SEMINAR

OPTIMUM DEGREE OF COOKING FOR BLEACLHABLE SULPHATE PULP FROM SWEETGUM

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Introduction

Many of the studies of pulping and bleaching optima have concerned themselves with quality differences within and between the various processes while ignoring the costs involved in obtaining the prescribed optima. In this study an attempt is made to determine the degree of cooking that yields the lowest total variable cost for the production of a bleached sulphate pulp from sweetgum (Liquidambar Styraciflua L.) wood. The permanganate number test was used in this study to determine the degree of cooking while simultaneously determining the bleach- ability of the pulp. A high permanganate number indicates a low degree of cooking which implies a low cooking cost and a high bleaching cost while a low permanganate number indicates a high degree of cooking which implies a high cooking cost and a low bleaching cost. Hence, a permanganate number must exist at which the total bleaching and cooking costs are at a minimum. However, there are costs which are permanganate number related which also affect the determination of the lowest total variable cost of production. A list of the major production costs that could be permanganate number related, and the factors that determined them follows:

1. Cooking Costs

a) Sodium and sulfur makeup chemical requirements
b) Lime makeup requirements
c) Lime kiln fire requirements
d) Steam to digester

2. Bleaching Costs

a) Chlorine requirements
b) Caustic requirements
c) Chlorine dioxide requirements
d) Bleach plant effluent qualities

3. Wood Costs

a) Unbleached yields
b) Bleached. yield

4. Recovery Steam Credit

a) Unbleached yields
b) Evaporator steam costs

5. Pulp Runability Costs

a) Optical properties
b) Strength properties
c) Dirt Content

Previous studies were made by Valeur (1); and Chollet, Powell, Duffy, and Buser (2) to find the optimum degree of cooking for bleachable sulfate pulps from softwoods. In these studies not all costs listed above were considered. Valeur held cooking chemical charge and temperature constant and cooked to varying Roe chlorine numbers by varying the cooking time. In his study wood costs, bleaching costs excepting effluent treatment cost and steam credits and costs were considered in arriving at the total variable cost versus Roe chlorine number relationship. Valeur found that the total variable cost of pulp production was nearly constant between Roe numbers of 5 to 7 (permanganate number of 21 to 27, roughly) with increasing costs on either side of this range. Chollet, Powell, Duffy and Buser held cooking time and temperature constant and varied the cooking chemical charged to achieve variations in the permanganate number. Their study considered wood costs, bleaching costs excepting effluent treatment costs, and the cost of salt- cake makeup. They found that the lowest total cost of production occurred at a permanganate number equal to 20 which was the softest pulp considered. They considered this the optimum permanganate number but qualified it as follows:

> "It appears that in both mills, A and B the least total cost corresponds to the production of soft pulp of permanganate number of about 20. It may, therefore, be concluded that the extent of pulping should be the maximum consistent with good product quality and this will usually be in a range from 20 to 25 permanganate number. In particular cases, additional factors must be considered. Among these are (a) the method of recovering screenings (b) the capacity of the recovery system (c) the extent of nonuniformity in pulping and (d) effect on the quantity of steam generated. Nevertheless, the information presented is probably representative of operations in many mills utilizing similar wood."

Scheme of 0ptimization and Experimental Procedure

The major process variables of the sulphate process, which affect the degree of cooking of the pulp, are:

1. Cooking time
2. Cooking temperature
3. Chemical charge
4. Chemical concentration
5. Sulfidity
6. Wood species

In mill operations the allowable cooking time is limited by mill design and the demand placed on the mill for pulp production. Cooking temperature is limited by mill steam service design. The type of chlorine dioxide generation, type of makeup chemicals used, and the efficiencies of the sulfur recovery in the recovery boilers determine the sulfidity. The forests surrounding the mill determine the wood species. This leaves only chemical charge and chemical concentration as variables affecting the permanganate number. In the experimental portion of this study all the mill imposed constraints on the variables affecting permanganate number have been observed by assigning fairly typical mill conditions to them.

