

# Low sulfidity and additive pulping by modified batch cooking

Paul A. Watson, Richard R. Gustafson, William T. McKean, and Ethan K. Andrews

**ABSTRACT:** *This study investigated the effect of white liquor sulfidity on modified batch pulping performance of southern pine. The sulfide concentration affected pulping at low sulfidities, although strong pulp resulted with an acceptable pulping rate at only 15% sulfidity. The authors also investigated use of soluble anthraquinone for reducing white liquor sulfidities. They found that sulfidity could decrease to 10% while still producing a good quality pulp by use of this catalyst.*

**KEYWORDS:** *Additives, anthraquinone, bibliographies, cooking liquors, pulping pinus, sulfidity, white liquors.*

## Introduction

Modified batch (MB) cooking processes such as Beloit's Rapid Displacement Heating (RDH) pulping have faster delignification and the capacity to realize lower kappa numbers than conventional pulping (1-6). This rapid delignification relates to high bulk delignification alkalinity and high sulfidity throughout the cook. It is conceivable, however, that the sulfide concentrations experienced throughout an MB cook are higher than required to achieve the benefits of MB pulping. Reducing the sulfidity may have the advantages of reducing recovery boiler corrosion (7), SO<sub>2</sub> emissions (8), and digester total reduced sulfur (TRS) emissions (9). The objective of this study, therefore, was to investigate

the effect of the sulfide charge on modified batch pulping behavior. The specific objective was determination of the lowest sulfidity level while still maintaining the benefits associated with MB pulping.

Previous studies have shown that small amounts of anthraquinone (AQ) added to conventional kraft pulping permits the use of lower white liquor sulfidities while maintaining pulp quality (10-13). Furthermore, use of AQ may permit a reduction in the required effective alkali charge and an increase in the pulp yield (12-17). Accordingly, a second objective of this research was to investigate the effectiveness of soluble anthraquinone (SAQ) (18) in MB pulping particularly when coupled with low sulfidity.

In the RDH and other modified batch processes, liquor recycles from batch to batch primarily for energy conservation. This liquor recycle permits considerable flexibility in the SAQ addition point for an MB cook. Although SAQ is not truly catalytic in nature, because pulping reactions consume it, the use of reduced SAQ charges to maintain an effective chemical concentration throughout the pulping is a possibility. As part of this research, we determined the optimum addition point of SAQ in MB pulping. Furthermore, we measured the consumption of SAQ during pulping to determine how much of the catalyst would recycle with the pulping liquors.

## Discussion

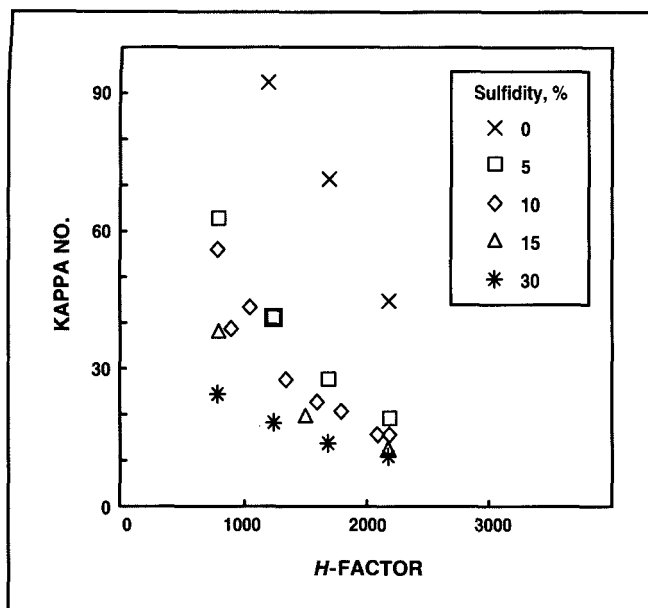
### Low sulfidity MB pulping

Figure 1 presents the kappa number versus *H*-factor data for laboratory MB cooks (19) performed at 15.7% effective alkali (as Na<sub>2</sub>O) while varying the white liquor sulfidities with the appropriate black liquor pretreatments. One can see that there is a large acceleration in pulping rate when the white liquor sulfidity increases from 0% to 5%. Past 5% sulfidity, however, the increase in pulping rate diminishes with increasing sulfidity. Similar results occur with conventional cooks (20).

