CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECTIVENESS OF ULTRA-FINE ANTHRAQUINONE IN THE KRAFT PULPING OF EUCALYPTUS WOOD

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This paper reports on an investigation of the effectiveness of ultra-fine anthraquinone (UF-AQ) in the kraft pulping process of eucalyptus wood. The results of the pulping process using UF-AQ are compared to the results of pulping with commercial AQ (C-AQ) and using no AQ. The delignification in the pulping process using UF-AQ is more effective than that of the C-AQ involving process. The use of UF-AQ also improved pulp yield, albeit to a lesser degree than the improvement in delignification, and had no significant effect on fiber length. The study also showed that the UF-AQ pulping significantly reduced the consumption of the effective alkali. In summary, the application of UF-AQ shows great promise for improving the AQ-assisted kraft pulping process in terms of increased effectiveness of energy, chemical consumption and raw material utilization.

Keywords: anthraquinone, ultra-fine particles, kraft pulping, effectiveness, energy efficiency

INTRODUCTION

Challenges posed by the energy crisis and environmental problems are forcing researchers to deeply investigate the utilization of lignocellulosic biomass, one of the world's most abundant and environmentally friendly resources.[1] These efforts can be seen in the development of new technologies for biofuel production,[2-3] as well as research to further optimize the existing pulping process in terms of material- and cost-effectiveness in mill operations.[4-5]

Kraft pulping is still the dominant process employed in the production of chemical pulps.[6] Anthraquinone (AQ) has been proved to be one of the most effective additives in the industrial application,[7] because it not only accelerates the delignification during alkaline pulping process, but also helps to stabilize the carbohydrates from further degradation.[8-9] As a result, the pulp yield is preserved. Currently, the yield from AQ-assisted kraft pulping can reach nearly 50% for hardwood species; e.g., eucalyptus.[6] However, it is still an interesting subject to further improve the effectiveness of the present AQ-assisted pulping process, i.e., on the energy/chemical consumptions and raw material utilization.

Many studies have been conducted on the improvement of pulp yield in alkaline-AQ pulping, including the optimization of process conditions and the use of polysulfides, surfactants and AQ derivatives. The major results from these studies indicate that: AQ is more effective to the pulping with lower sulfidities or lower H-factors (i.e., shorter cooking time);[10-13] there is a synergistic effect between polysulfides and AQ in pulping of softwoods;[14] surfactants are helpful in AQ-assisted pulping;[15] AQ derivatives (e.g. 2-methylanthraquinone,[16] 2, 6/7-dimethyloctahydro anthraquinone, and dimethylanthraquinone[17]) are more effective than AQ. However, there are also some weaknesses in the processes mentioned above. For example: the optimized process conditions can lower the delignification rate, and the resulting pulps possess poor uniformity;[10,18] the aid of polysulfide is not available for hardwood[19] and has little effect on the delignification rate;[14] surfactants show little or even a negative effect on the screen pulp yield;[20-21] the synthesis of AQ derivatives is quite complicated, and the yields are very low.[16-17,22-23] Despite these limitations or problems with the processes, AQ is still the major pulping-assistant additive used in the mill operations today.

It is well known that AQ is insoluble in aqueous solution and that it is important to increase the mass transfer of AQ particles into wood chips in order to improve the AQ effectiveness in pulping. In 2007, we proposed a new mechanism of AQ mass transfer during alkaline pulping,[10] as schematically described in Fig. 1.

This proposal was supported by our findings by the redox reaction based AQ mass transfer behavior in a membrane (Nafion) interface;[24] i.e., very high concentrations of anthrahydroquione (AHQ) were created at the surface of the membrane from the reaction between adsorbed AQ on the membrane surface and dithionite anions penetrating from the acceptor stream. This condition enabled the AHQ to partially penetrate through the membrane and enter the acceptor stream, as the membrane was swamped by sodium ions from the caustic and sodium dithionite solution.

According to the pathway shown in Figure 1, the adsorption of AQ particles on the surface of wood chips is the first step in transferring AQ into the hood chips and plays an important role in improving the effectiveness of AQ in pulping. Clearly, AQ with smaller particle sizes is not only more evenly distributed in the pulping liquor, but it also has a stronger adsorption to the surface of solid.[25] Therefore, we believe that the use of the AQ with small particle sizes is important for the AQ-assisted pulping process. However, until now, there has been a lack of research on the effect of AQ particle size on the outcome of alkaline pulping, which is actually a key part of the study of the mechanism by which AQ affects alkaline pulping.

