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Vapor-Liquid Equilibrium of VOC's in Kraft Mill Streams

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EXECUTIVE SUMMARY

The emission of volatile organic compounds (VOC's) in pulp and paper mills has been an environmental concern. VOC content and the vapor-liquid phase equilibrium (VLE) of VOC's in mill streams are the two key factors that dictate VOC emissions. Unfortunately, few methods are available to quantify the VOC content in various mill streams because of the corrosive nature of most mill streams, such as black liquor, which prevents direct composition analysis using traditional analytical methods, for example, direct injection into gas chromatography (GC). Measurements of VOC VLE is also not trivial.

This study reports on the investigation of VOC content and VLE partitioning coefficients of methanol in mill streams based on vapor-liquid phase equilibrium of the species to be measured using a commercial headspace GC system. The methods are rapid, accurate, automated, and do not require calibration.

For the developed method for VOC contents measurement in solutions, experimental data showed excellent an agreement between the quantity measured and the amount known in several standard VOC-water mixture solutions. The liquid methanol contents measured in four black liquor samples using the present method also agree with our previous study using the method developed by NCASI. Measurements of VOC contents in various mill streams from two Georgia mills are conducted using the developed methods.

For the VLE partitioning coefficient measurement method developed in the present study, mathematical analysis and experimental data indicated that the present method has a very high precision. Measurements of methanol Henry's constants in six samples from four kraft mills and five samples collected from our laboratory batch pulping processes under known pulping conditions are conducted. These samples have a good representation of black liquors yielded from hardwood and softwood, kraft and soda pulping processes. We found that temperature and total solids content are the two major factors that affect the Henry's constant of methanol in black liquor samples. Linear regression analysis indicates that the methanol Henry's constant in black liquors increases exponentially with the inverse of temperature in Kelvin and decreases linearly with the total solids content.

Keywords: VOC; Henry's law; phase equilibrium, partitioning coefficient, headspace; GC; standard addition, black liquor, methanol, mill streams.

OBJECTIVES

The overall objective of this research project is to develop a thermodynamic database of vapor-liquid phase equilibrium for organic compounds (VOC's) in various kraft mill streams. The data can be used as inputs of mill VOC simulation computer models to predict VOC emissions when mill processes change. For the one year funding from The Georgia Consortium for Pulp and Paper Competitiveness, the specific objectives of the project are to:

1. Develop a measurement technique to quantify VOC contents in various mill streams,
2. Develop a method to determine VOC Henry's constants in various mill streams,
3. Validate the methods developed,
4. Conduct detailed studies of VOC contents in various mill streams, and
5. Develop empirical correlation for VOC Henry's constants in various mills.

DELIVERABLES

All the objectives have been met as discussed in this report that contains two parts: Part I measurement methods for the quantification of the contents and vapor-liquid phase partitioning of VOC's, and Part II vapor-liquid equilibrium partitioning of methanol in black liquors.

BACKGROUND

With the increasingly restrictive environmental regulations, maintaining environmentally sound and technologically competitive operations in pulp and paper mills is the key to the success of the U.S. pulp and paper industry. The new toxic and permit provisions of the 1990 amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. Many VOC's are now considered hazardous air pollutants (HAP's). Several studies on VOC emissions at Kraft mills have been conducted. Venketash et al. [1] reported a millwide VOC prediction using a process simulation technique. The U.S.-based National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted a series of studies on VOC emissions at Kraft mills. NCASI's studies indicated that the release of VOC's during mill operations is determined by several factors [2]: (1) the VOC content in mill streams, (2) the fundamental thermodynamic vapor-liquid phase equilibrium behavior of the VOC's in mill streams, (3) the mass transfer associated with specific mill processes, and (4) the mill operating conditions, such as wood species, pulping chemicals used, water reuse in operation, etc. Some of the factors pertain to unit operating conditions and specific mill processes such as mass transfer in a unit operation. It is very difficult to generalize all the specific situations. However, the thermodynamic behavior of the VOC's should not depend on the characteristics of specific unit operations. Current vapor-liquid equilibrium (VLE) data on mixtures of VOC's and water overpredict VOC release for mill operations as will be shown in this report. Therefore, it is important to be able to measure VOC content in mill streams and understand the thermodynamic behavior of vapor-liquid phase equilibrium.

It is not trivial to analyze samples from various mill streams using conventional direct analytical methods with delicate laboratory instruments through calibration because some of the mill streams are corrosive in nature. Gunshefki and Cloutier [3] developed a method to measure MeOH contents in black liquor. However, their method modifies the sample matrix through the addition of chemicals to precipitate the solids in weak black liquors. The method has several disadvantages: (1) the amount of chemicals added (mass ratio of chemical over black liquor = 30:1) significantly dilutes the VOC concentration in the sample and reduces the measurement accuracy; (2) the method is only suitable for the analysis of weak black liquors as the solid precipitation method may not be used for other mill streams; and (3) the method is tedious, time-consuming, and not applicable for on-line analysis.

There are many methods available to study vapor-liquid phase equilibrium. Mackay and Shiu [4] presented a comprehensive review of the common methods to measure Henry's constants and their respective merits and deficiencies. Turner et al. [5] and Sherman et al. [6] separately presented their own comprehensive reviews of various methods for vapor-liquid equilibrium (VLE) studies—along with detailed comparisons of VLE data of aqueous organic systems obtained using these methods. Sherman et al. [6] also presented application limits of various available methods for VLE studies. The headspace gas chromatographic (HSGC) method gives a direct quantitative analysis of the vapor of a liquid sample matrix and therefore is very suitable for VLE studies. Much research on vapor-liquid phase equilibrium has been conducted using headspace GC systems [7-10]. The traditional HSGC method [7-10] for vapor-liquid equilibrium study requires quantitative determination of the equilibrium solute concentration both in the vapor and in the liquid phase through direct measurements using error-producing calibration procedures. To obtain experimental simplicity and high accuracy for practical applications, automated indirect HSGC methods will be desirable. Unfortunately, most of the existing indirect HSGC methods have practical difficulties to implement [11]. In this study, we report on the development of indirect methods for rapid, automated, and precise determination of the contents and the vapor-liquid phase equilibrium partitioning of VOC's in mill streams using a commercial headspace gas chromatography system.