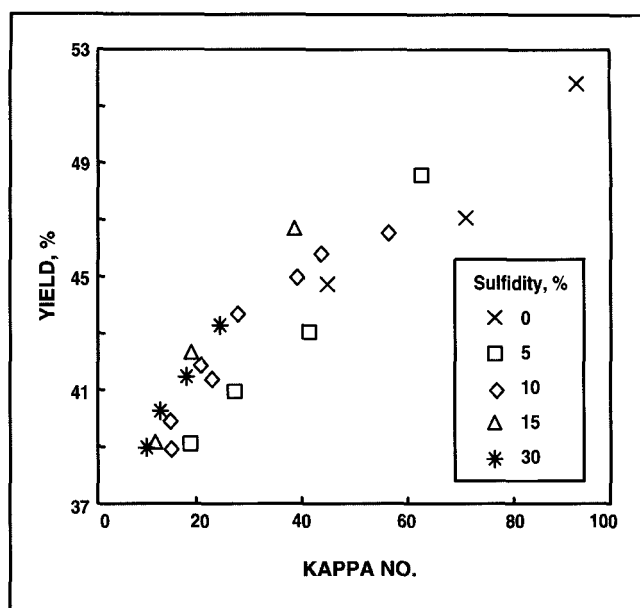
When pulping into the extended delignification range, i.e., kappa numbers less than 20, the effect of liquor sulfidity on the *H*-factor required to achieve a given kappa number further decreases. Figure 1 suggests that it is

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1. Kappa number vs. *H*-factor for low sulfidity MB pulping



2. Yield vs. kappa number for low sulfidity MB pulping



possible to produce low kappa number pulp with reasonable *H*-factors with a 15% white liquor sulfidity.

Figure 2 shows a comparison of the pulp yield at a given kappa number as a function of the white liquor sulfidity charge. It indicates that the 30% and 15% sulfidity cooks result in identical relationships between kappa number and yield. Reducing the sulfidity below 15%, however, results in a lower yield at a given kappa number. In the extended delignification range, the pulps with 5% sulfidity liquor have yields 1-2% lower at a given kappa number than those pulps with 15% or 30% sulfidity.

## Pulp quality

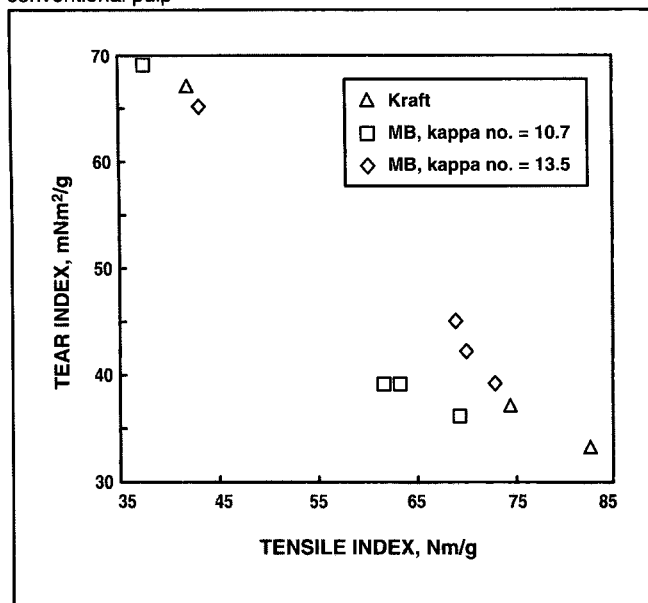
Modified batch processes produce strong pulp even with pulping into the extended delignification range (6). It was of interest to investigate the strength properties of some of the pulps produced in this study. Table I presents the mechanical strength properties for representative MB and conventional pulp samples. Note that all the pulps assessed for mechanical properties had low kappa numbers in the extended pulping range.