For the experimental cooking in this study the cooking schedule was held constant at 45 minutes heating time from 1000C to 176 C and 55 minutes cooking time at 176 C. The blow down at the end of the cook took ten minutes. The H-factor of this cooking cycle is 1900. The sulfidity of the experimental cooks was held constant at 25 percent. The wood species used in this study was sweetgum. The water to wood ratio was held constant at 3.5 to one. This left only chemical charge and hence concentration as the variables used in obtaining variations in the degree of cooking. 1'he active alkali charge was vari ed between 13 and 24 percent to obtain the various permanganate numbers (40 ml test, Tappi standard T-214 m-50) 1n the range of 7.6 to 15.7. The cooked chips were disintegrated for 10 minutes in a laboratory disintegrator, screened through a 0.010 cut flat screen. washed and centrifuged.. Screened and total yields were determined for each pulp. Permanganate numbers were determined on the screened, washed pulp. Residual active alkali was determined on black liquor samples taken at the end of each cook. The bleaching of sulphate pulps requires a multistage bleaching process using chlorine *(C),* chlorine dioxide (D), Hypo chlorite (H),and caustic extraction (E). The use of these chemicals is aimed at the removal of colored materials in the pulp that are for most part lignin compounds. Since the permanganate number which was used to determine the degree of cooking of the pulp roughly measures the lignin content, the demand of the pulp for bleaching chemical can be determined from the permanganate number. Popular bleaching sequences for sulfate pulp are CEHD, CEHDED, CEDED. All of these sequences begin with CE stages. Since CE bleach1ng is less expensive than the chlorine dioxide *or* hypo chlorite bleaching of the later stages, an increase in chlor1ne demand from a higher permanganate number is usually absorbed in the CE stages. In th1s study CEDED bleaches were carried out according to the conditions 1isted in Table 1. The chlorine and caustic charges were made to the CE stages in such a way that the various permanganate number pulps all had the same CE permanganate number (a 20 ml test) of 2.5

after CE bleaching. The BOD of the effluent from the CE stages was determined since it was believed that any variation in the total bleach plant effluent BOD due to initial permanganate number variations would occur most significantly from these stages. Final brightness and bleached yields were also determined on each of the various permanganate number pulps bleached. The dirt content, optical properties, and strength properties of the pulp are to some degree permanganate number related and hence must affect the optimum permanganate number. In actual mill operations, however, where paper is made from mixtures of softwood pulp, hardwood pulp, and filler, the optical and strength properties of the final sheet are for the most part determined by filler and softwood content rather than physical properties of hardwood pulp. The effect of optical and strength properties of the sweetgum pulp on the optimum permanganate number have been ignored in this study since the physical properties of the sweetgum pulp are probably overshadowed by the other components of the final product.

Results of Experimental Pulping and Bleaching

Relationships were found for total unbleached yield, screened yield, active alkali charge, residual active alkali, chlorine and caustic consumptions to a constant CE permanganate number of 2.5, bleached yield, and CE effluent BOD with the unbleached screened pulp permanganate number. The relationships are as follows:

Total Yield (%)	=	35.87 +	K*
Screened Yield (%)	=	[K<11.5]:	35.77 + K
		[K>11.5]:	$23.30 + 3.646 (K) - 0.1360(K^2)$
Active Alkali Charge (%)	=	35.55 - 1.398 (K)	
Residual Active lilkali Charge (%)	=	7.878 - 0.4737 (K)	
Chlorine Consumption (.%)	=	0.2960 + 0.2332 (K)	
Caustic Consumption (%)	=	0.1275 (K) - 0.2256	
Lbs. CE BOD per ADT	=	1.758 (K) - 8.165	
Bleached Yield (% Unbleached)	=	100.0 - 0.679 (K)	

NOTE: *K = Permanganate Number

The above relationships were determined by a linear least squares fit with the exception of the screened yield function. It was necessary to make a second order polynomial fit for this function above permanganate numbers of 11.5. All the linear relationships had correlation coefficients of above 0.9 that indicated reliable relationships. Table 2 demonstrates the reliability of the assumption that different permanganate number pulps, which are bleached to the same CE permanganate number and treated identically thereafter, yield the same final brightness. Table 2 presents the final brightness of pulps bleached in this way and their initial permanganate numbers.

