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Influence of Sulfidity and Active Alkali Charge on the Properties of Pulp Produced from *Eucalyptus camaldulensis*

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Abstract: The influence of cooking liquor parameters as independent variables, i.e., active alkali and sulfidity was investigated on the properties of pulp produced from *Eucalyptus* camaldulensis. The pulp properties were cooking yield, kappa number, rejects rate, brightness and viscosity. The multiple nonlinear regression of independent and dependent variables were conducted with MATLAB software using least square method. According to the results, by increasing sulfidity from 20 to 40% and decreasing active alkali from 25 to 19% on o.d. wood it was possible to improve the pulping yield significantly but simultaneously reject rate increased. However, the effect of decreasing active alkali charge was more influential than increasing sulfidity in all cases. By using D_0ED_1 bleaching sequence averagely 262% improvement in brightness and only 6.5% reduction in viscosity were observed.

Key words: Active alkali, sulfidity, cooking yield, kappa number, reject rate, brightness, viscosity, multiple nonlinear regression

INTRODUCTION

Kraft pulping process has been known for decades. It has higher market value and compatibility with most of the wood species and gives high strength pulp and better operation in chemical recovery system. It is desirable for many paper products and produces a stronger sheet of paper thus being able to compete with the other pulping processes such as sulfite (Yusup, 2004). Many parameters can affect the pulp properties but there are also some disadvantages in Kraft pulping for instance; pulp must be bleached and low yield due to carbohydrate losses (Kusuma, 2003).

From 400 species of *Eucalyptus* in Australia, only 17 species are more useful for pulping. However, growth rate is a main factor in chemical properties of wood (Rashidi, 2002). *Eucalyptus* can grow well on various soils. *Eucalyptus camaldulensis* is easily planted in tropical zone and has good suitability with different climate and ecological conditions especially in Thailand. It contains higher holocellulose (72-76.8%) which makes it one the most competitive hardwoods to be used for pulping (Ona *et al*., 1996).

There is a general agreement that high alkali concentration in the initial phase and a leveled out effective alkali concentration in the bulk phase result low lignin concentration in the residual stage of cooking (Saucedo and Kishanagopalan, 2002). The higher residual alkali charge is required to prevent the recondensation of lignin on the fibers. It has been found that the amount of residual alkali charge in the case of high alkali charge was high (Minh, 2000). Previous study on pulping characteristics of

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Eucalyptus camaldulensis showed that the highest cooking yield can be obtained at low alkali charge, lower temperature, shorter cooking time, higher liquor to wood ratio (L:W). The delignification rate slowed down due to decrease in Effective Alkali (EA) charge in the cooking process. This effect was more pronounced at high L:W ratio (Kusuma, 2003). In the Kraft pulping, the rate of delignification strongly depends on temperature and time so that the most part of delignification is done in the bulk delignification phase. H-factor, area under relative reaction rate curve against time, is a valuable parameter not only including both cooking time and temperature, but it also helps to control pulping process for a target kappa number (Gullichsen and Fogelholm, 1998). In this study all experiments were conducted at the same H-factor.

The viscosity of pulp depends on the hemicelluloses content of pulp and it has been found that the pulp viscosity at a given kappa number increases with increasing sulfide sorption in the wood (Heaing, 2000; Olm *et al*., 2000). It has been found that the ECF bleaching sequence ($D_0E_0D_1D_2$) of delignified Kraft pulps made from *Eucalyptus* gave higher pulp brightness (>90% ISO) (Camilla and Ulf, 1991).

The sulfidity and active alkali charge are two effective parameters that influence the pulp properties (Gullichsen and Fogelholm, 1998). From the delignification in Kraft pulping, sulfide and hydrosulfide ions facilitate the reaction of lignin removal and sulfur works mainly as a catalyst which is not consumed or transformed much (Bhowick, 1993). It has been found that the efficiency of lignin removal increases with increasing sulfidity. In practice, sulfidity is most often determined by chemical balance of the mill: higher in closed cycle and lower in open mills. The optimum sulfidity also depends on several factors, such as wood species, alkali charge, cooking temperature and properties desired in the final product. The upper limit is typically determined by odor release from the plant (Mirshokraee, 2003). Thus both active alkali charge and sulfidity play an important role in the Kraft pulping.