Table I shows a marked difference in the relationship between tear index

I. Handsheet properties of MB and kraft pulps of southern pine

| Pulp type                           | Freeness, ml | Basis wt., g/m <sup>2</sup> | Caliper, mm | Density, g/cm <sup>3</sup> | Bulk, cm <sup>3</sup> /g | Tensile index, Nm/g | Tear index, mNm <sup>2</sup> /g | Burst index, kPa |
|-------------------------------------|--------------|-----------------------------|-------------|----------------------------|--------------------------|---------------------|---------------------------------|------------------|
| 30% sulfidity MB<br>kappa no. 10.7  | 745          | 63.5                        | 0.127       | 0.500                      | 2.00                     | 38                  | 69                              | 245              |
|                                     | 550          | 61.5                        | 0.096       | 0.639                      | 1.56                     | 63                  | 39                              | 418              |
|                                     | 405          | 63.0                        | 0.095       | 0.663                      | 1.51                     | 62                  | 39                              | 454              |
|                                     | 225          | 60.6                        | 0.092       | 0.659                      | 1.52                     | 69                  | 36                              | 450              |
| 30% sulfidity MB<br>kappa no. 13.5  | 723          | 63.1                        | 0.130       | 0.487                      | 2.06                     | 43                  | 65                              | 252              |
|                                     | 593          | 60.0                        | 0.094       | 0.641                      | 1.64                     | 69                  | 45                              | 421              |
|                                     | 460          | 60.0                        | 0.092       | 0.655                      | 1.53                     | 70                  | 42                              | 434              |
|                                     | 240          | 62.7                        | 0.092       | 0.682                      | 1.47                     | 73                  | 39                              | 475              |
| 15% sulfidity MB<br>kappa no. 12.5  | 740          | 61.1                        | 0.121       | 0.503                      | 1.99                     | 47                  | 58                              | 247              |
|                                     | 600          | 61.8                        | 0.093       | 0.662                      | 1.51                     | 70                  | 42                              | 396              |
|                                     | 440          | 60.0                        | 0.089       | 0.674                      | 1.48                     | 72                  | 34                              | 416              |
|                                     | 230          | 60.4                        | 0.086       | 0.701                      | 1.43                     | 75                  | 35                              | 423              |
| 10% sulfidity MB<br>kappa no 15.1   | 755          | 64.0                        | 0.113       | 0.457                      | 2.05                     | 40                  | 62                              | 254              |
|                                     | 525          | 62.1                        | 0.101       | 0.615                      | 1.63                     | 63                  | 38                              | 432              |
|                                     | 395          | 60.8                        | 0.095       | 0.639                      | 1.57                     | 63                  | 36                              | 426              |
|                                     | 200          | 62.1                        | 0.099       | 0.626                      | 1.60                     | 68                  | 34                              | 448              |
| 5% sulfidity MB<br>kappa no. 18.8   | 750          | 63.4                        | 0.132       | 0.480                      | 2.08                     | 37                  | 57                              | 225              |
|                                     | 570          | 62.5                        | 0.106       | 0.590                      | 1.70                     | 58                  | 38                              | 386              |
|                                     | 378          | 62.2                        | 0.095       | 0.653                      | 1.53                     | 60                  | 34                              | 390              |
|                                     | 193          | 61.9                        | 0.092       | 0.674                      | 1.48                     | 63                  | 35                              | 418              |
| 30% sulfidity kraft<br>kappa no. 20 | 750          | 63.8                        | 0.125       | 0.509                      | 1.97                     | 42                  | 67                              | 250              |
|                                     | 400          | 61.7                        | 0.094       | 0.656                      | 1.52                     | 74                  | 37                              | 463              |
|                                     | 200          | 60.3                        | 0.087       | 0.693                      | 1.44                     | 82                  | 33                              | 465              |

3. Tear index vs. tensile index for 30% sulfidity white liquor MB and conventional pulp



and tensile index for the two MB pulps produced with 30% sulfidity white liquor. **Figure 3** presents this observation graphically. It indicates that the extensive pulping required to reach kappa no. 10.7 from kappa no. 13.5 (approximately 500 *H*-factor) resulted in some degradation of the pulp. It is interesting, however, that the low kappa pulps produced by the MB process were as strong as a conventional pulp with kappa no. 20.

**Figure 4** presents the tear index vs. tensile index data for MB pulps produced at different white liquor sulfidity levels. The 30% sulfidity curve is for the pulp cooked to kappa no. 13.5. This figure shows that higher sulfidity does produce a stronger pulp. The difference between the 15% and 30% sulfidity pulps is slight, however, with more refined pulp.

