

# Reaction Parameter Effects on Metal-Salt-Catalyzed Aqueous Biphasic Pulping Systems

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Metal salts ( $\text{MgSO}_4$  and  $\text{Li}_2\text{SO}_4$ ) that serve to catalyze wood delignification and also contribute to the formation of aqueous biphasic systems (ABSs) have been studied. The influence of treatment conditions on the pulp properties (measured as the kappa number, residual pulp yield) has been determined by means of a  $2^4$  factorial design. The effects of the variables (temperature, time, salt, and polymer concentration) have been determined. Wood and pulp samples and lignin resulting from this process have been characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

## Introduction

Current industrial production of cellulosic materials for paper, board, and viscose applications is based almost entirely on a variety of chemical pulping methods dominated by the Kraft process.<sup>1</sup> As a result of the impact of increasing environmental regulations, manufacturers have developed chlorine-free bleaching steps and are moving toward effluent-free bleaching operations.<sup>2</sup> This has encouraged an interest in alternative pulping technologies. Our own developments in chemical pulping using a wholly aqueous solvent extraction system are most closely related to the organosolv process but do not employ any organic solvent.<sup>3–5</sup> Organosolv processes have certain advantages over traditional chemical pulping processes, including the release for use, as opposed to the consumption by burning, of the lignin fraction and the implementation of a generally less polluting technology, which have not yet been realized in practical operations.

As a result of the work of Paszner, the use of salts of alkaline earth metals as efficient catalysts in organosolv processes has been discussed.<sup>6</sup> The application of alkaline earth metal catalysts leads to exceptionally high yields of cellulose for a wide range of species including softwood (55%), hardwood (60%), and bagasse (55%).<sup>6</sup> In these processes, 0.001–0.5 M solutions of an alkaline earth metal salt catalyst are added to alcohol at a temperature of 453–513 K, giving pulps with high hemicellulose contents and low residual lignin contents.<sup>7</sup> According to Paszner, magnesium, calcium, or barium chlorides, sulfates, or nitrates can act as the alkaline earth metal catalysts. It has been suggested that the success of these processes in recovering high yields of cellulose is related to the control of the final pH of the reaction due to the added metal salts and the prevention of extensive acid hydrolysis.<sup>8</sup> It has also been suggested that the divalent anions are adsorbed onto the carboxylic acid groups of the wood and that the resulting stabilized pH regime prevents hydrolytic degradation and deacetylation of hemicelluloses and condensation of lignin.<sup>8</sup>

The applicability of aqueous biphasic systems (ABSs) to the delignification and simultaneous extraction of lignocellulosic materials has been demonstrated.<sup>3–5</sup> ABSs represent critical phenomena occurring in aqueous solution, resulting in the spontaneous phase separation of certain polymers in water either in the presence of other polymers or promoted by the presence of salts.<sup>9–11</sup> They are also promoted by increasing temperature, and thus most molecular weights of poly(ethylene glycol) (PEG) and many other polymers will form aqueous biphasic mixtures at the temperatures typical of chemical and catalytic pulping processes, even in the absence of salt. The effectiveness of polymer-based ABSs in separating lignin from the cellulose fraction of wood has been demonstrated under temperatures and pressures equivalent to those used in current alkaline paper pulping practice. Both pine and hardwood mixtures can be successfully pulped in ABSs formed by the addition of polymer to the pulping solution.<sup>3–5</sup>

Here, we report the effectiveness of aqueous biphasic systems containing catalysts that simultaneously separate and extract lignocellulosic materials during the pulping process.

## Experimental Section

**Materials.** Hardwood was obtained from Gulf States Paper Company in Demopolis, AL. (Although the exact mix of species is not known, and thus comparison with the work of others is rendered more difficult, this does not affect the comparisons and conclusions drawn about the different process examined here and in our other papers.<sup>4,5</sup>) The wood chips were produced using a conventional hammer mill and then sieved by screen to a final chip size of 10–14 mesh. The chemicals NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{S}$ ,  $\text{MgSO}_4$ ,  $\text{Li}_2\text{SO}_4$ , and PEG-2000 were obtained from Aldrich (Milwaukee, WI) and were of reagent grade. All water used was purified using a Barnsted commercial deionization system (Dubuque, IA).