In this work, we conducted an investigation of the effect of AQ particle sizes on the kraft pulping of eucalyptus wood chips and compared those results with the results obtained using the commercial (C) AQ. Ultra-fine (UF) AQ particles were prepared by the reduction of AQ to AHQ with dithionate in alkaline solution, followed by re-oxidation of AHQ to form UF-AQ by aeration in a strongly stirred medium. The main focus of the present study was on the effectiveness of UF-AQ-assisted kraft pulping of eucalyptus wood.

EXPERIMENTAL

Chemicals and sample preparations

All chemicals used in the experiment were from commercial sources. Distilled water was used in solution preparation. 1 g of C-AQ, 2.5 g of sodium dithionite and 8 g of sodium hydroxide were mixed with 50 mL black liquor (from eucalyptus kraft pulping with EA = 17%, as NaOH, sulfidity = 20% at H-factor = 650) and 50 mL distilled water in a flask followed by stirring at 80 °C until the color of the solution turned from red to yellow, at which point the preparation of UF-AQ was finished.

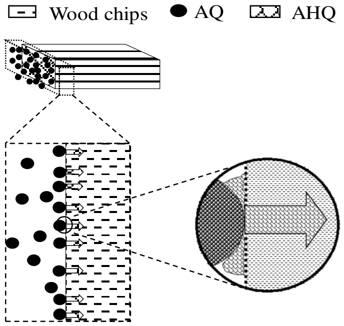

Figure 1: AQ mass transfer mechanism during alkaline pulping

Pulping

All of the pulping experiments were carried out as batch cooks in a laboratory digester system with circulating cooking liquor. The total volume of the Greenwood digester used is 10 liters. One thousand grams of oven-dried wood chips were put into the digester. The effective alkali (EA) charge ([NaOH] +1/2 [Na_2S] expressed as NaOH) was maintained at 17 wt% of wood; i.e., 17 g of EA/100 g chips. The sulfidity was maintained at 20% (sulfidity = [Na_2S]

/ ([Na_2S] + [NaOH]) all expressed as NaOH). The AQ dosage, from 0.025% to 0.2%, was based on the oven-dried weight of wood. The liquor-to-wood ratio was 4:1 in all of the experiments. The cooking liquor (white liquor) was prepared in the lab using sodium hydroxide and sodium sulfide. The remainder of the water in the system was made up by the water in the wood chips and de-ionized water. The cooking temperature was increased from 25 °C to 160 °C within 60 min and then held at 160 °C for 40 to 90 min. The pulps with no AQ were used as control.

Analysis

The kappa number and intrinsic viscosity of pulp were determined, respectively, by TAPPI standard method T236 om-06, SCAN-C 15:62. The content of residual effective alkali (REA) was measured using published methods.[26] Fiber morphological characteristics were analyzed with a fiber analyzer (Mesto Kajaani FS300, Finland).

Determination of anthraquinone particle size distribution followed the procedure: 0.3 g C-AQ or UF-AQ was added into 50 mL water solution containing 30% sodium dodecylbenzenesulfonate employed as disperser followed by stirring for 30 min. After settling, the supernatant was siphoned off for further characterization by means of a back-scattering laser granulometer (Mastersize 2000, Malvern Instrument).

RESULTS AND DISCUSSION

Particle sizes and distributions of UF-AQ and C-AQ

Figure 2 shows the particle size distributions of the UF-AQ made in this work and C-AQ. It can be seen that the particle size distribution of UF-AQ is between 1 and 200 µm, in which about 65% of particles are less than 20 µm. In contrast, the C-AQ has two regions of particle size distribution: the first, ranging from 30 to 320 µm, (accounting for 60% of the mass) and the second, from 700 to 2200 µm (accounting for the other 40%). Fig. 2 clearly shows that the UF-AQ prepared in this study not only has much smaller particle sizes, but also is more uniform than C-AQ, having a single modal distribution. Therefore, it is expected that UF-AQ will have a better performance in the pulping process.

Effect of AQ and its dosage on delignification

Figure 3(a) shows the effect of AQ charge on the delignification. The difference between UF-AQ and C-AQ addition is not significant when the AQ charge is below 0.025%, although both of the processes are more effective than the process without AQ; i.e., at zero addition. However, at charges greater than 0.025% the UF-AQ process is more effective than that of C-AQ; e.g., at the charge of 0.1%, the difference in kappa number is about 3.6. The results also indicate that when the charge is greater than 0.1%, the improvements on the delignification for both the C-AQ- and the UF-AQ-assisted processes become less significant.