Modeling strategy allows developing empirical models as a function of various independent variables (Navaee-Ardeh *et al*., 2004). Such a modeling can aim improving the pulping operation as well as minimizing extra experimental attempts thus saving a lot of time and costs. It has been reported that the strength properties of Kraft made pulps can be improved under optimized cooking conditions (Akgul *et al*., 2007). Proper mathematical models can be used to control the pulping process for a given product or specific pulp mill. In spite of extensive experimental investigations on Kraft pulping process, the modeling of pulp characteristics of *Eucalyptus camaldulensis* versus pulping variables is yet missing. In this study, the effect of various sulfidity and active alkali charges of cooking liquor were investigated on the produced pulp properties. Furthermore, the multiple nonlinear modeling of experimental data was performed to illustrate the effect of each independent variable on pulping properties.

MATERIALS AND METHODS

Experimental

Pulping and Screening

Fresh screened (according to standard SCAN-CM 40: 94) mill chips of *E. camaldulensis* collected from a local pulp mill near Pulp and Paper Center at Asian Institute of Technology (AIT) were used for the pulping process. The dry matter content of the chips was determined according to the standard SCAN-CM 39:94. Wood chips were cooked in an air heated 6-2.5 L autoclave digester with 400 g o.d. chips charge in each autoclave. The sulfidity and active alkali were changed in the range of 20-40% (as NaOH) and 19-25% (on o.d. wood), respectively. The pulps were prepared at a liquor to wood ratio of 4:1. The time from room temperature to 80°C was 20 min and from 80°C to the cooking temperature (160°C) was 55 min followed by a further 2 h at the cooking temperature. After cooking the pulp of each sample was washed using 8 L tap water for 5 times. The washed pulp then was centrifuged and homogenized. The homogenized pulp was weighted and dry matter content of pulp was determined (SCAN-C 3:78) and yield calculated. Then it was disintegrated and followed by a screening with a 0.2 mm slotted flat screen. Kappa number was measured according to the standard SCAN-C 1:77.

Bleaching

Fifty gram of each screened pulp was used for bleaching by a D_0ED_1 sequence in plastic bag in water bath. Pulp and distilled water before bleaching were preheated in microwave oven. The bleaching conditions have been summarized in Table 1. After each stage, the pulp was washed with distilled water using suction bottle. Brightness and viscosity were measured according to the standards SCAN-C 11:75 and SCAN-CM 15:88, respectively.

Experimental Design

In this study, all the independent variables were normalized according to the following formula (Navaee-Ardeh *et al*., 2004):

$$x_i = \frac{X_i - X_{min}}{X_{max} - X_{min}} \tag{1}$$

The normalized independent variables and experimental data of pulping and bleaching processes were used for developing the best empirical models to fit the curve in which the dependent variables were evaluated by the following formulas:

$$y_1 = a_0 + \frac{a_1}{a_2 + x_2} + a_3x_1 + a_4x_1^2 \tag{2}$$

$$y_2 = b_0 + \sum_i b_i x_i + \sum_j \sum_i c_{ij} x_i x_j \tag{3}$$

Where, y_1 and y_2 are dependent variables, x_i is the normalized independent variable and X_{min} and X_{max} are the minimum and maximum value of corresponding independent variables, respectively. Unknown linear and non-linear coefficients (a_i, b_i and c_{ij}) were found using experimental data

Table 1: Bleaching conditions

Parameters	D_0	E	D_1
Reagents	ClO_2	NaOH	ClO_2
Temperature (°C)	60	80	70
Time (min)	60	60	180
Conc. of reagent on % o.d. pulp	0.25*KN	2.5	1.5
Consistency o.d. (%)	8	8	10

