Spectroscopic Determination of Anthraquinone in Kraft Pulping Liquors Using A Membrane Interface

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ABSTRACT

A spectroscopic technique for determining AQ in pulping liquor was developed to effectively separate AQ from dissolved lignin. This technique is based on a flow analysis system with a Nafion membrane interface. The AQ passed through the membrane is converted into its reduced form, AHQ, using sodium hydrosulfite. AHQ has distinguished absorption characteristics in the visible range, whereas spectral contribution from the small lignin molecules that penetrate through the membrane is insignificant. It was found that AQ can be dissolved in dissolved lignin-enriched alkaline solutions, which makes calibration of AQ using standard aqueous alkaline AQ solutions possible. The solubility of AQ in a lignin-enriched solution is approximately 0.14 g/L at 90°C. Time-dependent dissolved AQ measurements in the kraft-AQ pulping process were demonstrated using the present method.

INTRODUCTION

Anthraquinone (AQ) is an important catalyst that has been widely used in alkaline wood pulping for its effectiveness in accelerating delignification and preserving pulp yield [1-4]. When AQ is added to alkaline pulping liquor, the dosage of sulfide applied in kraft pulping can be reduced without sacrificing pulping performance [5]. Therefore, applying AQ to the alkaline pulping process is environmentally sound because air emissions of total reduced sulfur (TRS) compounds at kraft pulp mills are reduced due to reduced sulfide application. Despite extensive research conducted on AQ pulping, AQ chemistry during the alkaline pulping process is not fully understood. Thus, the effectiveness of using AQ to improve pulping performance is limited. One of the main obstacles to research progress is the lack of an effective method for measuring AQ in kraft pulping liquors.

GC/MS [6] and liquid chromatographic (LC) methods [7] have been developed for AQ determination in black liquors; however, these methods are complicated and require time-consuming sample preparation. The GC/MS method involves an exhaustive extraction procedure using chloroform [6]. The LC method [7] requires pretreatment of the black liquor sample with acetonitrile to dissolve AQ solids as well as filtration of the diluted solution prior to LC analysis. Fleming et al. [4] reported a polarographic method for determining AQ in soda pulping liquors. Based on this polarographic method, AQ concentrations in the soda pulping liquors at different pulping times have been described. However, the method cannot be applied to the kraft-AQ pulping process due to the presence of sulfide ions in kraft pulping liquors. Furthermore, chromatographic methods usually can provide only the sum of the quantities of AQ and its reduced form, AHQ, in samples and cannot provide the quantities of AQ and AHQ separately. Because of the performance advantages of kraft-AQ pulping in terms of delignification, pulp yield, and insensitivity to wood species, it is important to be able to determine AQ in kraft pulping liquors.

We have developed a spectroscopic method using a Nafion membrane interface to determine anthraquinone-2-sulfonate (AQ-S), a catalyst that is similar to AQ but is soluble in alkaline solutions [8]. AQ-S was effectively separated from dissolved lignin in alkaline pulping liquor using the membrane, which makes spectroscopic determination of AQ-S possible. The objective of the present study is to demonstrate the Nafion membrane-based spectroscopic technique for AQ determination in kraft pulping liquor. Because of the limited solubility of AQ in aqueous solutions, the key technical difficulty related to reaching the objective will be sample calibration.

EXPERIMENTAL

Apparatus

The same experimental apparatus described in our previous study [8] for AQ-S measurement was used. The carry stream (10 mmol/L $Na_2S_2O_4$ + 0.1 mol/L NaOH solution) was pumped through a tubular membrane, Nafion 811 (Perma Pure, Toms River, NJ, USA), by a peristaltic pump (PR-1, Rainin, Woburn, MA, USA) at a flow rate of 0.5 mL/min, while AQ in the sample liquor (donor solution) permeated through the membrane into the carry stream to constitute the acceptor stream, as shown in Figure 1. The membrane tubing was 46 cm long and was placed in a 20-mL sample vial that was submerged into a water bath heated to a controlled temperature of 90°C throughout the experiment to achieve a constant and high AQ-S transport rate through the membrane. The acceptor stream flows through a cooling unit to bring the temperature of the flow down to room temperature. It was found that bubbles were formed after cooling. A debubble unit (Poreflon, Sumitomo Corp., Japan) was used to eliminate bubbles so that absorption measurements could be taken. The acceptor stream finally reached the flow cell with 1 cm optical path length. The absorption signal is collected by the spectrophotometer (HP-8453, Agilent Technologies, Palo Alto, CA, USA). Absorption spectral signals in the

UV-visible range were continually recorded by the spectrophotometer.