As reported earlier,[27-29] the effect of AQ on delignification kinetics is proportional to the square root of the AQ charge on wood weight. By plotting the inverse of kappa number versus the square root of AQ charges (using the data shown in Fig. 3), we also found that this relationship is also applicable when using UF-AQ. Eqs. (1) and (2) represent this relationship for C-AQ and UF-AQ, respectively:

$$K^{-1} = 0.0328\sqrt{d_{C\text{-}AQ}} + 0.0345 \quad (R^2=0.92) \qquad (1)$$

$$K^{-1} = 0.0653\sqrt{d_{UF\text{-}AQ}} + 0.0328 \quad (R^2=0.94) \qquad (2)$$

where K is the kappa number, $d_{C\text{-}AQ}$ and $d_{UF\text{-}AQ}$ are the dosages of C-AQ and UF-AQ respectively, in %. The slope of Eq. (1) is two times that of Eq. (2), indicating that the delignification with UF-AQ is more effective than that with C-AQ.

Figure 3(b) shows the kappa number of the pulps during the pulping processes without AQ, with C-AQ and with UF-AQ addition. It is clear that while C-AQ is effective on the delignification, UF-AQ is even more effective; e.g., comparing the kappa number of the pulps from the control process (AQ = 0) at H = 300, the kappa numbers in the C-AQ and UF-AQ assisted processes are decreased by 31% and 41%, respectively. In order to achieve the same target kappa number, the UF-AQ assisted process does so at a significantly reduced value of the H factor, indicating that the UF-AQ added process is also more effective in saving energy than is the C-AQ added process.

Effect of AQ on pulp yields

Figure 4 shows the screened pulp yields and reject yields at different pulping H factors. Among the three processes, the UF-AQ process exhibits the best performances in both pulp yield and reject yield at all H factors.

Figure 5 is the plot of pulp yield vs. kappa number. It can be seen from Figure 5 that, for the pulp yield, the AQ involving processes are much more effective. Comparing the results of the two

AQ involving processes, the pulp yield from the UF-AQ process is slightly better than the C-AQ process at a given kappa number.

Effect of AQ on pulp viscosity

Viscosity is a direct index related to the carbohydrate degradation. Figure 6 shows the change of pulp viscosity versus kappa number. It can be seen that the viscosities of pulps from the C-AQ, UF-AQ, and the controlled processes are essentially the same, basically decreasing with increasing kappa number. As generally known, there is a large uncertainty in the viscosity measurement of high kappa pulps (>20 for hardwood pulp), which is caused by lignin interference in the dissolution of cellulose in cupriethylenediamine solution.[30] Therefore, it can be concluded that there is no significant difference between the effects of C-AQ and UF-AQ on the pulp viscosity.

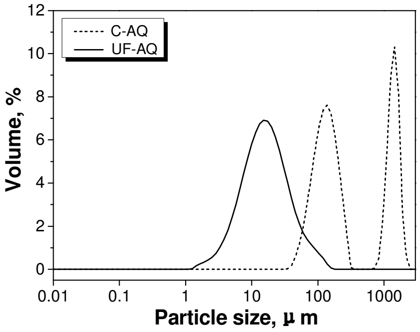

Figure 2: Particle size distributions of C-AQ and UF-AQ

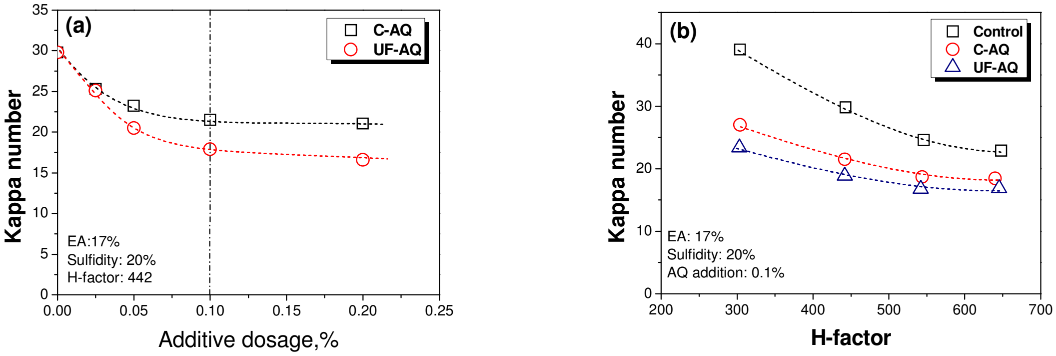

Figure 3: Kappa number variation as a function of (a) additive dosage; (b) H-factor

Effect of AQ charge on fiber length

Fiber length is an important property of papermaking furnishes, making great contributions to the paper strength through fiber-fiber bondings.[16] Figure 7 shows the average fiber length of pulp vs. kappa number from the present pulping processes. These data show that the AQ does not significantly affect the fiber length of pulps.

