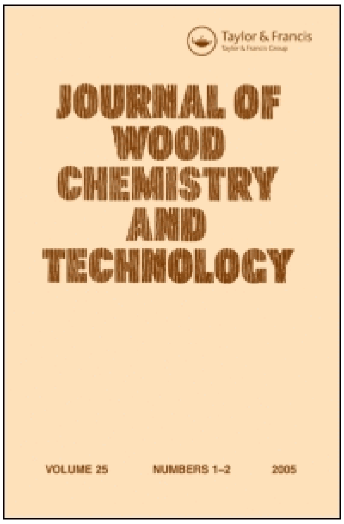

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Effects of Multiple Pulping Variables on the Molecular Weight and Molecular Weight Distribution of Kraft Lignin

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EFFECTS OF MULTIPLE PULPING VARIABLES ON THE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF KRAFT LIGNIN

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ABSTRACT

The effects of pulping variables on the molecular weight and molecular weight distribution of dissolved lignin have been studied. Kraft lignins were prepared by cooking Slash pine (Pinus caribaea) wood chips in a pilot-scale batch circulation digester. Four pulping variables, effective alkali, sulfidity, cooking temperature, and time-at-temperature, were arranged in a very broad input space under a central composite experimental design, and their effects on the molecular weight of dissolved lignin were examined by means of fifteen-parameter quadratic models.

It was found that, generally, the molecular weight of dissolved lignin increases in both bulk and final phases as delignification proceeds. Prolonged cooking at the end of final phase delignification causes degradation of lignin in the liquor and reduces the molecular weight of Kraft lignin. Discussions of pulping effects on the molecular weight of dissolved lignin are presented in detail.

INTRODUCTION

It is generally agreed that Kraft delignification is a first order reaction with respect to lignin concentration[1,2] and that the entire process consists of three phases: the initial, bulk, and final phases[2]. The initial phase is believed to be a diffusion controlled process[3]. The bulk phase delignification appears to be chemically controlled[4] and proceeds at a practicable rate only at temperatures above 150C[5,6]. The final phase delignification has the lowest reaction rate[1]. In the case

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of pine, the initial, bulk, and final phases correspond to H factors of about 100, 100 to 1000, and 1000 to about 2000, respectively[2].

Chiang and his colleagues[7-10] studied the isothermal pulping kinetics under an instantaneous isothermal condition, and found that[8] the Kraft delignification curve can not be resolved unambiguously by three intercepting straight lines. By using nonlinear regression techniques, they regressed the data points of Kraft delignification of Douglas-fir into a single equation for the entire delignification process, and found that[8] the amounts of lignin removed during the initial, bulk, and final phases are 18.8, 71.4, and 3.8%, while the rest (6%) was physically dissolved by alkali prior to chemical reactions. Recently, Labidi and Pla[11,12] reported the results of alkaline delignification of hardwoods in a flow-through reactor at a low residence time. They regressed the weight fraction of lignin remaining in the wood into exponential equations according to the three kinetic stages, and confirmed that the initial phase is a diffusion-controlled process.

Even though the molecular weight of lignin is one of the traditional topics in the study of lignin, the effects of multiple pulping variables on the molecular weight of lignin and its distribution have received little study, due to the complexity and multivariable nature of pulping, the heterogeneity of the chemical reactions, and the difficulty and uncertainty of the characterization techniques. Studies of the optical effects (fluorescence, anisotropy, absorption) of lignin solution on the determination of molecular weight of lignin with LALLS were reported in our previous paper[13], and we developed a reliable method to characterize the molecular weight of lignin. The current investigation attempts to develop correlations of the molecular weight of lignin with respect to pulping variables, under a 2^k+2k+1 ($k=4$) central composite experimental design.

Cooking time has been the single variable studied most often for its effect on the molecular weight of lignin. Experiments conducted in continuous flow reactors have shown that the molecular weight of dissolved lignin increases as delignification proceeds in Kraft[14-16], soda[15], acid sulfite and bisulfite[17] pulping of Spruce wood. Brown[18] reported that the molecular weight of lignin in the middle lamella region is higher than that in the secondary wall. An organosolv cooking of Spruce chips also indicated that[19] the molecular weight of residual lignin is considerably higher than that of the corresponding soluble lignin, and is dependent on yield and/or isolation procedure; however, it is not representative of the total lignin in the pulp[19]. Moreover, lignin fractions of very high molecular weight, from 230,000 to 410,000 Dalton, leached from an unbleached Kraft pulp were found to be still increasing in molecular weight as the washing of pulp proceeded[20]. However, Ahlgren, Yean and Goring[21] observed that the weight-averaged molecular weight of lignin remained constant during the course of reaction in an acidified sodium chlorite pulping of Spruce wood in a continuous flow reactor. This contradiction was explained as being due to the effects of diffusion. Lindberg[22] observed that soda liquor yielded lignin of higher molecular weight than Kraft liquor. In contrast, Obiaga[15] reported that Kraft liquor contains lignin of higher molecular weight than soda liquor.

There exist two alternative theories[23] in regard to the fundamental structure and size of lignin macromolecules: lignin is an infinite cross-linked three-dimensional network or it is a branched molecule of relatively small size. The latter treats delignification as a process of functionalization and subsequent dissolution of the lignin molecule, for which the molecular weight and molecular weight distribution have been predetermined by the process in the wood cell[23]. The former views delignification as a process of degradation or cleavage of the infinite network, and the degraded lignin is dissolved as macromolecules in a wide range of sizes[23]. Yan[24-26] developed a molecular theory of delignification. Ahlgren, Yean and Goring[27], Stone and Scallan[28] emphasize the physical factors and visualize the delignification occurring in two steps: cooking chemicals first degrade and dissolve the hemicellulose in the cell wall, thus creating a porous structure in the wood fibers; and then lignin is degraded and diffuses out through these pores. Therefore, there is a correlation between the pore size and the molecular weight of degraded lignin.

Most of the previous studies reported in literature investigates the effect of a single pulping variable with other variables fixed. In a multivariable pulping process, the effect of a single variable is not comparable unless all other conditions are fixed at the exact same conditions. Therefore, it is very necessary to analyze the effects of different factors simultaneously , which was the objective of this study.

EXPERIMENTAL

Kraft Pulping Experiments

Slash pine (Pinus caribaea) wood chips (95% at 2.86cm x 0.48cm), provided by the George-Pacific Corporation, were cooked in a vertical batch digester with a total volume of 0.10(m^3). The digester was equipped with a liquor circulation pump to provide forced liquor circulation. The four input variables investigated are effective alkali, EA, sulfidity, S, cooking temperature, T, and the time-at-temperature, t, respectively. The variable ranges for the EA, S, T, and t were designed as 11.5 to 17.5 (% O.D.W.), 12.5 to 42.5 (% active alkali), 160.0 to 182.2 ^{0}C (320 to 360 ^{0}F), and 20 to 100 minutes, respectively.

Kraft pulping experiments were conducted under a 2^k+2k+1 (k=4) central composite design(see Table 1). The coded values are defined by equations 1 to 4 as:

$$EA_{code} = \frac{EA-14.5}{1.5} \qquad [1]$$

$$S_{code} = \frac{S-27.5}{7.5} \qquad [2]$$

$$T_{code} = \frac{T-171.1}{5.6} \qquad [3]$$

$$t_{code} = \frac{t-60}{20} \qquad [4]$$

Notice that the EA, S, T, and t are in unit of "% O.D.W", "% active alkali", "degree Celsius", and "minutes", respectively; the EA_{code}, S_{code}, T_{code}, and t_{code} are the corresponding coded variables and each has five values of -2, -1, 0, 1, 2; the increasing steps for EA, S, T, and t are 1.5%, 7.5%, 5.6 ^{0}C (10 ^{0}F), and 20 minutes, and their center point values are EA=14.5%, S=27.5%, T=171.1 ^{0}C (340 ^{0}F), and t=60 minutes, which correspond to EA_{code}=0, S_{code}=0, T_{code}=0, and t_{code}=0, respectively.