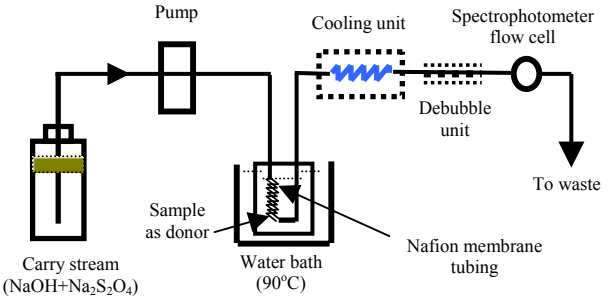

Fig. 1. Schematic diagram of the flow analysis and membrane interface system.

Chemicals and samples

All chemicals used in the experiment were from commercial sources. Distilled water was used in solution preparation. The carry stream was prepared by dissolving 10 mg of sodium hydrosulfite ($Na_2S_2O_4$, Fisher) in 1 liter of 0.1 mol/L sodium hydroxide (NaOH) solution. Paraffin oil was added to cover the surface of the carry stream source tank to prevent air from coming into contact with the stream. A set of anthraquinone standard solutions were prepared by dissolving different amounts of AQ in 1.5 ml/L of sodium hydroxide solution (containing 50 g/L lignin) for calibration. Sample pulping liquors were withdrawn at different times from conventional batch kraft-AQ pulping processes of loblolly pine. All pulping experiments were conducted under an active alkali (AA) charge of 18%, liquid-to-wood ratio of 4:1, and an AQ charge of 0.1% (on wood). Three sulfidity levels of 10, 20, and 30% were used. Four black liquor samples were taken from each pulping process at 20, 45, 70, and 100 minutes after the temperature reached 170°C. Standard AQ solutions with different known concentrations were used for calibration.

RESULTS AND DISCUSSION

Spectrum of anthrahydroquinone (AHQ)

Anthraquinone (AQ) is regarded as an insoluble compound in aqueous solutions; however, its reduced form, anthrahydroquinone (AHQ), yielded through AQ reaction with sodium hydrosulfite (a reducing agent), is soluble in water and gives a reddish color. Figure 2 shows the spectra of AHQ and a diluted black liquor from kraft pulping of loblolly pine. Similar to the spectrum of AHQ-S, as shown in our previous study [8], AHQ has distinguished spectral absorption characteristics in the visible range with two absorption peaks at wavelengths 416 and 505 nm, respectively. The absorption spectrum of a diluted black liquor (with a dilution factor of 1000), which is mainly contributed by the absorption of dissolved lignin in the liquor, covers the entire UV-visible range. As can be seen in the figure, the presence of dissolved lignin can interfere with spectroscopic determination of AHQ in black liquors.

Separating AQ from black liquor using a Nafion membrane

In a previous paper, we demonstrated that AQ-S (soluble) can penetrate through a Nafion membrane [8]. Its reduced form, AHQ-S, however, cannot pass through the membrane. Experiments were conducted using AQ kraft liquor as a donor in this study to examine the effectiveness of separating AQ from AHQ by the membrane. The same experimental apparatus shown in Figure 1 was used to conduct the experiment. The absorption of AHQ converted by the hydrosulfite in the carry stream from the AQ contained in the kraft liquor sample was measured. Then, hydrosulfite was also directly added into the donor sample to convert the AQ in the sample to AHQ to verify if AHQ could penetrate the membrane. It was observed that the measured absorption signal at 505 nm decreases rapidly after the addition of sodium hydrosulfite in the donor sample. No signal was detected at about 80 minutes into the reaction, indicating complete conversion of AQ to AHQ that cannot penetrate the membrane. Because the donor sample and the hydrosulfite are placed in an open container, the newly formed AHQ can be easily oxidized in air to form AQ. As soon as AQ was formed, absorption was observed again as shown in Fig. 3. The above experiments demonstrate that only dissolved AQ rather than AHQ can penetrate through the Nafion membrane.

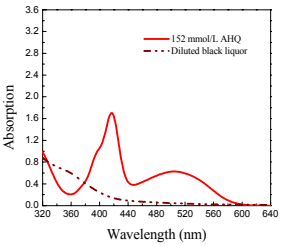

Fig. 2. Spectra of anthrahydroquinone and diluted black liquor.