### AQ in MB pulping

The addition of AQ to kraft pulping lowers the required sulfidity of the cook (10, 11). This study used the water soluble AQ derivative—generally called SAQ (1,4-dihydro-9,10-dihydroxyanthracene). SAQ provided ease of handling and minimized any complications associated with poor initial AQ solubility in the liquor charg-

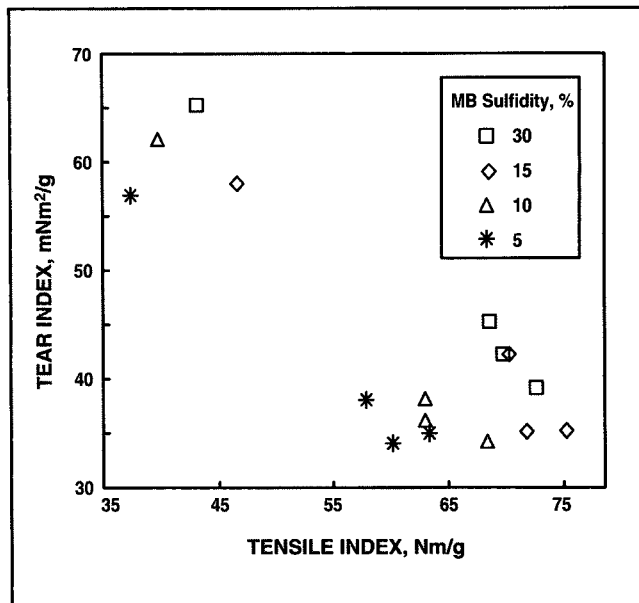
ing (18). It was of interest to determine whether the addition of SAQ to low sulfidity MB cooks would enhance the pulping rate, pulp yield, and pulp properties. We also considered factors such as the SAQ charge, the appropriate SAQ addition point, and SAQ recycling.

### Optimization of the SAQ addition point

Laboratory MB pulping, a simulation of the RDH process, consists of three phases. There is a warm black liquor fill to 120°C, a hot black liquor pretreatment to 155°C, and the white liquor cooking phase at 170°C (19). Since the addition of AQ to pulping reactions enhances delignification during the initial phase of pulping reactions (21), we expected that either the warm or the hot black liquor phase would be the optimum point at which to add SAQ.

To minimize the effects of overcharging the system with sulfide and thus mitigating the effect of the SAQ, we used a white liquor sulfidity of 10% to optimize the SAQ addition point in the MB liquor cycle. To avoid carryover with SAQ addition to either the warm or the hot black liquor, we prepared fresh black liquor solutions for these experiments. There was no recycling of black liquors. **Figure 5** shows the

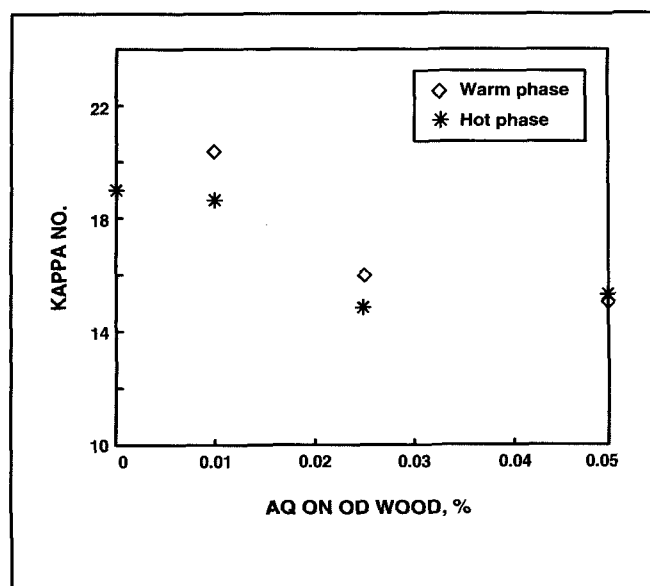
4. Tear index vs. tensile index for low sulfidity MB pulps



kappa numbers of pulps cooked to 1900 *H*-factor with different SAQ addition levels. For these cooks, we added the SAQ to either the warm or hot black liquors. One can see that addition of SAQ to the warm or hot black liquor resulted in a similar delignification enhancement. In addition, SAQ charges as low as 0.025% on wood accelerated the delignification resulting in a reduced kappa number pulp. There were similar results to those in Fig. 5 for MB pulping with SAQ to 1250 *H*-factor. These results show that the benefits of SAQ addition to either the warm or the hot black liquor are the same. Addition of the SAQ to the hot black liquor would be more advantageous because of the liquor recycling in the MB system. This agrees with the recent findings of Chang and coworkers (22).