**Phase Diagram Determination.** Stock solutions of polymer and salt were prepared on a mass percent basis. Phase diagrams of PEG with salt solution were determined by the cloud-point method,<sup>12</sup> and the tie lines and binodal curve were described using an empirical expression derived by Merchuk.<sup>13</sup>

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**Table 1. Factorial Design Experimental Results for Hardwood Pulping with the  $\text{MgSO}_4$ /PEG System**

$T$ (°C) A	time (min) B	$\text{MgSO}_4$ (mol/L) C	PEG (% w/w) D	residual pulp yield (%)	kappa number
160	45	0.5	40	$88.81 \pm 0.86$	$28.02 \pm 0.12$
160	90	0.5	40	$82.98 \pm 0.09$	$30.87 \pm 0.87$
180	45	0.5	40	$72.99 \pm 0.70$	$34.26 \pm 0.76$
180	90	0.5	40	$64.75 \pm 0.31$	$34.70 \pm 0.46$
160	45	1.0	40	$86.95 \pm 0.35$	$30.39 \pm 0.52$
160	90	1.0	40	$77.36 \pm 0.45$	$34.91 \pm 0.85$
180	45	1.0	40	$71.80 \pm 0.11$	$36.46 \pm 0.57$
180	90	1.0	40	$61.19 \pm 0.83$	$40.04 \pm 0.93$
160	45	0.5	30	$87.93 \pm 0.71$	$26.33 \pm 0.91$
160	90	0.5	30	$83.99 \pm 0.38$	$31.64 \pm 0.52$
180	45	0.5	30	$74.84 \pm 0.64$	$37.68 \pm 0.32$
180	90	0.5	30	$67.07 \pm 0.45$	$41.41 \pm 0.22$
160	45	1.0	30	$87.77 \pm 0.14$	$25.28 \pm 0.87$
160	90	1.0	30	$85.19 \pm 0.39$	$30.60 \pm 0.62$
180	45	1.0	30	$74.22 \pm 1.02$	$36.21 \pm 0.82$
180	90	1.0	30	$65.76 \pm 1.01$	$44.26 \pm 0.20$

**Batch Reaction.** The descriptions of batch reaction methods and apparatus are reported in a previous paper.<sup>4</sup> For each run, the mass of wood was 5 g. Equal volumes of PEG solution (40% w/w) and salt solution (1.0 or 0.5 M) were mixed together to give a total solution-to-wood ratio of 6:1. Sixteen runs with  $\text{MgSO}_4$ /PEG ABSs under different conditions (time, temperature, and concentration, as summarized in Table 1) were carried out to determine the effects of the parameters on the reaction. Pareto charts were used to analyze the pulping results. The Pareto bar chart is useful for comparing classes or groups of data. For each bar in the chart, the height represents the value in the series. In most cases, two or three categories will tower above the others. These few categories, which account for the bulk of the problem, will be the high-impact points on which to focus.

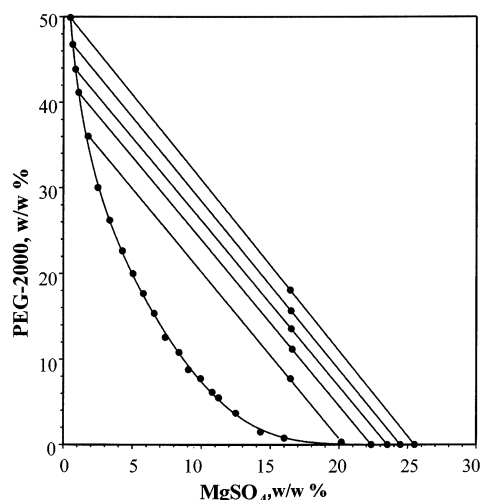
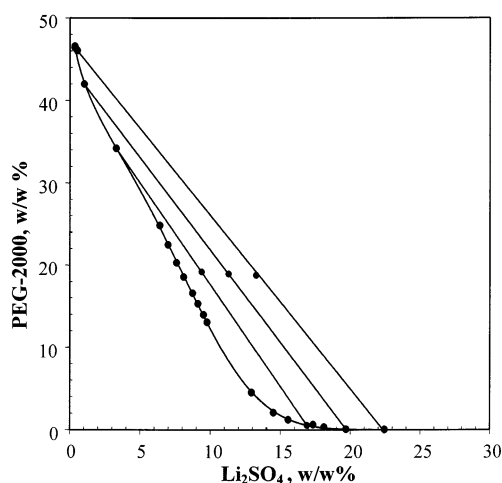
In a subsequent series of experiments,  $\text{Li}_2\text{SO}_4$  was used to study the effect of pH on metal salt ABS pulping because, at high pH, most alkaline earth metal salts will precipitate. The concentration of  $\text{Li}_2\text{SO}_4$  used was 1.0 M. The system pH was controlled by the addition of several drops of NaOH solution (10 wt %). The kappa number of the wood was obtained by Tappi Standard Method T-236. The residual pulp yield was calculated and is expressed as lignin free yield.<sup>4</sup>