Table 2: Summary of the white liquor components and corresponding pulping, screening and bleaching processes results

Cooking						
Sulfidity % (as NaOH)	30.00	30.00	30.00	30.00	20.00	40.00
Active Alkali charge % (on o.d. wood)	19.00	21.00	23.00	25.00	21.00	21.00
Cooking yield (%)	50.00	44.50	44.70	45.20	45.10	47.10
Kappa number	34.40	23.40	19.93	20.64	22.91	26.92
Residual EA (as NaOH mL^{-1})	0.00	1.20	2.72	0.055	1.86	0.70
Screening						
Reject rate (%)	2.10	0.20	0.30	0.50	0.10	0.40
Screened yield (%)	47.90	44.30	44.40	44.70	45.00	46.70
Bleaching						
Brightness (bleached pulp) % ISO	87.24	80.50	83.59	82.04	83.46	84.56
Brightness (unbleached pulp) % ISO	21.45	23.75	23.21	25.29	24.13	20.96
Viscosity of bleached pulp (mL g^{-1})	894.00	692.00	653.00	557.00	682.00	836.00
Viscosity of unbleached pulp (mL g^{-1})	926.00	770.00	588.00	706.00	796.00	827.00

Table 3: Linear and non-linear coefficients of dependent variables according to Eq. 2 and 3

	Variables	a_0	a_1	a_2	a_3	a_4	b_0	b_1	b_2	c_{11}	c_{22}	c_{12}	r^2
†	KN	11.10	9.91	0.5	4.90	-0.89							0.94
	CY (%)	43.75	0.59	0.1	-1.19	3.19							0.95
	RR (%)	-0.35	0.20	0.1	1.32	-1.02							0.94
‡	UBPV (mL g^{-1})						538.60	-234.60	1769.00	4964.10	270.00	-63811.00	1.00
	BPV(mL g^{-1})						729.00	2293.00	-2667.00	-10168.00	-2461.00	13168.00	1.00
	UBPB (% ISO)						21.85	-33.00	47.84	169.30	25.25	-209.81	1.00
	BPB(% ISO)						84.51	26.27	-34.30	-178.33	-74.89	263.96	1.00

KN = Kappa Number, CY = Cooking Yield, RR = Reject Rate, UBPV = Unbleached Pulp Viscosity, BPV = Bleached Pulp Viscosity, UBPB = Unbleached Pulp Brightness, BPB = Bleached Pulp Brightness, †: x_1= Normalized sulfidity (% as NaOH); x_2 = Normalized active alkali (% on o.d. wood), ‡: x_1 = Normalized kappa number; x_2 = Normalized screened pulp yield, r^2 = Pierson's coefficient (Lapin, 1990)

(Table 2) and were summarized in Table 3. Six conducted experiments with the corresponding independent and dependent variables have been summarized in Table 2.

RESULTS AND DISCUSSION

Normalization of the independent variables provides better estimates for the regression coefficients by reducing correlation between linear and quadratic interaction terms. Multiple nonlinear regression analysis to find the best model for experimental data was performed by MATLAB software (version 6.1) using least square method. Kappa number has two roles: independent and dependent variable. The results of this process have been summarized in Table 3.

Based on the experimental results, independent variables were changed over the following ranges:

- Active alkali charge (on o.d. wood): 19-25%
- Sulfidity (as NaOH): 20-40%
- Kappa number: 20 -34.4
- Screened pulp yield: 44.3-47.9%

In these experiments, cooking time, temperature and liquor to wood ratio were kept constant. The best advantage of multiple nonlinear regression is related to considering the effects of both sulfidity and active alkali charge at the same time on the dependent variables. Kappa number as a function of active alkali charge and sulfidity has been shown in Fig. 1. It can be seen that by increasing sulfidity, kappa number linearly increased, however kappa number varied nonlinearly in respect to the active alkali charge. At low active alkali charge, kappa number varied rapidly but its variation slowed down at the high active alkali charge. It can be inferred that the active alkali charge has reverse effect on kappa number, but sulfidity has positive effect (Fig. 1). It can also be seen that high kappa number was obtained at low active alkali charge and high sulfidity whereas low kappa number is achieved at high active alkali charge and low sulfidity.