TABLE 2

Permanganate Number	8	9.9	11.1	12.1	14.5
Final Brightness (%)	86.3	85.5	85.8	85.6	86.1

From the equations of the previous section and the operating costs and characteristics assumed in Table 3 an estimate of variable cost of pulp production with permanganate number can be calculated for the model pulp mill presented in Figure 1. Table 4 presents the variable cost of producing pulp at discrete permanganate numbers between six and sixteen at intervals of 2 units. If the total variable cost at various permanganate numbers is correlated by a second order polynomial regression against the permanganate number the following relationship results:

$$\text{Variable Cost Per ADT} = 49.294 - 1.328\,(K) + 0.045\,(K^2)$$

If this result is differentiated, set equal to zero, and solved for "K", the optimum permanganate number is found to be 14.6. Unfortunately this optimum is only a "local optimum" which predicts the optimum according to the assumptions and constraints of the search. If other cooking conditions, bleaching strategy, or chemical costs (which vary from location to location) are used some other optimum may result that is different than the one above. If that optimum is better than any other, it is a "universal optimum." However, if the costs and conditions used in the above analysis are considered typical, why then are permanganate number targets *for* southern hardwood pulps typically between 11 and 12 and not nearer the optimum of 14.6. One answer to this question involves the fact that hardwoods in the South are usually pulped in run of the wood mixtures. The optimum permanganate number for sweetgum of course may not be the optimum for the mixture. Another answer requires consideration of mill operations in achieving a target permanganate number. There is some variation in obtaining the target permanganate number; the degree of that variation can be expressed by the standard deviation from the mean. From the authors experience the standard deviation for cooking southern hardwoods as described is about one. This means that 95 percent of the cooks will occur between 12.6 and 16.6 with the mean occurring at the target of 14.6. The mill operating problem that would result from such a variation occurs in rejects handling. On the basis of *500* ADT, the rejects handling capacity must be designed to handle instantaneous loadings of up to 62 tons per day *for* cook blown at a permanganate number of 16.6. Such large amounts of rejects can not usually be handled within the present design of many rejects handling systems. Still more problems may come from screen room operations where very hard pulps and soft pulps of course require different screening strategies. All the problems of course apply constraints on the optimum which have not been considered previously and hence they could justifiably yield a different optimum than was found above.

Summary

The optimum permanganate number for the conditions specified and costs assumed in this study was found to be 14.6. However, certain costs and operating constraints were neglected and hence it is conceivable that if these constraints were considered or changed another optimum would result. Nonetheless, the results should be significant in finding what constraints need definition or modification to actually identify and achieve the optimum permanganate number.

1. Valeur Christian; Svensk Papperstidning; 54 (18): 613;(1951).

2. Chollet, J. L.; Powell; F.. G.; Duffy, M. G.; and Buser, R. C.; Pulp and Paper Magazine of Canada; 63 (10): T468; (1961).