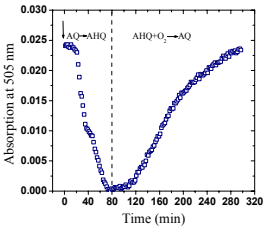

Fig. 3. Measured time-dependent absorption signal at 505 nm that show the passage of AQ not AHQ through the Nafion membrane.

In a previous study [8], we also found that the Nafion membrane can be used to separate AQ-S from large lignin molecules to effectively eliminate spectral interference from dissolved lignin with AHQ-S absorption for AQ-S determination. Based on the previous work [8] and the work by Danielsson and Chai [9, 10], it is feasible to use a Nafion membrane to effectively eliminate spectral interference from dissolved lignin for spectroscopic determination of AQ in pulping liquors. Figure 4 shows a spectrum of a kraft-AQ black liquor (without dilution) after membrane separation. Clearly, as indicated by a spectral absorption below 480 nm, the small lignin molecules can pass through the membrane. To verify that the absorption intensities at a

wavelength above 480 nm are from the AHQ yielded through the reaction of AQ in the donor stream with the sodium hydrosulfite in the carry stream, we subtracted the spectrum of the kraft-AQ black liquor from the absorption spectrum of an equivalent black liquor (obtained from kraft pulping under the same pulping conditions except without AQ addition) using membrane separation. As can be seen from the figure, the resultant spectral profile at a wavelength greater than 400 nm is very similar to that of the AHQ shown in Fig. 2. The results in Figure 4 also indicate that the membrane is very effective at eliminating spectral interference of dissolved lignin from AHQ at a wavelength range beyond 500 nm. Consequently, the absorption peak at 505 nm can be used for spectroscopic determination of AHQ and, therefore, dissolved AQ in black liquor, provided that sodium hydrosulfite does not absorb in a wavelength range greater than 400 nm as demonstrated in our previous study [8].

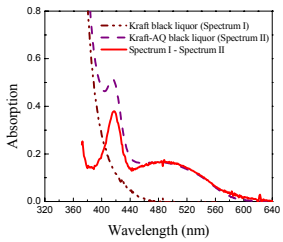

Fig. 4. Membrane separation of anthraquinones from kraft and kraft-AQ pulping liquors.

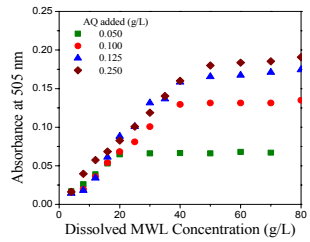

Fig. 5. The absorbance at 505 nm upon lignin addition. Four concentrations of AQ were chosen, and lignin solids were added to the respective solutions.

The solubility of AQ

AQ is generally regarded as an insoluble species in aqueous solutions. However, a limited amount of AQ was found to be soluble and detected by the spectrometer after its reaction with reducing agent sodium hydrosulfite, as shown in Fig. 4. We hypothesize that the dissolved lignin in black liquor is responsible for increasing the solubility of AQ. We conducted a detailed study on AQ solubility at 90°C to prove our hypothesis. Different amounts of alkaline wood lignin prepared from kraft pulping of softwood to linerboard grade pulps (MeadWestvaco Corp., SC, USA) were added into a set of four alkaline AQ aqueous solutions with a sodium hydroxide concentration of 1.5 mol/L. (The lignin can only be dissolved in alkaline solutions.) The solution was heated on a heating plate to a constant temperature of 90°C. Complete dissolution of the lignin was observed. The AQ concentration was fixed for a given AQ solution. The present spectroscopic method with the Nafion membrane interface described above was used to qualitatively determine the amount of AQ dissolved in the alkaline solution. The alkaline AQ solution was used as the donor solution. The dissolved AQ in the donor solution penetrated through the membrane and then reacted with the reducing agent sodium hydrosulfite to form AHQ. The AHQ was detected by the spectrophotometer. Figure 5 shows the measured AHQ absorption intensities at 505 nm in the four AQ solutions with AQ concentrations of 0.05, 0.10, 0.125, and 0.25 g/L, respectively, under various dissolved alkaline wood lignin concentrations. The results indicate that the absorption intensity at 505 nm linearly increases with a dissolved lignin concentration in the solution up to a lignin concentration of 50 g/L for the four AQ solutions tested. Furthermore, the experimental data points from the four tested AQ solutions fall onto a single line, indicting that AQ solubility in alkaline solutions increases linearly with an increase in the amount of dissolved lignin in the solution. Figure 5 also indicates that further increases in MWL concentration beyond 50 g/L have only a marginal effect on AQ solubility, which perhaps indicates that the solubility of AQ reaches its limit under the conditions tested. The break point for each curve in Fig. 5 can be regarded as the saturation point of AQ dissolution. The behavior of AQ dissolving in lignin solution might be explained by AQ's structural similarities to that of lignin, similarities which could increase AQ's solubility in aqueous lignin solutions. In the absence of dissolved lignin, the solubility of AQ in alkaline solution is very low (about 0.02 g/L), as shown in Fig. 5. The solubility of AQ in a dissolved lignin-enriched solution (50 g/L) was reached at approximately 0.14 g/L at 90°C.