**Scanning Electron Microscopy (SEM).** Specimens were mounted onto a specimen stub and coated with carbon. SEM studies were performed on a Philips XL30 SEM instrument, using an accelerating voltage of 20 kV, a spot size of 5, and a magnification of 1000.

**Fourier Transform Infrared (FTIR) Spectroscopy.** Spectra of lignin samples taken from the black liquor were recorded with a BIO-RAD Digilab Division FTS-40 FTIR spectrometer. The KBr technique was used to prepare the samples. The spectrometer was operated at a nominal resolution of  $4\text{ cm}^{-1}$ .

## Results and Discussion

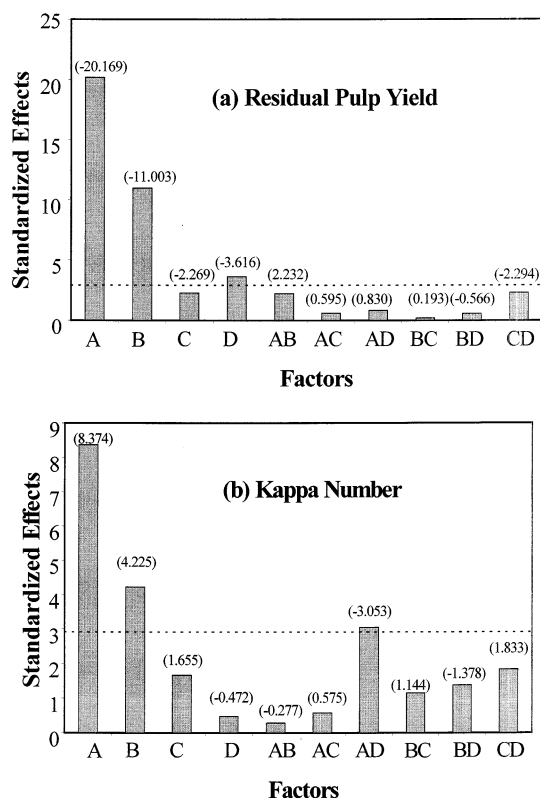
The phase diagram for a given ABS can be used to predict the phase behavior of that ABS. Useful information is obtained, including the relative amounts of the two phase-forming components needed to maintain a two-phase system, as well as the relative ratios of each component in either phase. Figures 1 and 2 show the PEG-2000/ $\text{MgSO}_4$ , and PEG-2000/ $\text{Li}_2\text{SO}_4$  phase diagrams. The curve in the phase diagram represents the

**Figure 1.** Phase diagram for PEG-2000/ $\text{MgSO}_4$  at 25 °C.**Figure 2.** Phase diagram for PEG-2000/ $\text{Li}_2\text{SO}_4$  at 25 °C.

binodal; below this curve a single homogeneous phase exists, whereas above the curve, two immiscible aqueous phases exist. The straight lines connecting two points (nodes) on the binodal are tie lines, representing the equilibrium condition between the phases. Preparing a system by adding the individual components in amounts shown anywhere along a given tie line will result in individual phase compositions represented by the composition of the nodes. The approximate phase ratio can be estimated as the ratio between the lengths of the tie lines from the system composition to the lower phase composition and from the upper phase composition to the system composition. As the salt concentration increases, the tie line lengths increase, resulting in an increase in the divergence of the phase compositions.

The phase diagrams indicate that the formation of ABSs for PEG-2000 with the selected salts occurs at modest concentration. For the  $\text{Li}_2\text{SO}_4$ /PEG system, the critical point is around 13% w/w of  $\text{Li}_2\text{SO}_4$  and 5% w/w of PEG. For the  $\text{MgSO}_4$ /PEG system, the critical point is around 8% w/w of  $\text{MgSO}_4$  and 10% of PEG. According to previous results,<sup>3,15</sup> lignin partitions to the polymer-rich phase, and cellulose partitions to the salt-rich phase, independent of the salt types and polymer molecular weight.<sup>3</sup> Thus, the  $\text{Li}_2\text{SO}_4$ /PEG and  $\text{MgSO}_4$ /PEG ABSs can be used for the separation of lignin from cellulose materials.