In the 2^k+2k+1 (k=4) input space, the 2^k term represents a full factorial design of 16 experimental runs (#1 to #16 in Table 1), which are defined by the combinations of coded values -1 and 1. The 2k term represents 8 "star points" (extreme conditions, #18 to #25 in Table 1), each consists a coded value -2 or 2 and three zeros for the other three variables, e.g. (-2, 0, 0, 0), (2, 0, 0, 0), etc. The last term is a center point (0, 0, 0, 0), i.e. EA=14.5%, S=27.5%, T=171.1 ^{0}C (340 ^{0}F), t=60 minutes (#17 in Table 1).

The liquor-to-wood ratio was fixed at 4/1, the causiticizing efficiency and reduction efficiency were maintained constant at 85% and 93%, respectively.

TABLE 1

A Four-Variable, Two-Level Central Composite Kraft Pulping Design and The Corresponding Pulp Yield and The Molecular Weight of Lignin.

	PULPING VARIABLES								RESPONSES		
No	Coded				Values				Pulp	Lignin	
	EA	S	t	T	EA %	Sulfidity %	Time Min.	Temp. F	Yield %	Mw Dalton	Mn Dalton
1	-1	-1	-1	-1	13	20	40	330	69.6	19,630	1,538
2	-1	-1	1	1	13	20	80	350	40.2	32,030	2,195
3	1	-1	1	-1	16	20	80	330	53.4	28,620	2,305
4	1	-1	-1	1	16	20	40	350	40.5	16,060	1,834
5	-1	1	1	-1	13	35	80	330	56.0	25,820	1,906
6	-1	1	-1	1	13	35	40	350	55.4	22,020	2,090
7	1	1	-1	-1	16	35	40	330	52.0	32,420	1,897
8	1	1	1	1	16	35	80	350	42.7	58,880	1,461
9	-1	-1	1	-1	13	20	80	330	59.1	21,930	1,684
10	-1	-1	-1	1	13	20	40	350	58.7	36,080	1,761
11	1	-1	-1	-1	16	20	40	330	59.7	23,270	2,033
12	1	-1	1	1	16	20	80	350	41.0	26,300	2,463
13	-1	1	-1	-1	13	35	40	330	60.0	20,090	2,169
14	-1	1	1	1	13	35	80	350	49.5	18,920	1,956
15	1	1	1	-1	16	35	80	330	52.8	48,440	2,048
16	1	1	-1	1	16	35	40	350	46.9	59,530	2,051
17	0	0	0	0	14.5	27.5	60	340	53.2	42,930	2,017
18	0	0	-2	0	14.5	27.5	20	340	68.3	21,210	1,560
19	0	0	2	0	14.5	27.5	100	340	-	-	1,516
20	0	0	0	-2	14.5	27.5	60	320	65.1	23,030	3,019
21	0	0	0	2	14.5	27.5	60	360	-	-	1,199
22	-2	0	0	0	11.5	27.5	60	340	60.5	17,780	1,011
23	2	0	0	0	17.5	27.5	60	340	41.9	17,760	1,681
24	0	-2	0	0	14.5	12.5	60	340	57.9	23,750	1,285
25	0	2	0	0	14.5	42.5	60	340	41.7	18,700	942

Although the time-to-temperature varied from batch to batch, typically it had a value of 20 to 25 minutes. In fact, temperatures were monitored and recorded with four thermal couples in different locations within the chip bed in both the time-to-temperature and the time-at-temperature phases. Subsequently, a temperature profile was developed and a H-factor[29] was calculated by equation 5.

$$H = \int_{o}^{t} \exp[43.2 - \tfrac{16113}{T}]dt \qquad [5]$$

Where, t is time in hours and T is temperature in Kelvin. More detailed information about the digester used and the pulping conditions can be found elsewhere[30,31].

Preparation of Lignin Samples

After each cook, black liquor was drained and filtered. The pulp was washed twice, and the two washes were combined with the black liquor. This fresh liquor was concentrated by evaporation at about 0.5 atmosphere, which results in a maximum temperature of 90C. Then, it was skimmed to separate soap substances. More detailed information about black liquor handling and evaporation can be found elsewhere[31].

Purified lignin samples were prepared from the skimmed black liquors. Black liquor samples at 10% solids with a pH of about 13 was filtered through a glass fiber filter to exclude fibril or particulate impurities, then it was titrated with 1.0N sulfuric acid slowly to a final pH of about 2.0 under stirring. The subsequent slurry was centrifuged and the supernate decanted; the lignin was washed with deionized water, centrifuged, and the supernate decanted. This precipitated lignin was redissolved in 0.1N sodium hydroxide and the solution pH was adjusted to about 13. It was then filtered through a filter paper to separate an insoluble substance. The subsequent filtrate was re-titrated with 1.0N sulfuric acid, the slurry was centrifuged, and the supernate decanted. The re-precipitated lignin was washed, centrifuged, and the supernate decanted with deionized water once, with 0.01N sulfuric acid twice, and with deionized water three more times. Then, the washed lignin was freeze dried. Finally, the dried lignin was extracted with hexane to reduce the organic impurities and freeze dried again.

Determination of Molecular Weight

In this study, primary (absolute) methods were employed to determine the molecular weights of lignin, and the molecular weight distribution was simply defined as the polydispersity index of lignin (the ratio of M_w/M_n). The weight-averaged molecular weight of Kraft lignin was determined with a KMX-6 low angle laser light scattering photometer(LALLS). In the early stage, we tested three kinds of solvents at different temperatures: dimethyl formamide (DMF) at 80C, pyridine at 50C, and 0.1N sodium hydroxide at ambient temperature, respectively. The optical effects of fluorescence, absorption and optical anisotropy of lignin solution were corrected, and the fully corrected molecular weight was used to develop correlations with pulping conditions. The detailed LALLS methodology and the correction procedure were described elsewhere[13]. Following the procedures developed, the determination of the molecular weight of lignin is very tedious and laborious. In fact it may take more than a man-week to prepare a lignin sample and to get a corrected weight-averaged molecular weight of lignin. For the present work, we did not repeat measurement. However, in the method-developing stage, we estimated that the measurement accuracy[13]would be within ±10%.

The number-averaged molecular weight of Kraft lignin was determined with a Wescan model 233 vapor phase osmometer (VPO) in dimethyl formamide (DMF) at 80.0C. Both the weight-averaged molecular weight and number-averaged molecular weight of lignins were summarized in Table 1.