We also studied the time-dependent AQ dissolution process. It was observed that the AQ dissolution process is very slow, even with the presence of dissolved lignin. It took about 45 minutes to achieve complete dissolution of 0.125 g of AQ in 1 L of alkaline solution at 90°C. Therefore, sufficient time should be taken to prepare calibration solutions to ensure that complete dissolution of AQ is achieved.

Calibration

A set of standard AQ solutions were prepared by adding different amounts of AQ powder (below the solubility limit of 0.14 g/L at 90°C) into an alkaline solution containing 50 g/L of dissolved MWL with an NaOH concentration of 1.5 mol/L. The solution was stirred for one hour on a heating plate to maintain the temperature at 90°C to ensure complete AQ dissolution. As discussed by Danielsson and Chai [9], the effect of sample matrix on the ability of species to penetrate the Nafion membrane is not significant if the ionic strength in the testing solution is higher than 1.2 mol/L. The ionic strength of pulping process liquor can easily meet the 1.2 mol/L ionic strength requirement. Therefore, actual pulping liquor was not needed as the base solution for preparing the standard AQ solution for calibration. Furthermore, some carbohydrates in the black liquor could convert a certain percentage of AQ into AHQ,

causing errors in calibration. Using the calibration procedure described in our previous study [8] for AQ-S measurements, a linear calibration equation was obtained in this study. Figure 6 shows a typical calibration equation of the system where only the data points with AQ concentrations below 0.14 g/L were used in linear regression.

Applications

Three kraft-AQ pulping processes of loblolly pine were conducted using a lab-scale bomb digester. Detailed descriptions of the pulping experiments can be found in our previous study [11]. Duplicate pulping experiments were conducted but terminated at different pulping times so that time-dependent information could be obtained. All spent pulping liquor was collected at the end of each pulping experiment. The dissolved AQ in the process liquor was determined using the present method. Figure 7 shows the results. A maximum concentration of AQ was detected in the early stage of pulping when the pulping temperature reached 170°C. As the process continues, the concentration of AQ in the cooking liquors decreases. However, more AQ was found in the cooking liquor for the process having an initial sulfidity of 10%. AQ consumption is higher in the process with higher initial sulfidities.

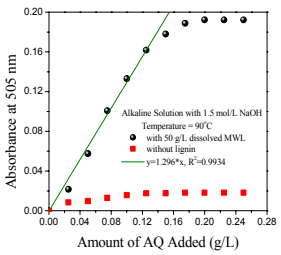

Fig. 6. The absorbance at 505 nm at different times when AQ was added to an alkaline lignin alkaline solution with a lignin concentration of 70g/L.

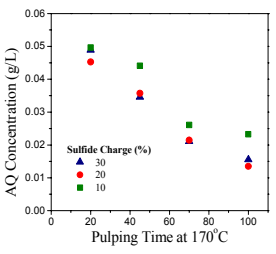

Fig. 7. The AQ concentrations in the cooking liquors withdrawn at different times from the pine kraft pulping process after the temperature reached 170°C.

CONCLUSIONS

This study reveals that AQ can be dissolved in dissolved lignin-enriched alkaline solutions. The solubility of AQ at 90°C in the solution is approximately 0.14 g/L with the presence of dissolved lignin greater than 40 g/L. The dissolution of AQ in lignin-enriched solution is a very slow process and takes about 45 minutes to reach its solubility limit. Based on the knowledge obtained from the AQ solubility study, calibration of AQ was achieved for spectroscopic determination of AQ in pulping process liquors using the technique developed previously for AQ-S analysis [8]. AQ concentrations in pulping process liquors of three kraft-AQ processes were determined. It was found that AQ concentration continuously decreases as pulping process proceeds. Furthermore, the dissolved AQ concentration at the end of the pulping process is highest in the final process liquor with the lowest initial sulfide charge of 10%.

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