As a result of the phase diagram studies, we elected to conduct batch reactions at salt concentrations of 0.5



**Figure 3.** (a) Pareto chart for residual pulp yield. (b) Pareto chart for kappa number: A, temperature; B, time; C,  $\text{MgSO}_4$  concentration; D, PEG concentration; AB, interaction of temperature and time; AC, interaction of temperature and  $\text{MgSO}_4$  concentration; AD, interaction of temperature and PEG concentration; BC, interaction of time and  $\text{MgSO}_4$  concentration; BD, interaction of time and PEG concentration; CD, interaction of PEG and  $\text{MgSO}_4$  concentrations. (The values in parentheses are the estimated effects.)

and 1.0 M. It was found that, in the latter case, the systems were biphasic at room temperature. In the former case, the systems were not initially biphasic at room temperature, but they undoubtedly became biphasic during the reaction and were found to be biphasic upon cooling once the reaction was complete. The salt was used, therefore, both as a phase-forming component and as a catalyst.

The characteristics of the pulp obtained from the 16 pulping runs using the  $\text{MgSO}_4$ /PEG ABS are summarized in Table 1. Data processing enabled estimation of the main effects and the interactions of the factors for the responses considered.

Pareto charts were employed to determine the significance of the statistically determined effects. In these plots (Figure 3a and b), each of the estimated effects appears as bars. The length of each bar is proportional to the standardized effect calculated as the estimated effect divided by its standard error. The horizontal line on the plot indicates the effects that are statistically significant at a 95% confidence level. In terms of absolute magnitude, the main effects tend to be larger than two-factor interactions, which, in turn, tend to be larger than three-factor interactions, and so on. In this work, only the main and two-factor interactions have been considered.

As seen in Figure 3a, the main effects (time, temperature, and PEG concentration) are statistically significant for residual pulp yield. No significant effects have been found for two-factor interactions. The values of the

effects show that higher residual pulp yields can be obtained at low cooking temperature, short cooking time, and low PEG concentration. An increase in severity of the pulping conditions results in a loss of residual pulp yield as a result of increased dissolution of the wood component<sup>14</sup> and extensive hydrolysis of hemicelluloses and cellulose.<sup>8</sup> This result is the expected outcome, given knowledge of the pulping process.

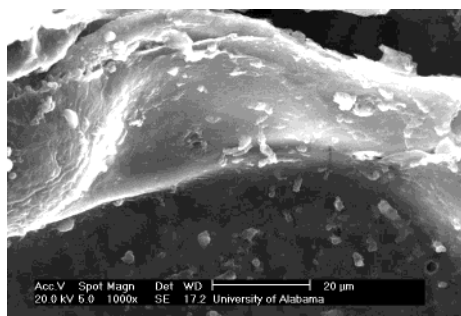
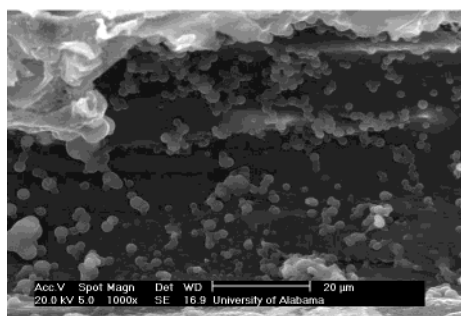
Figure 3b shows the Pareto chart for the kappa number. It can be seen that the main effects of temperature and time are statistically significant for the kappa number. A two-factor interaction (temperature and PEG concentration) is also statistically significant for the kappa number. The values of these effects are absolutely unexpected on the basis of the use of similar salts in organosolv systems,<sup>7,8</sup> and our own experiences of pulping in alkaline ABSs.<sup>4,5</sup> High temperature and long reaction time are not normally considered to result in a higher kappa number. Generally, a higher degree of severity of the cooking conditions will produce a lower kappa number. The reason for this will be explained below.

According to the results of the interaction of PEG and temperature, it was found that PEG concentration has a significant effect on kappa number at high temperature (180 °C). This indicates that an increased PEG concentration results in a lower kappa number at higher temperature. The reason for this appears to be that, as the temperature increases, the degree of phase divergence for this biphasic system increases, thus enhancing phase separation and increasing lignin dissolution in the polymer-rich phase of the ABS.<sup>15</sup> The result is that lignin condensation is reduced and the kappa number is lowered.