**Figure 6** has a comparison of the kappa number and *H*-factor relationship for three pulps: MB control, 0.025% SAQ added to the hot black liquor, and 0.025% SAQ added to the white liquor. We found that SAQ added to the white liquor did not enhance the pulping rate. The absence of rate enhancement by the SAQ added to the white liquor is consistent with the fact that AQ is most effective in accelerat-

5. Optimum SAQ concentration and addition point at 1900 H-factor



ing the initial phase of delignification (21). Simulations of the MB process suggest that the pulping is well into bulk delignification when the chips contact the white liquor (19).

One would expect the maximum benefits of the catalyst when adding SAQ to the white liquor, since this liquor would recycle through the hot and then the warm black liquor phases. We subsequently determined, however, that addition of 0.025% SAQ to the white liquor results in hot and warm liquor concentrations that translate to charges less than 0.01% of wood. At this concentration, Fig. 5 indicates that no enhancement in delignification would occur from the SAQ recycled into the black liquor pretreatments.

Figure 7 shows that the pulp yield at a given kappa number improves with the addition of SAQ to either the white or hot black liquor. The yield enhancement was greatest (2% at kappa no. 20) when we added SAQ in the hot black liquor. The yield improvement resulting from SAQ added to the white liquor indicates carbohydrate stabilization by SAQ during the high temperature portion of the cook (23, 24).

The results in Figs. 5-7 demonstrate that SAQ is most effective when added to the hot black liquor phase of an MB cook. We therefore conducted

all subsequent experiments with SAQ added to the hot black liquor phase.

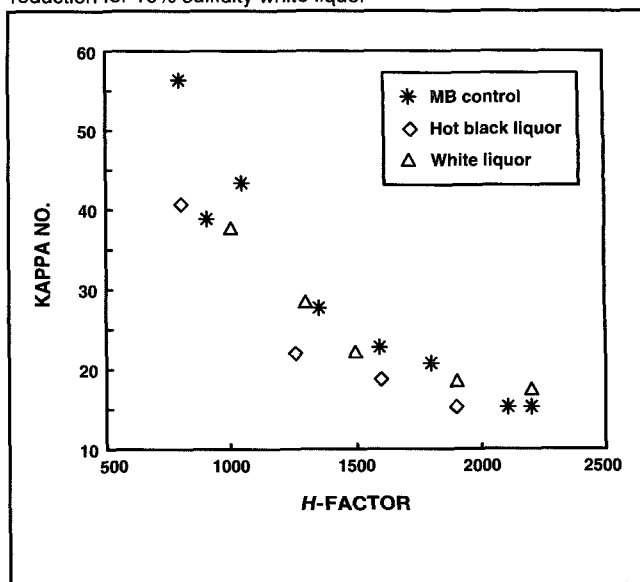
## Low sulfidity SAQ MB pulping

Figure 8 presents the effect of white liquor sulfidity on the delignification rate with SAQ added to the hot black liquor. The trend of decreasing pulping rate with decreasing sulfidity previously observed in Fig. 1 also appears in Fig. 8. Adding SAQ to the hot black liquor with a white liquor sulfidity level of only 10%, however, produced low kappa number pulp with little loss of pulping rate. In the absence of SAQ, the difference between the 30% sulfidity and 10% sulfidity pulping was greater. Comparison of the results in Fig. 1 to those in Fig. 8 shows that soda MB pulping with SAQ is considerably more rapid than soda MB pulping. As one would expect, the enhancement by SAQ appears to be greatest at lower sulfidities.

Figure 9 shows that the relationship for kappa numbers and yields for 10% and 30% white liquor sulfidity cooks is similar when SAQ is added to the black liquor. Pulp yield decreased marginally when using a white liquor sulfidity of 5% and more dramatically under soda MB conditions with SAQ.

