examination of Reaction Kinetics in Kraft Cooking, Paperi Puu, 61 (2) : 8 (1980).
13. Teder, A. and Tormund, D., The Equilibrium Between Hydrogen Sulfide and Sulfide Ions in Kraft Pulping, Svensk Papperstid., 76 (16) : 607 (1973).
14. Pekkala, O., Some Features of Residual Delignification During Kraft Pulping of Scotch Pine, Paperi Puu, 65 (4) : 251 (1983).
15. Westling, J. M. S. Thesis, University of Washington, P. 41 (1983)
16. Stockmann, V. E. Effect of Pulping on Cellulose Structure : Part I : A Hypothesis of Transformation of Fibrils, Tappi Journal, 54 (12) : 2033 (1971).
17. page, D.H. The Origin of the Differences Between sulphite and Kraft Pulps, Canadian Wood Chemistry Symposium, 1979, Extended Abstracts, 48.
18. Patterson, Richard R., B. S. Thesis, Western Michigan University, Kalamazoo, Michigan, p. 8 (1990).