Usually, the kappa number will decrease with increasing degree of severity of the reaction conditions. However, during the batch cooking process, condensation reactions appear to predominate under acidic conditions and often completely overshadow the effects of hydrolytic degradation. The tendency of lignin to undergo intermolecular condensation reactions is perhaps best illustrated by the fact that lignin readily condenses with various monomeric phenols.<sup>16</sup> The condensation of lignin can be verified by SEM results (Figure 4a and b). Figure 4a shows the SEM image of a sample obtained at 160 °C and 45 min, whereas Figure 4b is of a sample obtained at 180 °C and 90 min (all other conditions were identical). In these images, it can be seen that the pulp samples are covered by precipitated lignin. This precipitated lignin cannot be readily removed with solvent washing and requires more powerful lignin solvents for solubilization.<sup>8</sup> As time and temperature increase, the lignin condensed on the surface increases at the end of the process as a result of the reduced pH, thus explaining why the kappa number increases under more severe reaction conditions.

It is expected that lignin precipitation can be prevented by controlling the system pH, because lignin condensation occurs under acidic conditions.<sup>8,16</sup> An experiment was conducted using a  $\text{Li}_2\text{SO}_4$ /PEG ABS in which the pH level was controlled.  $\text{Li}_2\text{SO}_4$  was used in place of  $\text{MgSO}_4$  because  $\text{MgSO}_4$  will precipitate under basic conditions. Table 2 shows the results of a series of experiments in which  $\text{Li}_2\text{SO}_4$  replaced  $\text{MgSO}_4$  as the metal catalyst. The initial experimental pH was varied between 11 and 14 using NaOH as the titrant.



(a)  $\text{MgSO}_4$ -PEG ABS Pulping 160 °C, 45 min.(b)  $\text{MgSO}_4$ -PEG ABS Pulping 180 °C, 90 min.

**Figure 4.** SEM images of pulp samples: (a)  $\text{MgSO}_4$ /PEG ABS pulping at 160 °C, 45 min. (b)  $\text{MgSO}_4$ /PEG ABS pulping at 180 °C, 90 min.

**Table 2. Results of Hardwood Pulping with the  $\text{Li}_2\text{SO}_4$ /PEG System<sup>a</sup>**

initial pH	time (min)	kappa number	residual yield (%)	final pH
11	30	50.58 ± 0.51	95.14 ± 0.8	9.4
	60	52.57 ± 0.62	91.81 ± 1.3	8.9
	90	55.72 ± 0.67	89.32 ± 0.8	8.7
12	30	43.22 ± 0.54	84.34 ± 0.5	10.4
	60	45.18 ± 0.48	83.47 ± 1.2	10.3
	90	47.72 ± 0.44	81.62 ± 0.7	10.3
13	30	38.89 ± 0.61	82.07 ± 0.9	11.2
	60	35.75 ± 0.72	80.60 ± 0.8	11.4
	90	31.87 ± 0.76	79.58 ± 1.2	10.8
14	30	34.50 ± 0.80	76.13 ± 0.6	12.2
	60	25.80 ± 0.82	72.87 ± 1.1	12.1
	90	21.10 ± 0.85	68.54 ± 0.7	11.9

<sup>a</sup> Conditions: 1 M  $\text{Li}_2\text{SO}_4$ , 40% w/w PEG-2000, 160 °C.

Table 2 shows that, in all cases, the final pH was less than the initial pH as a consequence of the reaction and its duration. In every case, the pH fell by about 2 units regardless of the initial pH. The residual yield was found to depend on the final pH and the duration of the reaction, being lowest for the longest reaction time and highest pH. At the highest pH values (initial pH 13 and 14), the kappa number also decreases with reaction extent. However, at the lowest initial pH values (initial pH 11 and 12), the kappa number actually increases with extent of reaction, as lignin recondensation occurs. As the pH of the reaction conditions increases, the kappa number decreases with the extent of reaction, indicating greater delignification and reduced recondensation.

Figure 5 shows SEM results at different pH conditions. As expected from the results shown in Table 2, an increase in the system pH decreases the lignin condensation on the pulp surface. At pH 14 (Figure 5d), almost no lignin can be found on the surface. [The results obtained for kappa number vs residual pulp yield for pulping reactions conducted with the  $\text{Li}_2\text{SO}_4$ /PEG

ABS (initial pH = 14) are compared to those obtained with the  $\text{MgSO}_4$ /PEG ABS (pH not controlled) and Kraft conditions (initial pH > 14), later in this paper.]