Figure 10 presents the yield vs. kappa number comparison between

6. Optimum SAQ addition point determination and kappa number reduction for 10% sulfidity white liquor



MB and MB pulping with SAQ with 30% sulfidity white liquor. These results show that one would anticipate a yield improvement of approximately 1% when there is a 0.025% SAQ addition to the hot black liquor.

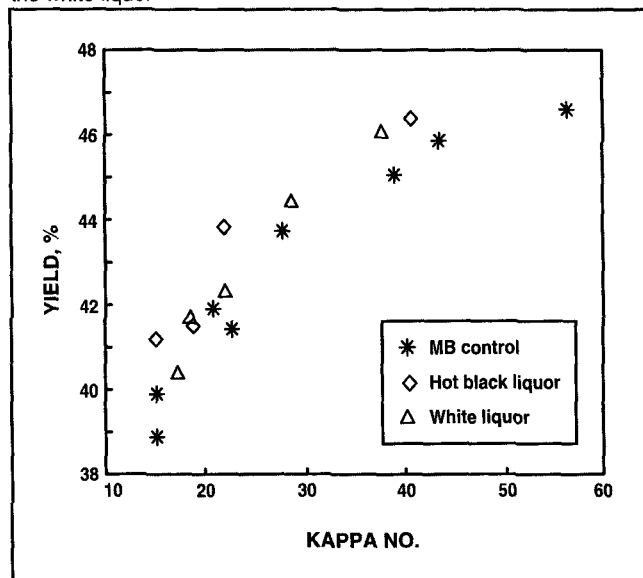
## Pulp strength

The addition of AQ to kraft pulping has little effect on pulp strength (12, 13). Figure 11 shows the effect of SAQ addition on pulp strength for pulps produced in this study. It is obvious that addition of SAQ significantly improved the relationship of tear and tensile of pulps produced at 10% sulfidity. At 30% sulfidity, the effect of SAQ on the pulp strength was minimal. The addition of SAQ does appear to produce a slightly stronger pulp. One can also see in Fig. 11 that the pulp produced with 10% sulfidity is about the same strength as that produced at 30% sulfidity when SAQ is present in the hot black liquor.

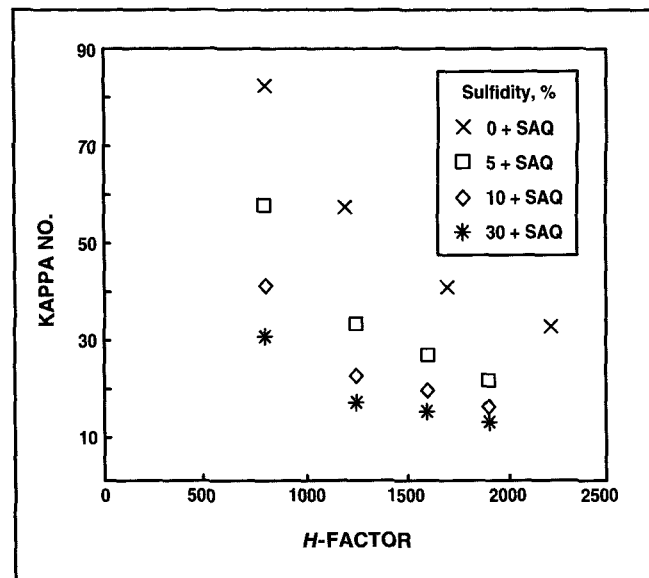
## Residual SAQ analysis

We measured residual SAQ levels as AQ using high-pressure liquid chromatography to estimate the amount of catalyst that might recycle through a commercial MB system. We found that changes in the sulfidity of the

7. Yield vs. kappa number for SAQ added in the hot black liquor and the white liquor



8. Effect of white liquor sulfidity on SAQ addition in the hot black liquor



cooking liquor had no effect on the amount of SAQ present in the resultant black liquors. The warm and hot black liquor conditions are mild. Consequently, we could recover 47–52% of the original SAQ charge from these liquor phases when adding either 0.025% or 0.05% SAQ to the cook. We also observed SAQ in the black liquor obtained at the conclusion of the white liquor cooking phase. The precise amount, however, was dependent on the cook *H*-factor, because SAQ degrades during the high temperature phase of pulping.