Effect on residual effective alkali (REA)

Effective alkali (EA) is the chemical driving force for the delignification in the pulping process. The right amount of EA must be present toward the end of the cooking in order not only to achieve the delignification to the desired degree, but also to avoid precipitation of dissolved lignin onto the fibers.[31] Figure 8 shows the relationship between the REA in the cooking liquor and pulp kappa number. It is clear that for a given kappa number the UF-AQ involving pulping preserved more REA in the cooking liquor. Thus, the UF-AQ process has the added benefit of saving EA in the pulping process.

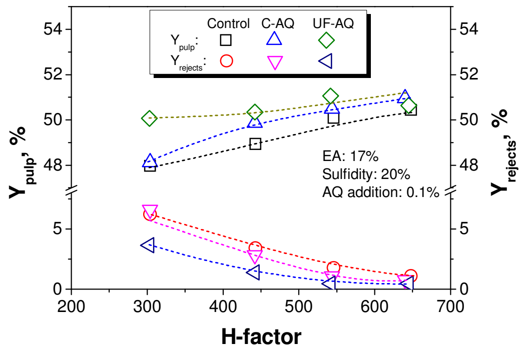

Figure 4: Variation of screened pulp yield (Y_{pulp}) and screened reject yield ($Y_{rejects}$) as a function of H-factor

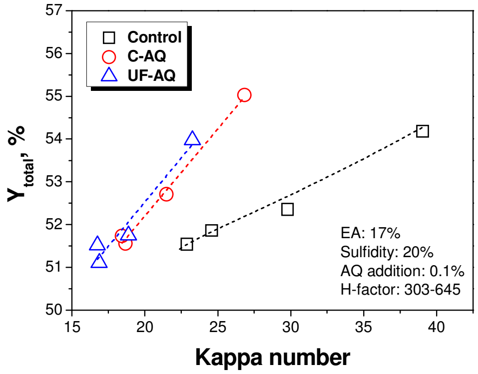

Figure 5: Variation of total pulp yields (Y_{total}) as a function of kappa number

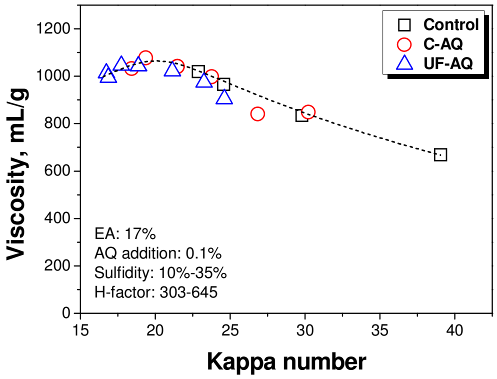

Figure 6: Variation of pulp viscosity as a function of kappa number

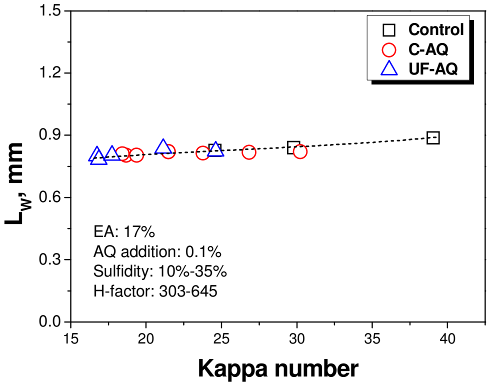

Figure 7: Variation weighted average fiber length (L_W) as a function of kappa number

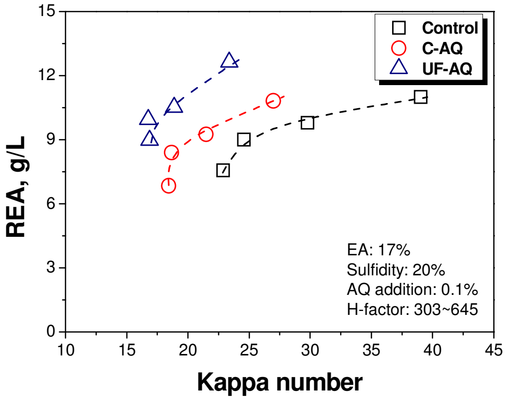

Figure 8: Variation of REA as a function of kappa number

CONCLUSION

The effectiveness of the UF-AQ involving kraft pulping process was investigated, and the data show that addition of UF-AQ results in a very significant positive effect on the delignification and a reduction in EA consumption. Therefore, the potential for UF-AQ-assisted pulping should be further explored with the goal of improving energy efficiency, reducing chemical consumption and maximizing raw material utilization in pulp mill operations.