RESULTS AND DISCUSSIONS

Molecular Weight versus Pulp Yield

Figure 1 shows a plot of the weight-averaged molecular weight of lignin with respect to the pulp yield. Surprisingly, it seems that a reasonable relationship between the weight-averaged molecular weight and the pulp yield exists, regardless of chemical levels. As shown in Figure 1 (the thick line), the weight-averaged molecular weight increases slowly as the pulp yield decreases from 70% to about 55%, then rises very sharply and reaches a maximum as the pulp yield further

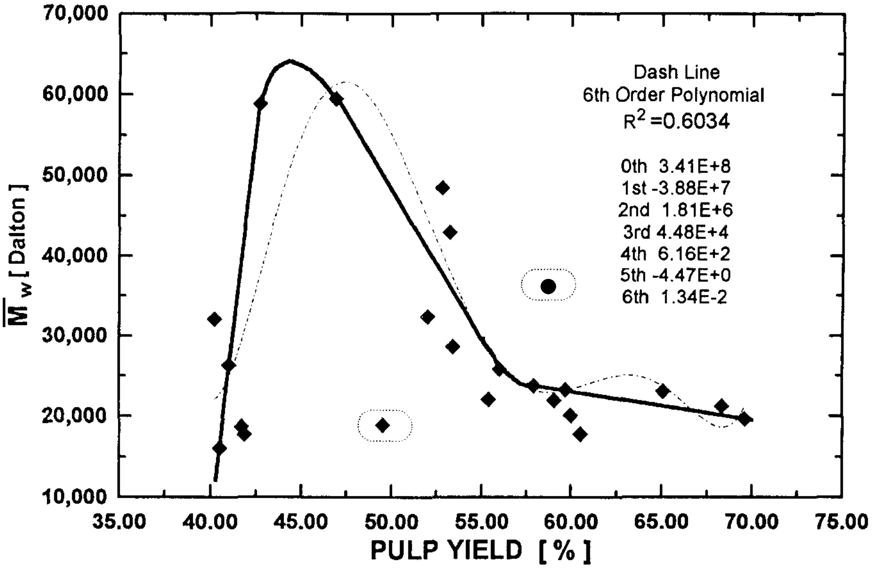

FIGURE 1. Dependence of the weight-averaged molecular weight of lignin on pulp yield for Kraft pulping of Slash pine.

decreases from 55% to about 45%, and finally it drops very sharply as the pulp yield decreases from 45% to 40%. Only two experimental points lie far from the curve plotted in Figure 1.

Probably, the most appropriate way to measure the degree of delignification in pulp is to determine the Klason lignin. However, the primary goal of our project (a project supported by the US Department of Energy) is to develop a data base for the composition and physical properties of black liquors and lignins at various pulping conditions. The project emphasized on black liquor instead of the pulp. We characterized the pulp yield and Kappa # only on the pulp side. we did not have Klason lignin available.

H-factor is a good measurement for the extent of delignification process if the chemical level is fixed. However, it is not proper to use H-factor to make comparisons with varying levels of cooking chemicals. On the other hand, since the chemical levels of a cooking liquor directly affect the lignin content of black liquor (it is defined as the percentage ratio of the dissolved lignin to the total solids

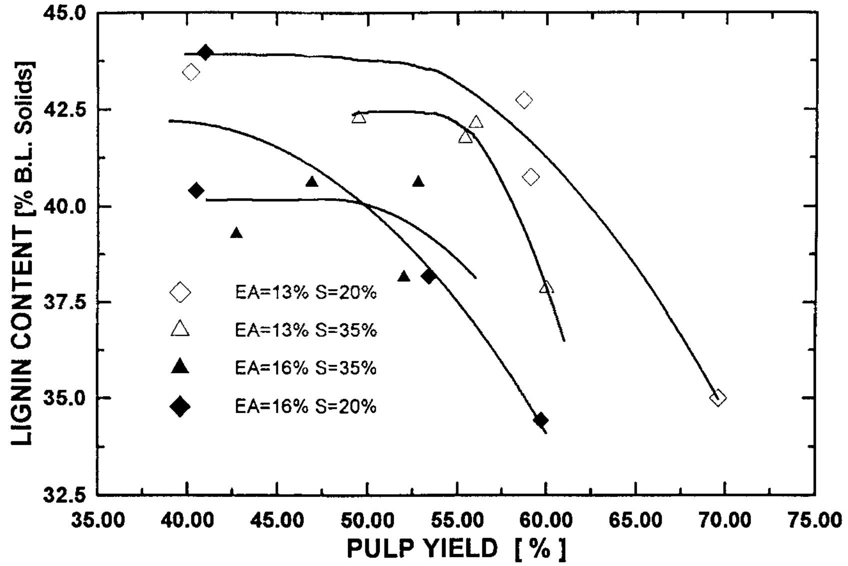

FIGURE 2. Lignin content of black liquor as a function of pulp yield at different chemical levels for Kraft pulping of Slash pine. (The black liquor content is defined as the percentage ratio of lignin to total black liquor solids.)

in the black liquor in this study[30]), it is not valid to use the lignin content of black liquor to compare the degree of delignification at different chemical levels. Also, practically, the experimental error in Kappa Number determination is not as easily controlled as pulp yield. That is why pulp yield is used as a variable in Figures 1, 3, and 4.

Logically, pulp yield is approximately inversely proportional to the total lignin available on the pulp, since cellulosic substances and lignin are the two main components of wood. In order to interpret the information shown in Figure 1, the lignin content of black liquor was plotted with respect to the pulp yield at different fixed chemical levels, as shown in Figure 2. Figure 2 indicates that, generally, the lignin content of black liquor (at fixed chemical levels) first increases sharply as pulp yield decreases, and then changes its slope and approaches a nearly constant value. It is very probable that the rapid increase with the decreasing yield at high pulp yield represents bulk phase delignification, the transition indicates a change from the bulk to the final phase of delignification, and the low rate change with decreasing yield at low pulp yield represents the final phase of delignification. Although the four curves plotted at different chemical levels appear to be different, it seems that a common transition point does exist near a pulp yield of 55%. Notice that the experimental design used in this study does not show the initial phase, since all experimental runs terminate beyond the initial phase. Therefore, it seems that the following conclusion can be reached: as delignification proceeds, the weight-averaged molecular weight of dissolved lignin slightly increases in the bulk phase and increases very sharply in the residual phase of delignification.

In the region of pulp yield from about 45 to 40%, the weight-averaged molecular weight decreases sharply as the pulp yield decreases (Figure 1). The experimental points in this region can be classified into two special cases: the H factor above 2500 regime and the extreme high chemical level (the 2k "star" location) points. This decrease in molecular weight generally occurs at or "after" the end of the final phase of delignification. If one visualizes a Kraft cooking process as the competition of the delignification reactions of the lignin in the pulp and the reactions of the dissolved lignin (degradations and condensations) in the liquor, there is essentially no lignin available in the pulp at the end of process and the reactions in the liquor predominate. Figure 1 suggests that, at the end of final phase, the degradation reactions of the dissolved lignin dominate.

Observation of the relation of weight-averaged molecular weight of lignin and pulp yield shown by Figure 1 led to relating the number-averaged molecular weight versus pulp yield, as shown in Figure 3. Again, there appears to be a reasonable relationship between the number-averaged molecular weight of lignin and the pulp yield. All data, except three points, follow the trend described with the curve as shown in Figure 3. These three points are (EA_{code}= -2, S_{code}=0, T_{code}=0, t_{code}=0), (0, -2, 0, 0) and (0, 0, -2, 0), respectively. Notice that they are all located at the 2k star positions and representing extremely low cooking levels of effective alkali of 11.5%, low sulfidity of 12.5%, and low cooking temperature of 160 ^{0}C(320 ^{0}F), respectively.