Figure 12 shows the SAQ concentration profile from an MB cook with addition of 0.05% SAQ in the hot black liquor. We attribute the apparently rapid consumption of SAQ during the hot black liquor phase to the absorption of SAQ by the wood chips. As the figure indicates, approximately 50% of the original SAQ charge was discarded with the displaced black liquor. With the white liquor addition, the SAQ present in the chips diffused into the pulping liquor until reaching the maximum cooking temperature at 90 min. Consumption of the chemical then occurred resulting in the observed depletion of SAQ in the pulping liquor.

The SAQ consumption results suggest that the steady-state AQ concen-

trations in an MB mill will be higher than in this study because of liquor recycling. One might expect that the enhancement of the pulping associated with use of SAQ will therefore be greater than shown here.

## Conclusions

The effectiveness of modified batch pulping increases significantly with sulfide concentration at low white liquor sulfidities, but this increase diminishes at sulfidities over 15%. The results of this study suggest a reduction in white liquor sulfidity in an MB mill to approximately 15% with no adverse effects on production or pulp quality. More work on the relationship between sulfidity and pulping rate and pulp properties in the 15–30% white liquor sulfidity range is necessary to determine definitively the sulfide concentration which produces an acceptable pulp.

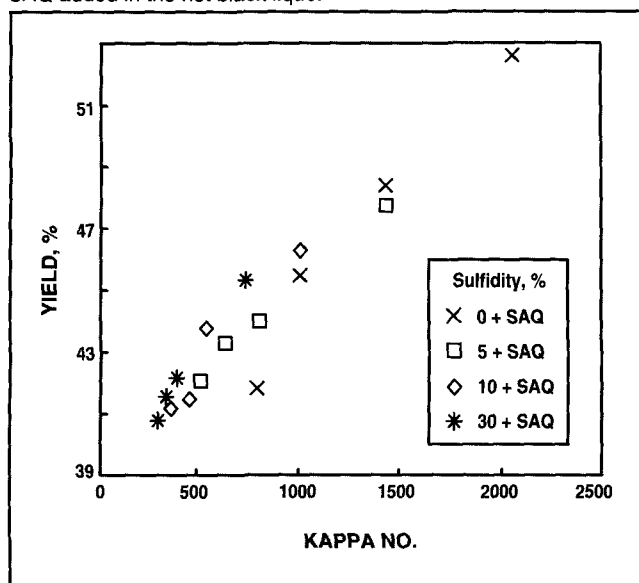
The addition of SAQ to the MB system enhances pulping similar to the enhancement achieved in conventional pulping with this catalyst. SAQ accelerates the pulping rate and increases the yield at a given kappa number. We also found that the addition of SAQ significantly improved the pulp strength when pulping at lower

sulfidities. SAQ was most effective with addition to the hot black liquor phase of the MB cycle. We found with addition of SAQ to the hot black liquor at a level of 0.025% the white liquor sulfidity could decrease to only 10% while still producing strong pulp. The addition of SAQ at this level also increased the pulp yield at a given kappa number by 1%. Reduction of the sulfidity to 10% in an MB cook without SAQ resulted in a significantly inferior pulp. Approximately 50% of the SAQ charged to the hot black liquor was recovered following this pulping phase. It is therefore possible to recycle it into a subsequent cook. We anticipate that liquor recycling in the MB system will enhance the efficacy of SAQ in a commercial mill to a greater extent than found in this study.

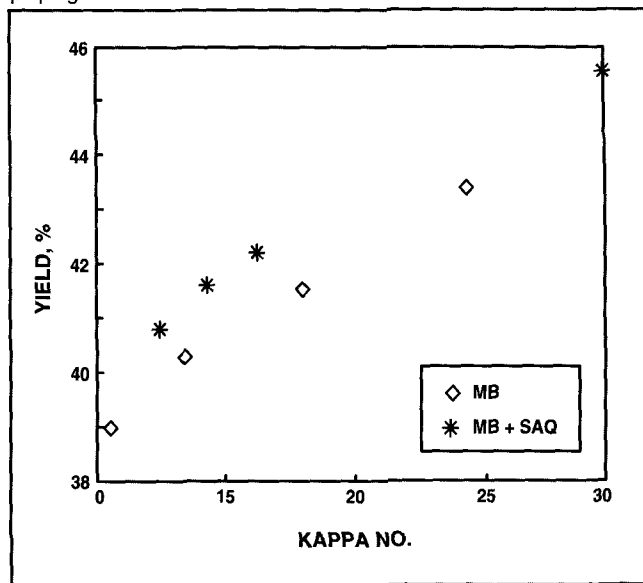
## Experimental

We dried and screened commercial southern pine chips and then removed knots and other irregularities by hand. We performed laboratory MB and conventional kraft pulping experiments using a dual vessel digester described elsewhere (19). For the low sulfidity cooks, we prepared synthetic black liquors as a percentage of both the 30% sulfidity MB black liquor and a soda

