

Study on the Mass Transfer Behavior of AQ and Its Effectiveness during AQ-Kraft Pulping Process

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ABSTRACT

Studies of the effectiveness of anthraquinone (AQ) in kraft-AQ pulping in terms of its mechanism of mass transfer have been conducted. Experiments performed have demonstrated an "apparent solubility" of AQ in caustic solutions of wood lignin. The adsorption behavior of AQ species was also analyzed. Anthraquinone-2-sulfonic acid (AQ-S), a water-soluble derivative of AQ, showed selective adsorption on wood. A mechanism for the transport of AQ into wood chips during kraft pulping are proposed, and some explanations for previously unexplained observations are addressed.

Key words: Kraft; soda; pulping; AQ; Mass transfer; delignification; kappa number; pulp yield; solubility; dissolved lignin.

INTRODUCTION

With the shortage of energy, raw materials, and the increasingly strict environmental regulations, there is an urgent need for pulping mills to be more effective in the energy and raw material use and reduce environmental impact in order to gain competitiveness in the world. Anthraquinone (AQ), as a chemical additive in the alkaline pulping process, was first introduced in the pulping industry in 1977 [1]. With the presence of AQ, the delignification rate and the preserved pulp yield can be improved. In our recent study, it showed that the AQ related kraft pulping process can also environmentally sound since it reduces the emission of volatile organic compounds (VOCs) such as methanol [2] and organic sulfur compounds (e.g., methyl mercaptan and dimethyl sulfide) [3], the latter can lead to a significant sulfur loss in the pulping production.

Traditionally, the positive effects in AQ pulping are mainly attributed to its redox cycle mechanism between oxidized and reduced anthraquinone, that is, AQ and anthrahydroquinone (AHQ). Through such a redox cycle, the aldehyde end groups of carbohydrates can be converted into aldonic acid groups, which stabilize the carbohydrates from the further degradation [4-5]. On the other hand, the reduced AQ (i.e., AHQ) reacts with lignin in wood chips, which accelerates the delignification. Since AQ is regarded as an insoluble chemical, the effectiveness of AQ during the alkaline pulping process could be limited by many factors, mainly the mass transfer. Many researchers have conducted various studies

in order to discover the reason for the impressive catalytic effect of AQ not only chemically, but also physically [6-8]. Unfortunately, the limited information was unable to explain some interesting and important phenomenon that they observed in their studies. The main reason might be the lack of a powerful analytical method that can efficiently determine the AQ content in the process liquors, especially in the sulfide-containing pulping liquors.

In our previous work [9], we have developed a novel method for determination of AQ in the alkaline cooking liquor. It is based on separating AQ species from cooking liquor using a Nafion membrane interface and then converting the AQ species to AHQ by reaction with dithionite in the acceptor solution, which is detected spectroscopically at a wavelength of 505 nm.

In this work, we have studied the behaviors of the apparent dissolution of AQ in different alkaline liquors and adsorption behavior on wood chips. The effectiveness of AQ on the delignification with different process conditions of pine and maple pulping has also been investigated.

EXPERIMENTAL

Chemicals and sample preparations

All chemicals used in the experiment were from commercial sources. Distilling water was used in solution preparation.

Sample liquors were withdrawn at different time from several alkaline pulping processes with various sulfidity (10, 20, 30%) and AQ charges (0.025, 0.05 and 0.10% on

wood) at different ending time (H-factor). The active alkaline is 18% for pine and 16% for maple cook, respectively, with a liquor to wood ratio of 4:1. In AQ or AQ-S adsorption study, the liquor to wood ratio is 5:1.

Apparatus and Procedures

The determination of AQ and anthraquinone-sulfonate salt (AQ-S) is conducted by a flow analysis method based on a membrane separation and spectroscopic measurement. A detailed description of the method is published in the reference [9].

RESULTS AND DISCUSSIONS

"Apparent solubility" of AQ in alkaline pulping process liquors

AQ is generally regarded as an insoluble specie in the aqueous solution. In this work, we defined those AQ particles with small enough size to freely migrate in the liquor (due to stirring and Brownian effects) as the "dissolved" AQ. Thus, the so-called "apparent solubility" of AQ represents the maximum limit of the amount of the "dissolved" AQ particles in the liquor. As shown in Fig. 1, the amount of the "dissolved" AQ particles in a NaOH solution is very limited, however, which can be greatly increased in a lignin-containing alkaline solution [9]. For the solution containing more than 40 g/L of alkaline dissolved lignin, the "apparent solubility" of the "dissolved" AQ can be up to 0.14 gram/L, at a temperature of 90°C. Fig. 1 also shows that the "apparent solubility" of AQ in a soda black liquor (H-factor = 1000) is lower than that in the alkaline lignin solution when adding the same amount of AQ solids. We believe it is because of the significant amount of carbohydrates that soda liquor contains, which can convert a part of AQ into AHQ form.