Figure 3 indicates that the number-averaged molecular weight of lignin increases as the pulp yield decreases from 70% to about 43%, then drops very rapidly as the pulp yield decreases further. A quite interesting fact observed is that the lignins with their number-averaged molecular weight in the sharply decreasing regime (pulp yield < 43%) correspond to the same two cases mentioned previously:

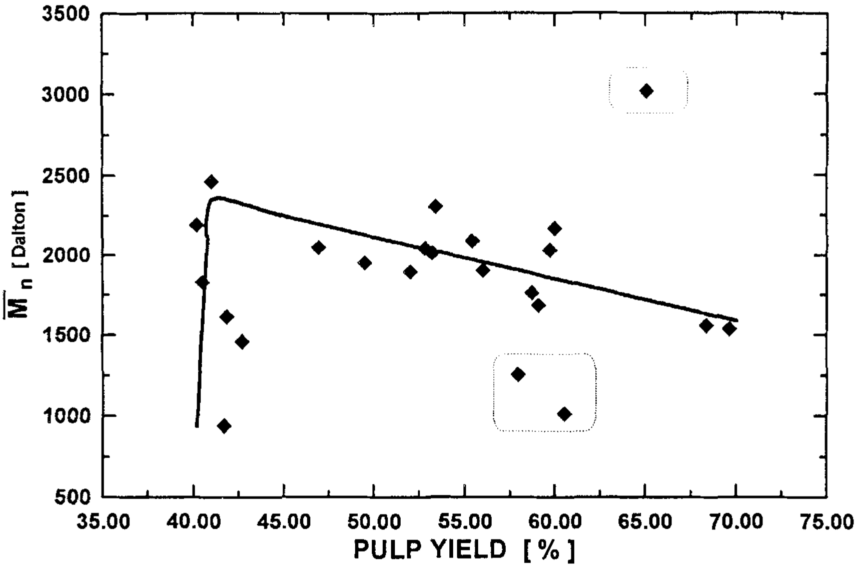

FIGURE 3. Dependence of the number-averaged molecular weight of lignin on pulp yield for Kraft pulping of Slash pine.

the H factor above 2500 regime and the extremely high chemical level (the 2k "star" location) points.

As discussed previously, the region of pulp yield from 70% to about 43% appears to cover both the bulk and final phases of delignification. Generally, therefore, the number-averaged molecular weight of lignin increases monotonically in both bulk and final phases as delignification proceeds, and prolonged cooking causes degradation of the dissolved lignin in the liquor, resulting in a decrease in the number-averaged molecular weight. Unlike the weight-averaged molecular weight, however, no transition point between the bulk and residual phases was observed for the number-averaged molecular weight of lignin.

It is not known why there does not exist a clear transition point between the bulk and final phase for Mn while there does for the Mw. A possible reason we can think of is that small amount of impurities associated with purified lignin sample may affect this. Since the VPO method is governed by the colligative properties of a solution, small amount of low molecular weight impurities may affect the Mn, while they barely affect the light scattering result (the Mw).

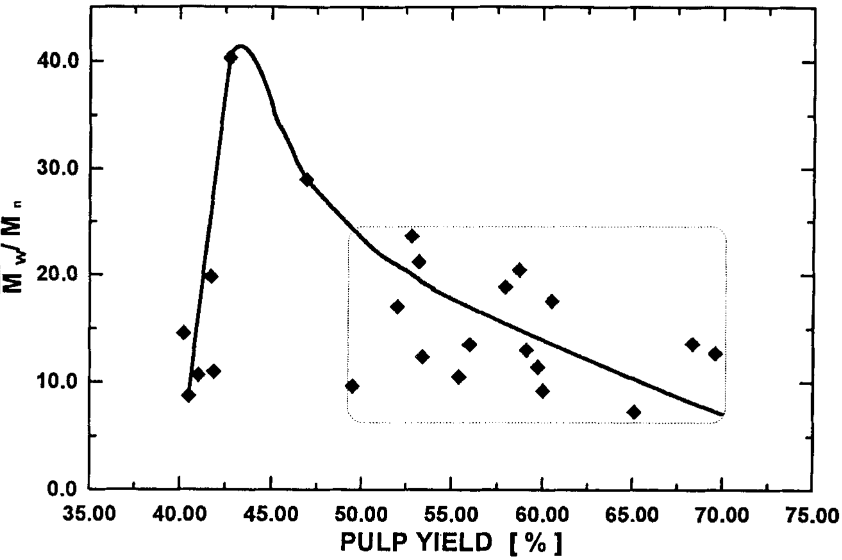

FIGURE 4. Dependence of the polydispersity index (Mw/Mn) of lignin on pulp yield for Kraft pulping of Slash pine.

Figure 4 shows the dependence of the polydispersity index of lignin, defined as the ratio of M_w/M_n, on pulp yield. It shows that, generally, this ratio increases monotonically as the pulp yield decreases from 70% to about 45%, then drops sharply with further decrease in the pulp yield to about 40%. Following the previous arguments, it is believed that the molecular weight distribution of dissolved lignin broadens as delignification proceeds in both the bulk and final phases up to the end of the final phase. At the end of the residual phase, the molecular weight distribution of lignin passes a maximum, and then decreases if the cooking is prolonged, possibly because the degradation reaction dominates the system, and the low molecular weight fractions increase at the expense of high molecular weight lignin.

Notice that, in Figure 4, the data points scatter around the plotted curve in the region of pulp yield from 70% to about 50%. It is very likely that the different reaction rates of dissolved lignin in the liquor cause this scattering. The depolymerization and condensation reactions of dissolved lignin in the liquor and the delignification reactions of wood chips take place simultaneously in the system.

However, variations in cooking variables, effective alkali, sulfidity, the cooking time and temperature, may greatly affect the rates of reactions in the liquor (homogenous reactions in a single phase), while affecting the delignification of wood chips less strongly. Therefore, the wide range of cooking conditions used in this study may have caused the scatter shown in Figure 4.

RESPONSE SURFACE ANALYSIS

Models and Response Surface

Due to the nature of the $2^k+2k+1(k=4)$ experimental design, it is ideal for development of a four-variable, full quadratic model for response surface analysis. The full quadratic model is defined in equation 6.

$$Y = a_0 + \sum_{i=1}^{k} a_i X_i + \sum_{i=1}^{k} a_{ii} X_i X_i + \sum_{i<j}^{k} a_{ij} X_i X_j \qquad [6]$$

Where Y is the estimate for a response (dependent) variable: the weight-averaged molecular weight, the number-averaged molecular weight, or the polydispersity index of lignin; k=4 is the total number of independent variables, X_is are the independent variables, effective alkali, sulfidity, cooking temperature and cooking time; and a_0 , a_i , a_{ii} , and a_{ij} are the estimates of regression parameters. The X_i terms in the equation account for the linear effects, the X_i X_i terms for the quadratic effects, and the X_iX_j terms for the two-variable interaction effects. Hence, this model contains one constant term, four linear terms, four quadratic terms, and six two-variable interaction terms, a total of 15 parameters.

A SAS (Statistical Analysis System) procedure, RSREG[32], was employed to perform statistical calculations, and the estimated parameters for the weight-averaged molecular weight, the number-averaged molecular weight and the polydispersity index of lignin are summarized in Table 2. It has to be pointed out that the parameters in Table 2 are based on real cooking variables (not the coded variables). As shown in Table 2, the regression coefficient of determination, R^2 ,

TABLE 2
Parameters in The Complete Quadratic Models of The Molecular Weight and The Polydispersity Index of Lignin for Kraft Pulping of Slash Pine.