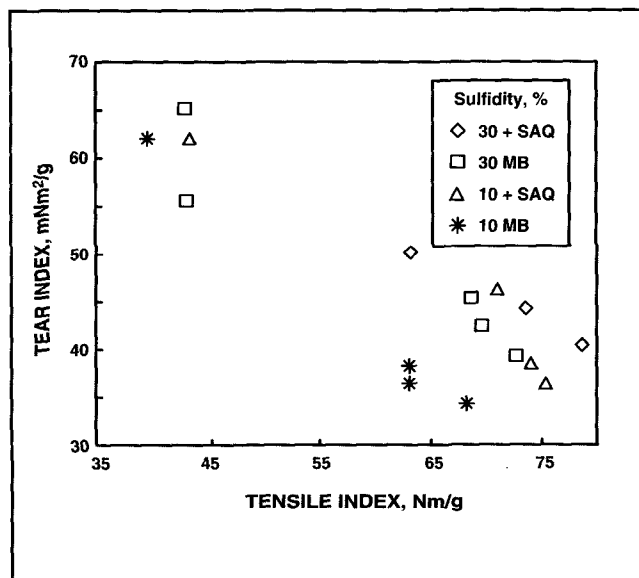
9. Yield vs. kappa number for changing white liquor sulfidities with SAQ added in the hot black liquor



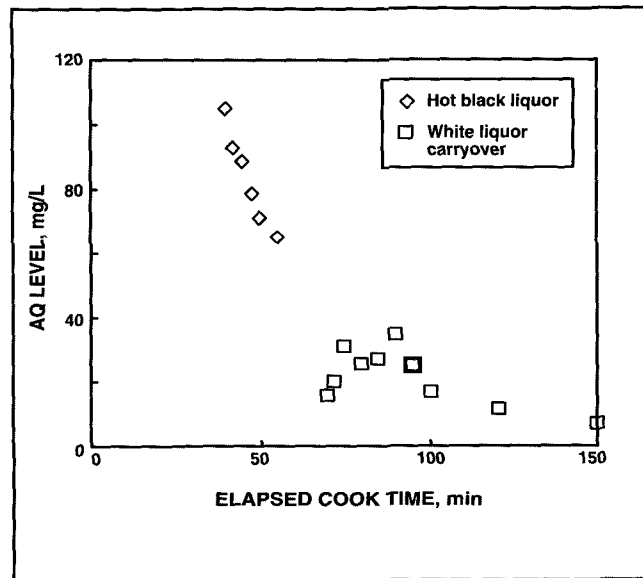
10. Yield vs. kappa number comparison between MB and SAQ MB pulping



11. Tear index vs. tensile index for SAQ MB pulping



12. SAQ consumption profile for SAQ addition in the hot black liquor



black liquor. For example, in a 10% sulfidity cook, we charged the black liquor with 34% of the 30% sulfidity black liquor and 66% of the soda black liquor. In this way, the white liquor phase would not become overcharged with sulfide ions carried over from the black liquor pretreatments to give misleading results.

We mixed the required volume of the 10% SAQ solution in caustic with the appropriate pulping liquor using a

syringe immediately before introduction of that liquor to the wood chips.

Conventional methods determined pulp yield and wood moisture content. TAPPI Test Method T 236 cm-85 determined kappa numbers. High-pressure liquid chromatography measured residual SAQ concentrations in the pulping liquors using a procedure based on that of Nelson and Cietek (25).

Following defiberization and screening, we beat the pulp samples in a mill and determined handsheet properties using the TAPPI Test Method T 220 om-88. TAPPI Test Method T 227 om-85 determined pulp freeness. □

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