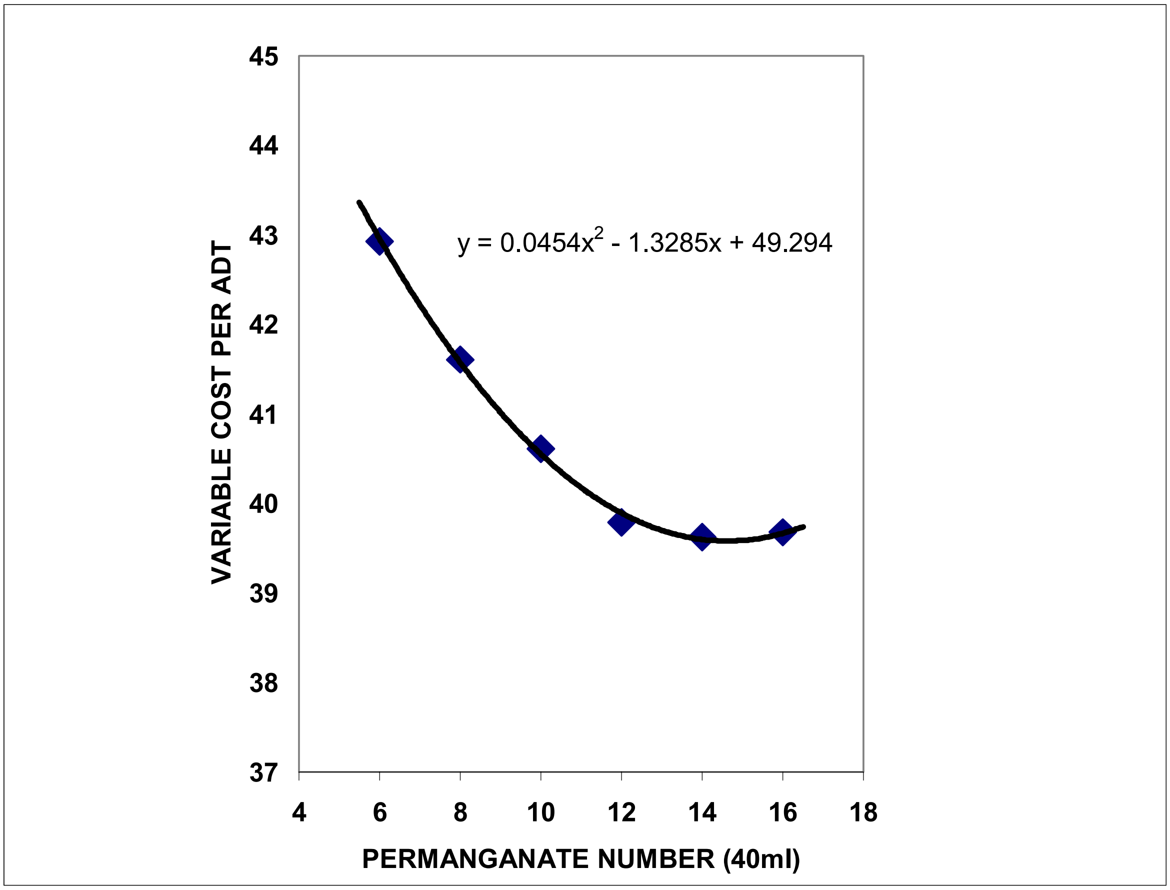

Figure 2
Net Variable Cost per Air Dry Ton Bleached
Sweetgum Pulp Versus Permanganate Number

Table 1

Bleaching Conditions

	Chlorination	First Caustic Extraction	First Chlorine Dioxide	Second Caustic Extraction	Second Chlorine Dioxide
Chemical Charge	*	*	1.0% as Available Chlorine	0.5%	0.5% as Available Chlorine
Consistency	3%	9%	9%	9%	9%
Temperature	75˚F	160˚F	160˚F	160˚F	160˚F
Time	45 min.	90 min	90 min	90 min	90 min

* As specified in Text

Table 3

Assumptions Made in Calculations

Assumptions:

Costs		
	Wood	$25.00 per cord
	Saltcake	$36.00 per ton
	Lime	$28.00 per ton
	Oil	$ 2.50 per bbl
	Chlorine	$75.00 per ton
	Caustic	$65.00 per ton
	BOD Reduction	$30.00 per ton
Material. Characteristics		
	Oil	5.83MMBTU per bbl
	Wood	5400 wet lb per cord
	Wood	50% moisture content
	Wood	Specific heat 0.33 BTU per lb °F
	Chemical	Specific heat 0.33 BTU per lb °F
	Black Liquor Organics	9500 BTU per lb
	White Liquor	As specified in Appendix V
	Rejects	Yield 50%
Operation Concepts		
	Evaporators Chemical Losses	5.7 Economy
	Chemical. Losses	1 lb. Saltcake per cubic foot white liquor based digester consumption
	Chemical Losses on usage	3% Lime loss in liquor room based
	Lime Kiln	10 MM B'l'U per ton lime
	Steam	1000 BTU per lb essentially in all steam (latent heat)
	Brown Stock Washer	All chemical and organics recovered (100% efficiency)

Table 4

Total Cost Variation with Permanganate Number

Permanganate Number	**6**	**8**	**10**	**12**	**14**	**16**
Wood Cost per ADT	$41.458	$40.063	$38.850	$37.878	$37.620	$37.705
Cooking Chemical Makeup Cost per ADT	$5.680	$4.895	$4.233	$3.590	$3.042	$2.512
Steam Cost to Digester per ADT	$1.147	$1.104	$1.067	$1.036	$1.024	$1.022
Total Cost of Bleach Plant Operation per ADT	$1.557	$2.112	$2.697	$3.282	$3.899	$4.489
Total Cost of Pulp Production per ADT	$49.842	$48.174	$46.847	$45.786	$45.585	45.728
Less Credit for Recovered Steam per ADT	$6.914	$6.563	$6.233	$5.996	$5.959	$6.050
Net Cost of Pulp Production per ADT	$42.928	$41.611	$40.614	$39.790	$39.626	$39.678