Variables	Parameters Mw (Dalton)	 Mn (Dalton)	 PI (Mw/Mn)
INTERCEPT	-1.95E+06	3.01E+05	-2.14E+03
EA	4.09E+04	4.01E+03	-1.82E+01
S	-9.90E+03	7.55E+02	-1.27E+01
T	9.71E+03	-2.00E+03	1.42E+01
t	2.77E+03	3.04E+01	2.27E-02
EA*EA	-2.44E+03	-6.89E+01	-7.34E-01
S*S	-8.21E+01	-3.71E+00	-6.77E-03
T*T	-1.41E+01	3.09E+00	-2.27E-02
t*t	-6.04E+00	-1.06E-01	-2.74E-03
EA*S	7.10E+02	-1.18E+01	4.70E-01
EA*T	2.68E+01	-4.91E+00	7.28E-02
EA*t	6.27E+01	5.81E-01	4.78E-02
S*T	1.30E+01	-9.63E-01	1.76E-02
S*t	1.74E+00	-9.65E-01	1.00E-02
T*t	-8.34E+00	1.03E-02	-1.76E-03
R-squared	0.7026	0.9121	0.7505

Note: EA--effective alkali (% O.D.W.), S--sulfidity (% Active Alkali), T--cooking temperature (F), t--time-at-temperature (minutes), Mw--weight-averaged molecular weight of lignin, Mn--number-averaged molecular weight of lignin, and PI--polydispersity index of lignin.

for the weight-averaged molecular weight, the number-averaged molecular weight, and the polydispersity index of lignin are 0.7026, 0.9121 and 0.7505, respectively.

Since the input space itself is four-dimensional, two independent variables have to be fixed if a three-dimensional response surface is prepared. Based upon the equations shown in Table 2, many three dimensional graphs can be prepared, depending on different needs. As examples, six three-dimensional response surfaces and their contour plots, Figures 5 to 10, are shown and discussed here (two for each of the three response variables). Figures 5 to 10 are all prepared for one response variable as a function of two pulping variables with the other two fixed at their center point values.

Weight-Averaged Molecular Weight

Figure 5 shows the response surface of the weight-averaged molecular weight of lignin and its contour plot with respect to effective alkali and sulfidity at a constant cooking temperature of 171.1 ^{0}C (340 ^{0}F) and cooking time of 60 minutes. This response surface is approximately a symmetrical rising ridge. As shown in Figure 5, the weight-averaged molecular weight is low in the region of low effective alkali and low sulfidity, since delignification probably terminates in the initial or bulk phase after the chemicals in the liquor have been exhausted. As both the effective alkali and sulfidity increase, the weight-averaged molecular weight increases. However, at a fixed sulfidity (or at a fixed effective alkali), there exists a corresponding EA_W^* (or S_W^*), at which the weight-averaged molecular weight reaches a maximum, and further increase in effective alkali (or sulfidity) above the EA_W^* (or S_W^*) results in a decrease in the weight-averaged molecular weight. For example, an extremely high effective alkali point, (EA=17.5%, S=27.5%, T=171.1 ^{0}C, t=60minutes), located at a 2k position has passed the EA_W^*. This cook produced a lignin of low weight-averaged molecular weight, which is in good agreement with the conclusion of qualitative analysis (Figure 1).

Therefore, there exist optimum ratios between the effective alkali and sulfidity in terms of high weight-averaged molecular weight of lignin, and these optimum ratios fall on the symmetrical line in the contour plot (Figure 5). Increases of both effective alkali and sulfidity along this line would increase the weight-averaged molecular weight of lignin. This can be explained as follows. The optimum ratio was defined under the conditions of a constant cooking time of 60 minutes and a cooking temperature of 171.1 ^{0}C (340 ^{0}F), which gives a limited H factor of about 946. Higher effective alkali and higher sulfidity accelerate the rate of delignification, and push the delignification process toward completeness at this limited H factor. Therefore, lignins of higher molecular weight are produced. These optimum ratios would vary if cooking time and temperature were changed.

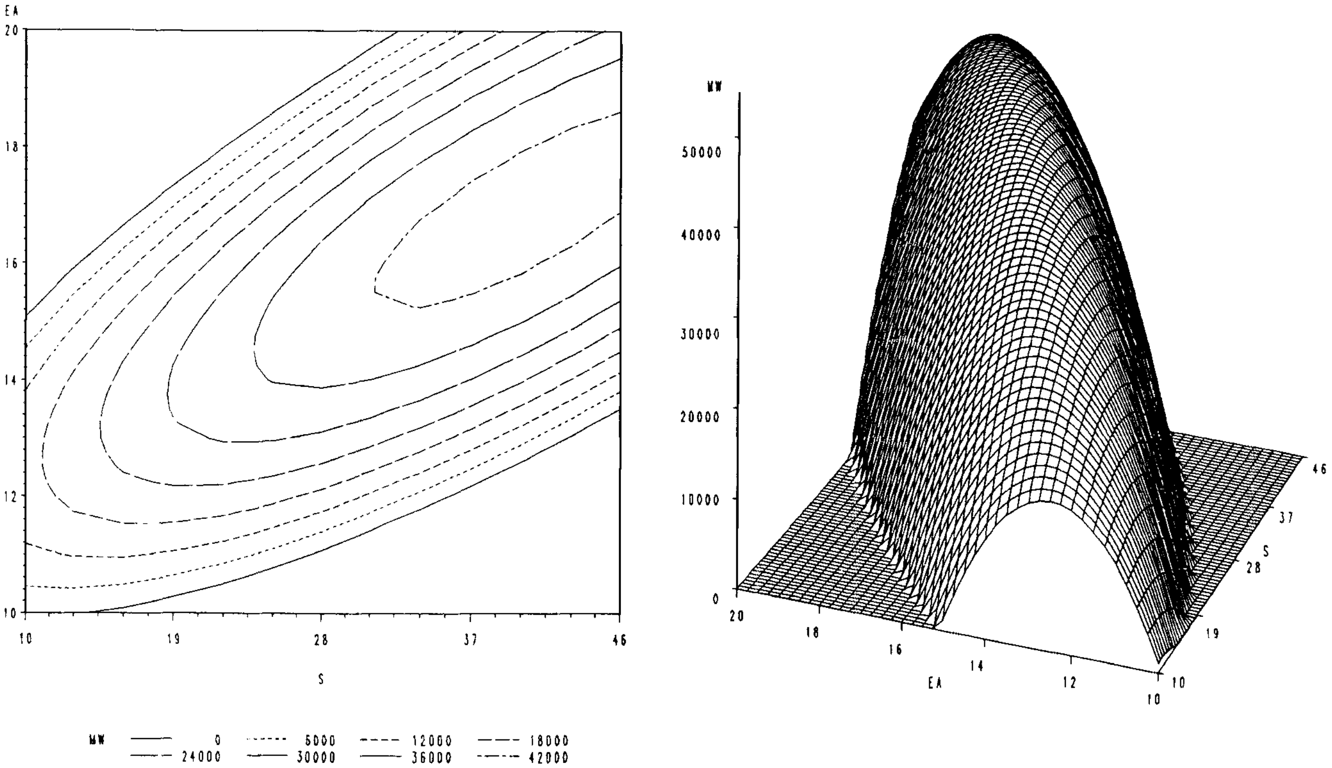

FIGURE 5. Contour plots of the effect of effective alkali (EA) and sulfidity (S) on the weight-averaged molecular weight of lignin at constant cooking time (t=60 minutes) and temperature (T=171.1 ^{0}C) for Kraft pulping of Slash pine.