The effect of sulfidity on cooking yield variation was marginal in comparison to the variation of cooking yield with active alkali charge. The variation of cooking yield was like the kappa number variation but it varied nonlinearly respect to the sulfidity. Moreover, the variation of cooking yield at low active alkali charge significantly increased (Fig. 2).

Insufficient cooking process generates higher rejects and results more shives, chop and debris in the screening process. There was a maximum reject rates at 33% sulfidity which needs to be avoided. Indeed it can be inferred that the kappa number, cooking yield and reject rate as dependent variables are more sensible to active alkali charge than sulfidity. However by increasing active alkali this sensibility decreased but there was a uniform change for these dependent variables with the variation of sulfidity.

At low screened pulp yield by increasing initial pulp's kappa number, the viscosity of unbleached pulp increased (Fig. 4). The main reason can be explained that the higher the kappa number, the lower the removal of lignin during pulping and therefore less hemicellulose dissolution occurs. The variation

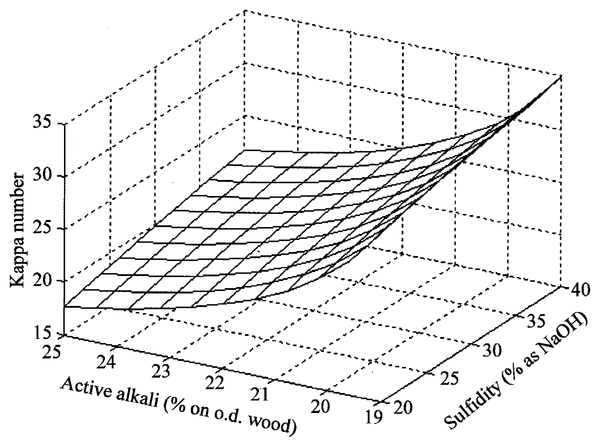

Fig. 1: Variation of Kappa number vs. active alkali and sulfidity

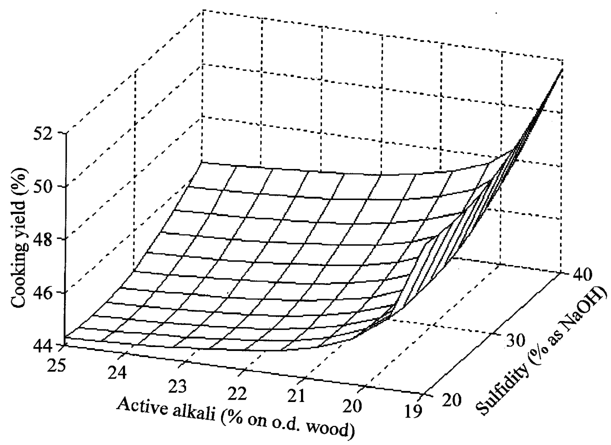

Fig. 2: Variation of cooking yield vs. active alkali and sulfidity

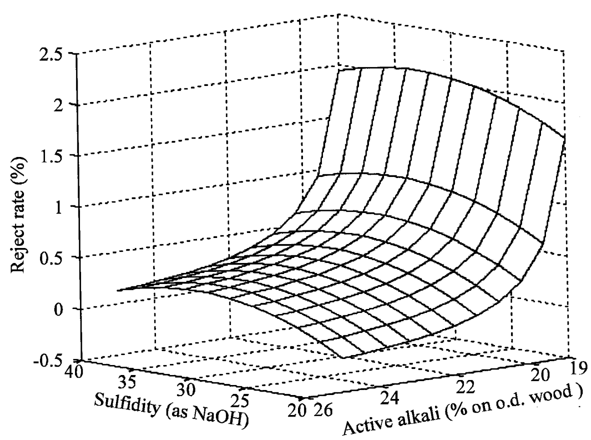

Fig. 3: Reject rate in pulp screening vs. active alkali and sulfidity

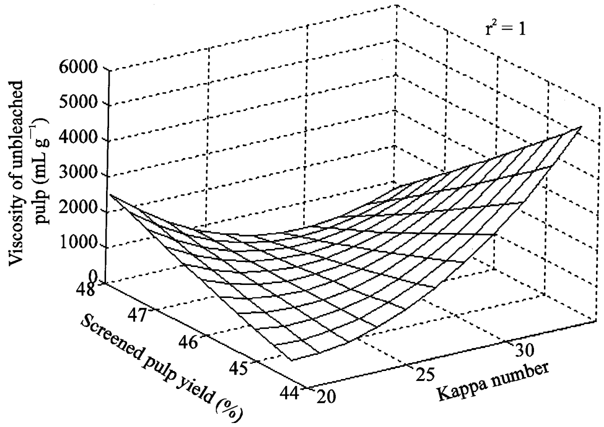

Fig. 4: Unbleached pulp viscosity vs. screened pulp yield and kappa number

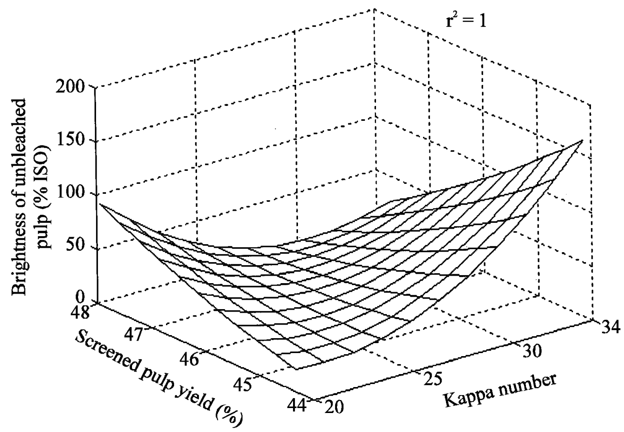

Fig. 5: Brightness of unbleached pulp vs. screened pulp yield and kappa number