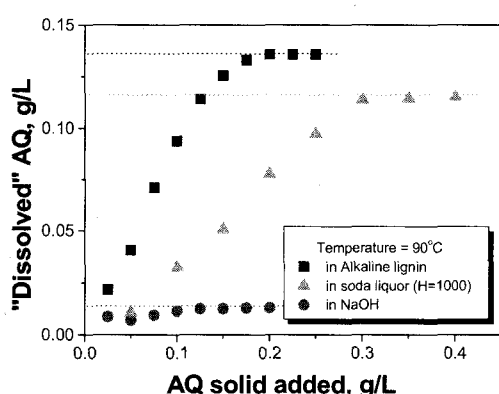


Figure 1. Apparent solubility of AQ in different alkaline mediums.

It was observed that the dispersion ("dissolving") of AQ powder is a slow process; a near-complete dispersion of 0.14 g AQ powder in one liter of the lignin-enriched alkaline solution takes about 40 minutes at a temperature

of 90°C. The rate of AQ "dissolving" is expected much faster at a higher temperature during the pulping process.

Possible mechanism for AQ "dissolving"

We believed that the AQ "dissolving" is due to a chemical reaction with the reducing species (i.e., carbohydrates) to form AHQ. If the amount of the reducing species in the system is not sufficient, some of AHQ can easily be oxidized back to AQ by air or the dissolved lignin in the cooking solution. As a result, much smaller size of AQ particles is formed. In pure NaOH solution, there are no reducing species available; therefore, the amount of the "dissolved" AQ in the liquor is very small. In the soda black liquor, there are plenty of reducing species available in the form of dissolved carbohydrates. Thus, a majority of AQ can be converted to AHQ and some of them remain stably in the liquor. The lignin we used in preparing the artificial (alkaline lignin) liquor was acid hydrolyzed from wood chips. This means that the lignin still contains some reducing groups in the form of the end units of lignin-carbohydrate complexes (LCCs), which having a reducing capability. Thus, AQ can react with LCCs to form AHQ, however it is instable due to a limit amount of reducing species in such as a liquor. Eventually, it is all in AQ solid form but with a much small particle sizes. This results in the highest "apparent solubility" of AQ of the three in shown in Fig. 1.

Study of AQ adsorption behavior on wood chips

Due to its solubility limitation of solid AQ in the solution, it is difficult to study the adsorption behavior of AQ on wood chips, in which both AQ deposition and adsorption on the wood chips take place at the same time. Instead, we use anthraquinone-2-sulfonic acid (AQ-S), a water-soluble derivative of AQ, to observe its adsorption behavior on the wood chips. The study shows that the AQ-S can adsorb onto the wood chips, and the amount of AQ-S adsorbed is a function of the time and temperature. The equilibration of adsorption can be achieved in about 20 minutes. The amount of AQ-S adsorbed is inversely proportional to the temperature of the system. Therefore, this adsorption should be regarded as physical adsorption. The study also showed that the adsorption of AQ-S on wood chips is selective, because its reduced form, anthrahydroquinone-2-sulfonic acid (AHQ-S) does not significantly adsorb on the wood chips under the same conditions.

We believe that AQ should have the similar behaviors as AQ-S, but can adsorb on wood chips more than AQ-S. However, the AQ "dissolving" can play a very important role to significantly affect its adsorption on wood chips.

Mass transfer of AQ in wood pulping

In a recent work, we have revealed the special AQ mass transfer phenomenon in Nafion membrane [10]. This is based on the adsorption of AQ tiny particles and reduction reaction on the membrane surface. As a result,

it creates a very high AHQ concentration near the membrane surface and provides a significant driving force to diffuse AHQ through the membrane by the concentration gradient. We believe that a similar AQ mass transfer mechanism involved during wood pulping.

Base on the special AQ behavior in membrane transportation, the following is proposed for the mass transfer of AQ during the alkaline pulping process. The “dissolved” AQ migrates in the liquor and adsorbed on the wood chips. It reacts with carbohydrates released from wood chips to form highly concentrated AHQ at the surface, which can penetrate into wood chips significantly where it further reacts with lignin in wood to form AQ. Then the AQ→AHQ→AQ redox cycle takes place in the wood phase. AQ will lose its functionality for pulping if the AHQ exits the chip into the bulk solution.

Effectiveness of AQ in kraft pulping processes.

According to our new hypothesis, the adsorption and reaction based AQ mass transfer plays an important role in improving the pulping effectiveness. The following discussions are about the effects of some process parameters on the pulping effectiveness.