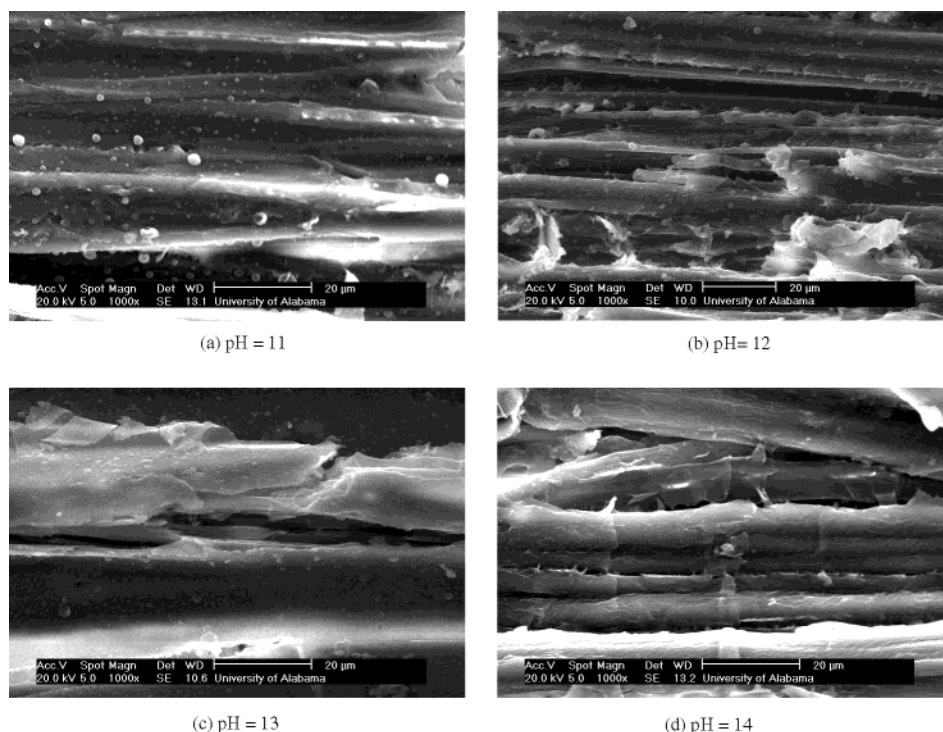
The FTIR spectra of lignin obtained by  $\text{Li}_2\text{SO}_4$ /PEG pulping are shown in Figure 6. The region from 2000 to 4000  $\text{cm}^{-1}$  does not provide any useful information other than the presence of broad hydroxyl and aliphatic C–H absorption and will not be considered further.

The peaks in the FTIR spectra can be assigned as follows: The 1708  $\text{cm}^{-1}$  band is a carbonyl (C=O) stretch in unconjugated ketones and in ester groups (frequently of carbohydrate origin); the 1653  $\text{cm}^{-1}$  band is also a C=O stretching band due to para-substituted ketones or aryl aldehydes; and the 1597  $\text{cm}^{-1}$  band is an aromatic skeletal vibration plus a C=O stretch. A strong absorption band at 1508  $\text{cm}^{-1}$  indicates the aromatic skeletal vibrations; the 1458  $\text{cm}^{-1}$  band is from C–H deformations; the 1423  $\text{cm}^{-1}$  band is from aromatic skeletal vibrations combined with C–H in-plane deformation; the 1366  $\text{cm}^{-1}$  band is the aliphatic C–H stretch in  $\text{CH}_3$ ; the 1328  $\text{cm}^{-1}$  band is from syringyl rings plus condensed guaiacyl rings; the 1222  $\text{cm}^{-1}$  band is from C–C plus C–O plus C=O stretches; the 1123  $\text{cm}^{-1}$  band is from aromatic C–H in-plane deformation; the 1033  $\text{cm}^{-1}$  band is from aromatic C–H in-plane deformation (guaiacyl type); and the 831  $\text{cm}^{-1}$  band is from aromatic C–H out-of-plane bending. It is important to note that the FTIR spectra for these lignins, shown in Figure 6 and obtained from  $\text{Li}_2\text{SO}_4$ /PEG pulping, are not in any way different from those of typical lignin samples obtained as a result of many other pulping processes including organosolv. Thus, although metal-catalyzed ABS pulping results in significant delignification at rather high residual yields, this does not seem to be the result of any significantly different reaction chemistry occurring in these systems.