Figure 6 graphically shows the dependence of the weight-averaged molecular weight of lignin on the cooking time and temperature at fixed effective alkali of 14.5% and sulfidity of 27.5%. It is very interesting that the weight-averaged molecular weight of lignin is a maximum at a cooking temperature of about 178 ^{0}C (352 ^{0}F) and a cooking time of about 70 minutes, which corresponds to an H-factor of about 2050. Notice that this graph is prepared at a typical (fixed) chemical level, and an H-factor of 2050 is probably right at the end of final phase delignification. Therefore, it suggests that a maximum weight-averaged molecular weight occurs at about the end of the final phase of delignification.

Starting at the bottom-left corner in the graph, the weight-averaged molecular weight of lignin increases as the cooking time or cooking temperature or both are increased until a maximum is reached. Further increase of either cooking time or cooking temperature would cause a decrease in the weight-averaged molecular weight, indicating that prolonged cooking causes degradation of dissolved lignin. Also, the response surface is quite flat around the maximum. This indicates a competition between the delignification reaction in the pulp,which gives lignin fractions of very high molecular weight towards the end of the final phase, and the degradation and condensation reactions in the liquor, which generally reduces the Mw of dissolved lignin. As the former approaches completion, the later gradually becomes a dominant factor in the system.

Number-Averaged Molecular Weight

Figure 7 shows contour plots for the effects of effective alkali and sulfidity on the number-averaged molecular weight of lignin at a constant cooking time of 60 minutes and a cooking temperature of 171.1 ^{0}C (340 ^{0}F). The number-averaged molecular weight of lignin response is a maximum (about 1400 Dalton) at an effective alkali of about 15% and a sulfidity of about 26.5%. The maximum value of 1400 Dalton is not high, because of a low H factor of about 946. Since the maximum point occurs in the region of medium effective alkali and medium sulfidity, stepping in any direction from the maximum will cause a decrease in the number-averaged molecular weight of lignin. Generally, the number-averaged molecular weight of lignin increases and reaches a maximum as both effective alkali and sulfidity increase simultaneously, then decreases as both effective alkali and

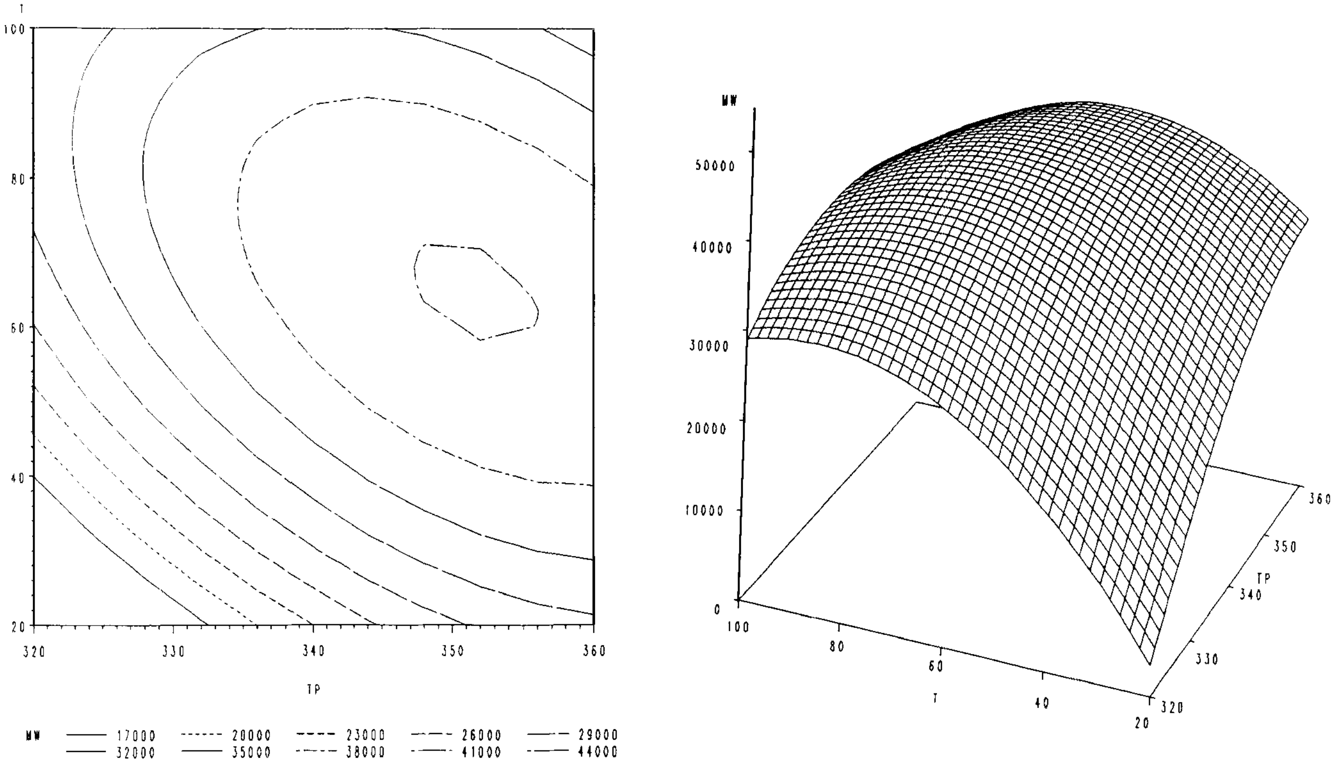

FIGURE 6. Contour plots of the effect of cooking time (t) and temperature (T) on the weight-averaged molecular weight of lignin at constant effective alkali (14.5%) and sulfidity (27.5%) for Kraft pulping of Slash pine.