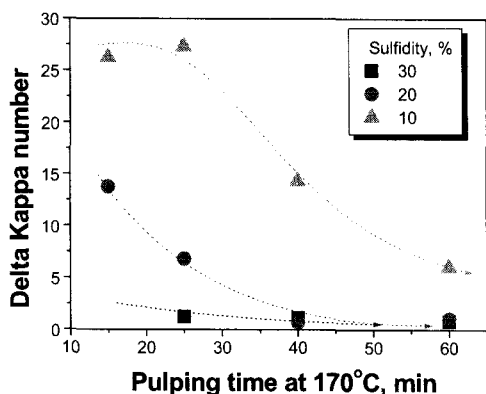


Figure 2. Sulfidity effect on AQ delignification during maple kraft pulping processes.

Sulfidity effect.

It has been reported that the effectiveness of AQ decreases as sulfidity of white liquor increases [11-13]. It is well known that sulfide is a reduction agent and could react with AQ, an oxidant. Previous work has shown that sulfide can readily reduce AQ at high temperatures [14,15]. Our experiment showed that the AQ reduction by a strong reducing agent, dithionite, is much easier than sulfide, at a temperature of 90 °C. We also conducted an experiment that using AQ-S, a soluble specie, to react with sulfide in the alkaline liquor. It was found that a complete conversion of AQ-S to AHQ-S occurred within a short time at a temperature above 50°C. Thus, we concluded that the dissolution rate of AQ solids is

affected by the reducing agent capability, its concentration, and temperature. In the early stage of kraft pulping, the release of the carbohydrates from wood chips and higher concentration of sulfide in the cooking liquor can convert more AQ into AHQ form, which remains stable. It decreases amount of “dissolved” AQ to the surface of wood chips. In Fig. 2, it shows the sulfidity effect on the delignification differences (Delta kappa number) between the processes with AQ and the controlled pulping without AQ addition, in the conventional pulping process. Clearly, at a low sulfidity, the AQ effectiveness in pulping is much higher that that of process with a higher sulfidity. Similar phenomenon was also observed in pine pulping process.

Process time effect during a conventional pulping.

Fig. 2 also shows that AQ is most effective during the early stage of the conventional pulping process. This further confirms the results that revealed by the work conducted by Sezgi et al., which tells the difference in kappa number for the pulp samples from kraft and AQ-kraft pulping processes at different H-factor as shown in Fig. 10 of that paper [16]. Their figure clearly indicates that the effect of AQ on delignification at an H-factor below 2000 is very significant. Cooks utilizing AQ displayed a reduction of six kappa number unit over the process without AQ. However, the benefit gained by the addition of AQ disappears when the H-factor reaches 2500. Here, cooks containing AQ produce pulps with the same kappa number as that from pulps without AQ.

In Fig. 3, it shows that the high charge of AQ can still effective to the delignification even in a cooking at a high sulfidity, especially in the early stage of the cooking. However, the benefit of AQ will be lost gradually as the cook continues. Therefore, we can conclude that the effectiveness of AQ is limited mainly to the initial stage during the conventional kraft pulping process.

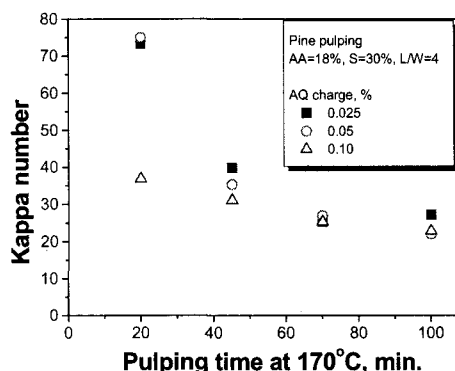


Figure 3. AQ charge effect on delignification during a high sulfidity conventional kraft pulping processes.

Effect of pulping mode.

It has been reported in a number of studies [16,17] that

AQ is less effective in the displacement batch pulping operations, such as RDH and SuperBatch™, than it is in conventional batch cooking. It can be easily explained by the phenomenon as we discussed above. First, the AQ adsorption on wood chips plays an important role to the delignification and a lower temperature is ideal to such an adsorption. Second, a significant amount of dissolved lignin and carbohydrates in the cooking liquor can limit the AQ to AHQ redox cycle within the cooking liquor and affect the adsorption of AQ on the wood chips. On the other hand, it was found that AQ or AHQ is consumed during the late stage of the cook as shown in Fig. 3. Therefore, only the process conditions at the early stage of conventional batch process is ideal to meet the requirements. Thus, we suggest that the AQ-containing pulping research should be focused on the early stage of conventional pulping processes.

CONCLUSIONS

This study has shown that AQ has an "apparent solubility" in caustic solutions of carbohydrates and wood lignin, in which the AQ dissolution is a slow process. The adsorption behavior of AQ derivative (AQ-S) on wood was also analyzed and a selective adsorption behavior was observed. A mechanism for the transport of AQ into wood chips based on a surface adsorption and reaction was proposed, and some well-known AQ-kraft pulping phenomena have been explained based on our new hypothesis.

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