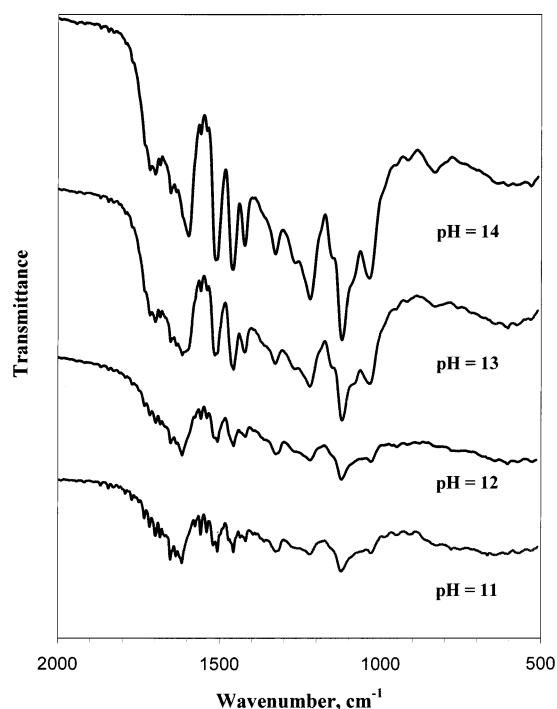
As the pH increases from 11 to 14, the 831  $\text{cm}^{-1}$  band becomes stronger, indicating that, as pH increases, more aromatic C–H out-of-plane bending occurs. The reasons behind this phenomenon are not clear and merit further investigation.

The delignification selectivities of different systems are compared in Figure 7, represented by the relationship of kappa number vs residual pulp yield. The kappa number correlates with the lignin content of wood/pulp, and the residual pulp yield is lignin-free yield, so Figure 7 provides a way to depict the relative selectivity of the delignification process.

Maximal selectivity would occur in an ideal pulping process if all lignin were removed (kappa number = 0) and at the same time no carbohydrate were removed (residual yield = 100%). However, this is hypothetical and does not occur in practice. Nonetheless, one can appreciate that, as the kappa number vs residual pulp yield line approaches the 0, 100% point (upper left-hand corner), a greater selectivity is obtained. For the  $\text{MgSO}_4$ /PEG pulping process, the trend of selectivity is different from those of the other systems in Figure 7. This can be explained by the factorial design experimental result, in which time is the main significant factor, which has a negative effect on residual pulp yield (reduction) and a positive effect on kappa number (increase). Thus, as the cooking time increased, the residual pulp yield is decreased, and the kappa number is increased (because of the lignin condensation on pulp, which was identified by SEM in Figure 4). Thus, the unexpected results can be explained by the condensation process.

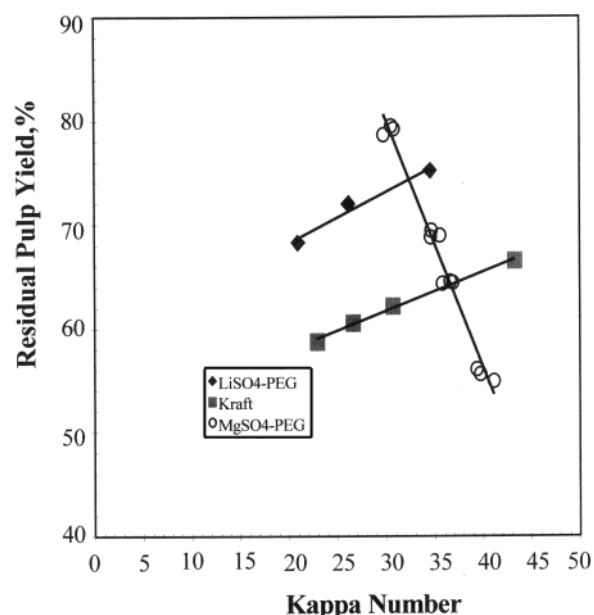


**Figure 5.** SEM images of pulp samples: (a)  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping at 160 °C, 60 min, pH = 11. (b)  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping at 160 °C, 60 min, pH = 12. (c)  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping at 160 °C, 60 min, pH = 13. (d)  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping at 160 °C, 60 min, pH = 14.