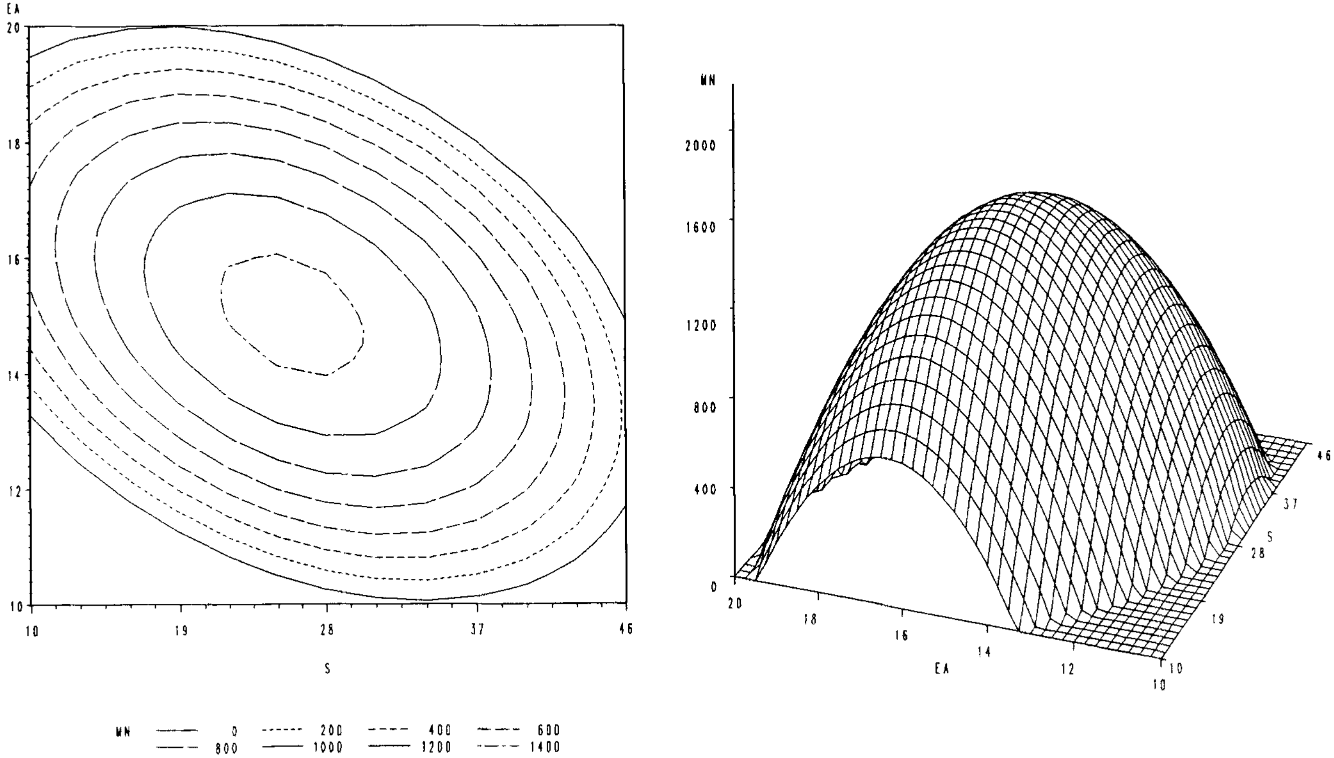

FIGURE 7. Contour plots of the effect of effective alkali (EA) and sulfidity (S) on the number-averaged molecular weight of lignin at constant cooking time (t=60 minutes) and temperature (T=171.1 ^{0}C) for Kraft pulping of Slash pine.

sulfidity increase further. Again, there exist optimum ratios between effective alkali and sulfidity in terms of high number-averaged molecular weight of lignin. At a fixed effective alkali (or at a fixed sulfidity), there appears to exist a corresponding S_n^* (or EA_n^*), as the sulfidity level (or effective alkali level) increases, the number-averaged molecular weight of lignin increases to a maximum at the S_n^* (or EA_n^*), and then decreases gradually.

The response surface of the number-averaged molecular weight of lignin and its contour plot with respect to the cooking time and cooking temperature at fixed effective alkali of 14.5% and sulfidity of 27.5% are shown in Figure 8. This response surface is approximately a stationary ridge. Figure 8 indicates that the cooking temperature strongly affects the number-averaged molecular weight of lignin, while the cooking time affects it slightly at fixed chemical levels. Also, this approximate stationary response of low number-averaged molecular weight of lignin occurs in the region of cooking temperatures from 165.6 ^{0}C (330 ^{0}F) to 176.7 ^{0}C (350 ^{0}F), which is the typical cooking temperature region for a Kraft process. The reason for this is not clear. It seems that degradation reactions of the dissolved lignin in the liquor take place at a maximum rate in this temperature region. However, more experimental evidence is needed to confirm this, since the weight-averaged molecular weight of lignin (Figure 6) does not show this behavior.

Polydispersity Index of Lignin

Figure 9 shows the response surface of the polydispersity index of lignin and its contour plot with respect to effective alkali and sulfidity at a constant cooking time of 60 minutes and a cooking temperature of 171.1 ^{0}C (340 ^{0}F). The response of the molecular weight distribution index of lignin is a minimax surface. Figure 9 indicates that the polydispersity index of lignin has low values in the following two regions: the low sulfidity and high effective alkali region, and the low effective alkali and high sulfidity region. In the region of both high effective alkali and high sulfidity, lignins of high polydispersity are produced. In the low sulfidity and low effective alkali region, the molecular weight distribution index has medium values.

The response surface of the polydispersity index of lignin and its contour plot with respect to the cooking time and temperature at constant effective alkali of

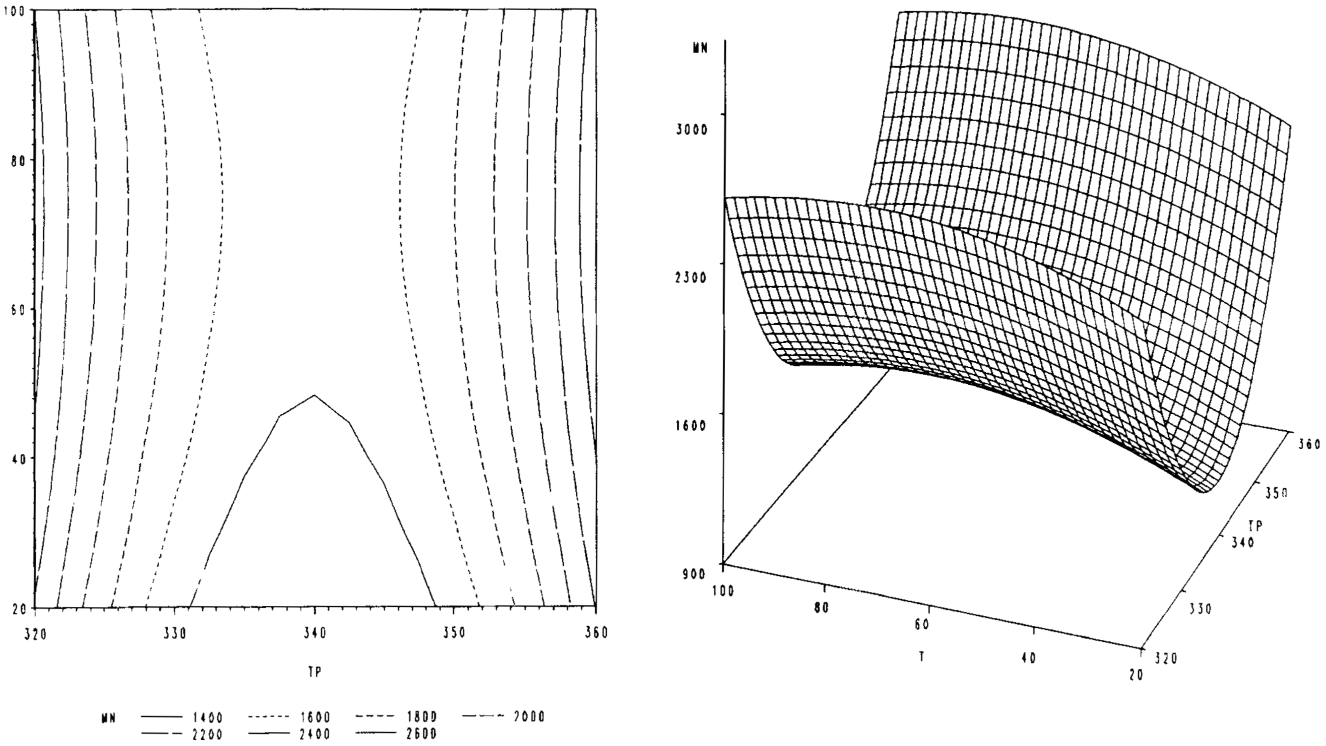

FIGURE 8. Contour plots of the effect of cooking time (t) and temperature (T) on the number-averaged molecular weight of lignin at constant effective alkali (14.5%) and sulfidity (27.5%) for Kraft pulping of Slash pine.