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REFERENCES

[1] P. C. Munasinghe and S.K. Khanal, *Bioresour. Technol.*, **101**, 5013 (2010).

[2] P. Tomani, P. Axegård, N. Berglin, A. Lovell and D. Nordgren, *Cellulose Chem. Technol.*, **45**, 533 (2011).

[3] C. Chirat, D. Lachenal and A. Dufresne, *Cellulose Chem. Technol.*, **44**, 59 (2010).

[4] A. Alfaro, F. Lopez, A. Perez, J. C. García, M. A. Pèlach *et al.*, *Cellulose Chem. Technol.*, **47**, 765 (2013).

[5] Z. Gonzalez, F. Vargas, L. Jimenez and A. Rodriguez., *Cellulose Chem. Technol.*, **47**, 603 (2013).

[6] H. Sixta, "Handbook of Pulp", Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.

[7] S. Saka, R. J. Thomas, J. S. Gratzl and D. Abson, *Wood Sci. Technol.*, **16**, 139 (1982).

[8] L. Löwendahl and O. Samuelson, *Svensk Papperstidn.*, **80**, 549 (1977).

[9] L. Löwendahl and O. Samuelson, *Polym. Bull.*, **1**, 205 (1978).

[10] X. S. Chai, J. Samp, Q. X. Hou, S. H. Yoon and J. Y. Zhu, *Ind. Eng. Chem. Res.*, **46**, 5245 (2007).

[11] G. W. Kutney, *Procs. Tappi 1984 Pulping Conference*, Tappi Press, Atlanta, 1984, pp. 65-73.

[12] L. Sturgeoff and S. Bernhardt, *Procs. Tappi 1998 Pulping Conference*, Tappi Press, Atlanta, 1988, pp. 25-29.

[13] N. J. Van Allen, J. V. Hatton and W. Y. Gee, *Tappi J.*, **64**, 64 (1981).

[14] Z. Li, H. Ma, G. J. Kubes and J. Li, *J. Pulp Pap. Sci.* **24**, 237 (1998).

[15] F. Gomes, *Tappi EPE Conference*, Jacksonville, October 2007.

[16] R. C. Francis, S. J. Shin, S. Omori, T. E. Amidon and T. J. Blain, *J. Wood Chem. Technol.*, **26**, 141 (2006).

[17] D. R. Dimmel, *U. S. Patent* 6156155 (2000).

[18] S. A. Rao and J. S. Upadhyaya, *J. Sci. Ind. Res.*, **61**, 231 (2002).

[19] C. Luthe, R. Berry and K. Parsons, *Pulp Pap. Can.*, **106**, 97 (2005).

[20] C. Baptista, N. Belgacem and A. P. Duarte, *Appita J.*, **57**, 35 (2004).

[21] Y. Hamzeh, A. Abyaz, M. O. Niaraki and A. Abdulkhani, *Bioresources*, **4**, 1267 (2009).

[22] D. R. Dimmel and J. C. Wozniak, *U.S. Patent* 5049236 (1991).

[23] D. R. Dimmel and J. C. Wozniak, *U.S. Patent* 5002634 (1991).

[24] X. S. Chai, J. Samp and Q. X. Hou, *J. Membrane Sci.*, **271**, 215 (2006).

[25] J. C. Samp, *ProQuest* (2008).

[26] S. L. Shi and F. W. He, in "Pulp and Paper Analysis and Detection", China Light Industry Press, Beijing, 2003.

[27] P. K. Bhattacharya, S. De, R. Haldar and R. Thakur, *Tappi J.*, **75**, 123 (1992).

[28] M. H. Waller and Y. N. Eyike, *Pulp Pap. Can.*, **84**,83 (1983).

[29] J. Abbot and H. I. Bolker, *Tappi J.*, **65**, 127 (1982).

[30] Paper and Boards Testing Committee, Scandinavian Pulp (1962).

[31] T. Radiotis, J. Sullivan, M. Macleod, S. Syed and T. O'Hagan, *Tappi EPE Conference*, Jacksonville, October 2007.