**Figure 6.** FTIR spectra of hardwood lignin obtained by  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping at pH = 11–14.

The other two systems,  $\text{Li}_2\text{SO}_4/\text{PEG}$  and simulated Kraft solution, were both investigated under basic conditions to prevent lignin precipitation; more lignin was removed from the wood, and almost no lignin was condensed on the pulp (identified by SEM in Figure 5). The increased severity of the pulping conditions results in a reduction in residual pulp yield due to the increased dissolution of wood components<sup>14</sup> and extensive hydrolysis of hemicelluloses and cellulose.<sup>8</sup> On the other hand, the higher degree of severity of the cooking conditions produces a lower kappa number. In Figure



**Figure 7.** Comparison of delignification selectivity for (◆)  $\text{Li}_2\text{SO}_4/\text{PEG}$  ABS pulping, (○)  $\text{MgSO}_4/\text{PEG}$  ABS pulping, and (■) simulated Kraft pulping.

7, as time increases, the residual pulp yield and kappa number both decrease.

A significant improvement in delignification selectivity was achieved by using  $\text{Li}_2\text{SO}_4/\text{PEG}$  with pH control, compared to a simulated Kraft process. The acidic condensation reactions of lignin mainly take place between the side-chain benzylic carbons and the electron-rich carbons on the aromatic nuclei. The reactivities of the aromatic carbons of the syringyl nuclei are higher than those of the guaiacyl nuclei.<sup>17</sup> This suggests that the hardwood lignin consisting of syringyl units forms condensation products very easily. Because acids generated by the wood can initiate lignin condensation and

undesirable lignin condensation reactions can occur at high temperature in the absence of alkali, it is very important to control the pH level during the cooking.<sup>18</sup> A salt/PEG ABS has been demonstrated that can improve the selectivity of delignification<sup>4,5</sup> because phase separation enhances the lignin extraction from cellulose.

## Conclusion

The phase diagrams for PEG-2000 and salts ( $\text{Li}_2\text{SO}_4$  and  $\text{MgSO}_4$ ) of importance in pulping processes have been constructed. Increasing the salt concentration increases the phase divergence of the resulting ABS. The results of batch cooking experiments ( $2^4$  factorial design) showed that the reaction time and temperature are the most significant main effects on the residual pulp yield and kappa number. The PEG concentration has a significant effect on the residual pulp yield, and no two-factor interactions are significant. For two-factor interactions, only the PEG concentration and temperature interaction has a significant effect on the kappa number. The system pH was found to be very important for the metal-salt-catalyzed ABS, resulting in improvements in the delignification selectivity and the prevention of lignin precipitation on the pulp surface. The structure of the lignin released during pulping was not obviously affected by pH as judged by the results of FTIR analysis.

Previously, we have examined alkaline and Kraft-like ABSs for the development of pulping processes and shown that these systems offer benefits in reduced kappa numbers and increased yields compared to conventional pulping processes.<sup>3-5</sup> Here, inspired by previous work in the development of organosolv processes,<sup>6-8</sup> we have attempted the implementation of metal-catalyzed pulping reactions in ABSs. At alkaline pH, these approaches appeared to be highly successful, although little is known about the fiber quality produced, in that yields were much higher than for comparable Kraft processes at the same kappa number.

Because of the high pH requirements for the metal-salt-catalyzed ABS pulping, most salts, such as Mg, Ca, and Al, that have the ability to catalyze delignification in organosolv pulping cannot be used. It has been suggested that lignin condensation is practically eliminated at neutral or even acidic conditions during organosolv pulping with metal salts.<sup>8</sup> This can be explained by the fact that the high methanol or ethanol concentration (80%) of the cooking liquor discourages carbohydrate dissolution and lignin condensation in the presence of metal salts. Although PEG has the ability to prevent carbohydrate degradation and lignin condensation at high pH, unlike methanol or ethanol, it does not appear to have this ability under acidic conditions. The reasons for this include the lignin solubility, the system pH, and the concentration of the PEG-based ABS. This suggests that exploring the effect of different polymers, e.g., Triton, in search of polymers that have the ability to prevent carbohydrate degradation and lignin condensation under neutral or acidic conditions similarly to methanol or ethanol and that, meanwhile, can form ABSs with salts to eliminate the problems arising from the use of organic solvents might be a worthwhile undertaking.

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