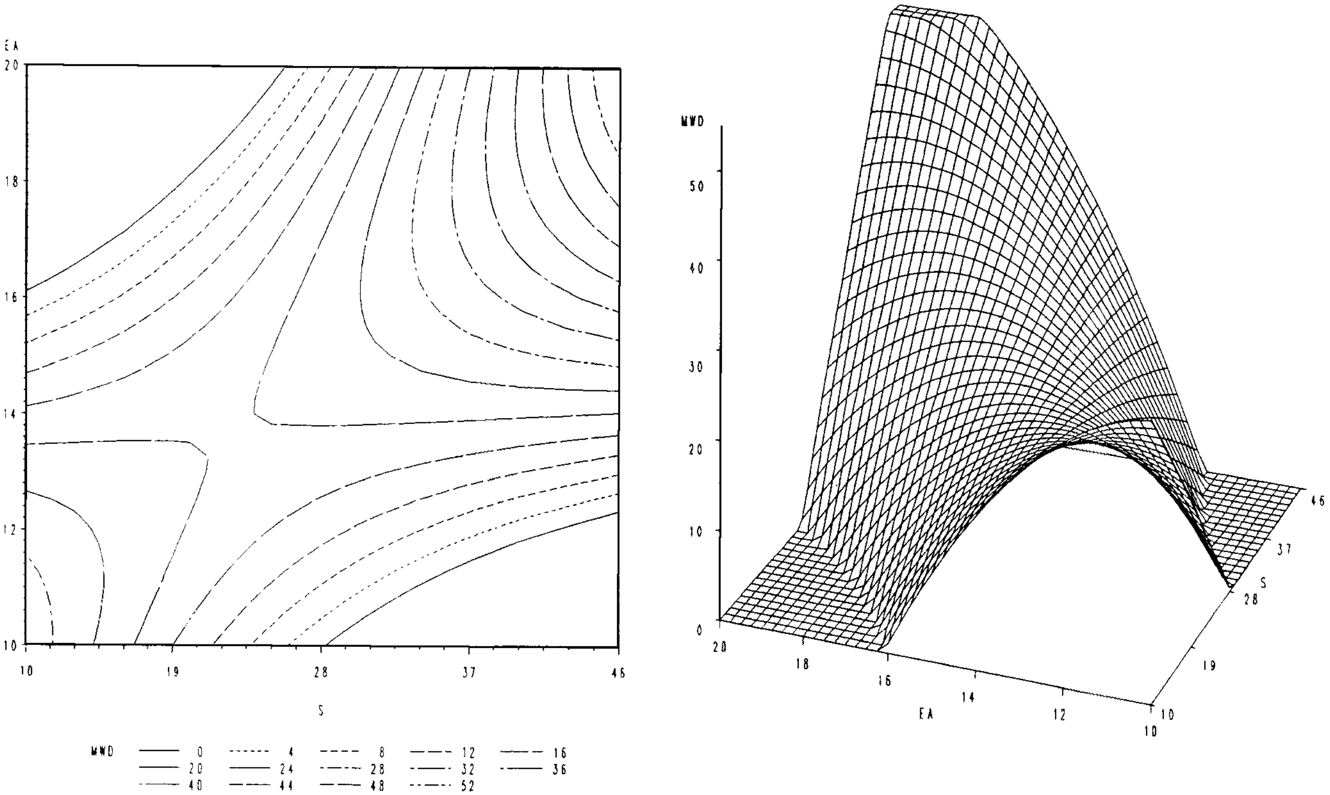

FIGURE 9. Contour plots of the effect of effective alkali (EA) and sulfidity (S) on the polydispersity index of lignin at constant cooking time (t=60 minutes) and temperature (T=171.1 ^{0}C) for Kraft pulping of Slash pine.

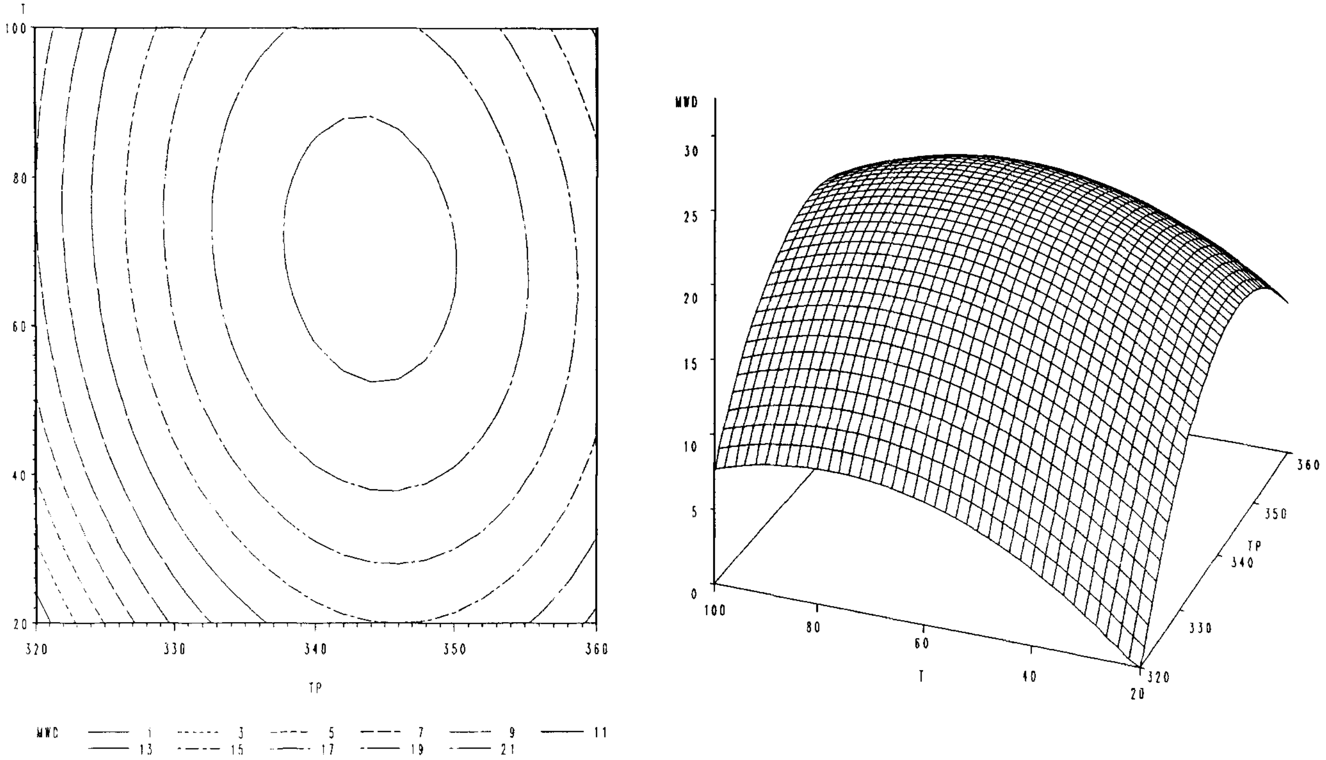

FIGURE 10. Contour plots of the effect of cooking time (t) and temperature (T) on the polydispersity index of lignin at constant effective alkali (14.5%) and sulfidity (27.5%) for Kraft pulping of Slash pine.

14.5% and sulfidity of 27.5% are shown in Figure 10. The lignin polydispersity index response is a flat maximum in the region of cooking times from 50 to 85 minutes and cooking temperatures from 170 ^{0}C (338 ^{0}F) to 176.7 ^{0}C (350 ^{0}F). Generally, at a fixed cooking temperature, the polydispersity of lignin will become broader as the cooking time increases form 0 to about 70 minutes, then remain stable or become narrower , depending upon the values of the cooking temperature , as cooking time is prolonged. It is evident that there exists a critical temperature of about 174 ^{0}C (345 ^{0}F), below which the polydispersity index of lignin increases as the cooking temperature increases, and above which it decreases as the temperature increases.

ACKNOWLEDGMENTS

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