of viscosity of unbleached pulp was completely fitted as a polynomial function of the normalized screened pulp yield and kappa number. There was a minimum viscosity and brightness for unbleached pulp showing lower hemicellulose content. At low kappa number by increasing screened pulp yield, the viscosity linearly increased. By increasing kappa number and decreasing screened pulp yield both viscosity and brightness of unbleached pulp increased (Fig. 3-5).

In contrast, the variation of bleached pulp viscosity and brightness was completely different than unbleached pulp (Table 3 and Eq. 3).

CONCLUSIONS

Different chemical charges in the pulping process of *E. camaldulensis* chips affected pulping yield, kappa number, viscosity and brightness, significantly. The average values of cooking yield, unbleached and bleached pulp brightness and viscosity were 46.1%, 23.1, 83.5 ISO%, 769 and 719 mL g^{-1}, respectively. It was possible to improve the brightness of the pulp using D_0ED_1 bleaching sequence 60.4 ISO% (261.47% improvement) compared to the unbleached pulp brightness whereas the reduction in viscosity (hemicellulose content) was only 50 mL g^{-1} (6.5% reduction). Generally the viscosity (hemicellulose content) of unbleached pulp was more than the viscosity of bleached pulp.

The empirical models facilitated to investigate the impact of different parameters on pulping properties. The models are also able to help controlling the pulping process for better results as well as minimizing the number experimental trials thus cost saving in the mill scale. The developed models can also be used to optimize the pulping process according to the requirements of a particular pulp mill.

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