PART I: MEASUREMENT METHODS

METHODOLOGY

Quantification of VOC Contents in Kraft Mill Streams

We developed an indirect measurement method for the quantification of VOC contents in liquids by headspace gas chromatography based on the thermodynamic vapor-liquid phase equilibrium. The method is schematically described in Fig. 1. We use two sample vials both filled with the same amount of sample solution. Then, we add a known small amount of concentrated solution into one of the vials. The volume of the solution added is very small compared with the volume of the original solution and therefore can be neglected. We conduct headspace GC analysis of each sample after a phase equilibrium was established within each vial. We can assume that the solute concentrations in these two sample vials are still very low or the solute concentrations are under infinite dilution, which is valid for most VOC's in mill streams even after the addition. Therefore, the solute VLE partitioning coefficients in these two vials are equal to the Henry's constant of the solute under consideration, which connects the two independent headspace measurements to determine the solute content in the original sample. The following is the derivation of the present HSGC method.

When a sample solution of volume V_l^0 with an unknown solute concentration of C_0 is introduced into a closed vial, the amount of solutes in the vapor at vapor-liquid phase equilibrium state can be described as:

$$n_1 = C_0 V_l^0 - \alpha C_1 V_l^0 = C_g^1 V_g^0, \tag{1}$$

where C_1 and C_g^1 are the solute concentrations in the liquid and vapor under equilibrium, respectively, a is the solution volume expansion factor due to temperature from state 0 to state 1, and V_g^0 is the headspace volume.

If a certain volume V_s of concentrated solution with a known solute concentration of C_s is added into this system, the existing equilibrium will be disturbed and a new equilibration state will be established after a while. The amount of solute in the vapor phase under the new equilibration state can be expressed as:

$$n_2 = C_0 V_l^0 + C_s V_s - \alpha C_2 V_l^0 = C_g^2 V_g^0, \tag{2}$$

where we assume that the total volume of the solution keeps the same as the volume of the concentrated solution added is negligible compared with the initial volume of the solution, i.e., $V_l^0 >> V_s$.

From Eqns. (1) and (2), we can obtain the concentrations of the solute in the liquid phase under the two equilibrium states,

$$\frac{C_1}{C_g^1} = \frac{C_0 V_l^0 - C_g^1 V_g^0}{\alpha V_l^0 C_g^1}, \text{ and} \tag{3}$$

$$\frac{C_2}{C_g^2} = \frac{C_0 V_l^0 + C_s V_s - C_g^2 V_g^0}{\alpha V_l^0 C_g^2}. \tag{4}$$

By assuming that the solute is infinite dilution in both vials, we can use the Henry's Law to connect Eqns. (3) and (4) as follows,

$$H_c = \frac{C_g^1}{C_1} = \frac{C_g^2}{C_2}. \tag{5}$$

Then, the initial solute concentration in the sample solution can be calculated from Eqns. (3)-(5) as,

$$C_0 = \frac{C_s V_s}{(C_g^2 / C_g^1 - 1)V_l^0}, \tag{6}$$

where, the ratio of the solute concentration in the vapor C_g^2 / C_g^1 is proportional to the ratio r_A of the peak areas *A1* and *A2* of the solute detected from the two HSGC measurements. We can rewrite Eqn. (6) as,

$$C_0 = \frac{C_s V_s}{(A_2 / A_1 - 1)V_l^0} = \frac{C_s V_s}{(r_A - 1)V_l^0}. \tag{7}$$

Eqn. (7) can be used to determine the VOC contents in various mill streams. The advantage of the present method is that it does not require calibration.

Determination of VOC Henry's Constants in Kraft Mill Streams

The VOC's in mill streams are small quantities and can be treated under infinite dilution. Therefore, the Henry's law in Eqn. (5) best describes the VLE partitioning of VOC's in Kraft mill streams. Determination of Henry's constants is the key to understanding the thermodynamic VLE behavior of VOC's in mill streams.

The indirect GSGC method we developed uses two sample vials both filled with the same sample solution but with a significant variation in volume as schematically shown in Fig. 2. We conducted a headspace analysis of each sample after a phase equilibrium was established within each vial. The solute of the two systems has the same VLE Henry's constant as the two systems are identical, which can be used to connect the two independent headspace measurements to determine the solute concentration in the original sample. The derivation of the present method is very simple. We can express the total moles M of the solute under equilibrium in the two vials using Eqns. (1) and (5),

$$M_1 = C_l^0 V_l^1 = C_l^1 V_l^1 + C_g^1 V_g^1 = C_g^1\left[\left(V_l^1 / H_c\right) + V_g^1\right], \tag{8}$$

$$M_2 = C_l^0 V_l^2 = C_l^2 V_l^2 + C_g^2 V_g^2 = C_g^2\left[\left(V_l^2 / H_c\right) + V_g^2\right], \tag{9}$$

where C_g is the concentration of solute in the vapor phase, and V_g is the vapor volume in the vial.

The dimensionless Henry's constant *Hc* can be derived from Eqns. (8) and (9),

$$H_c = \frac{V_l^1\left(1 - C_g^1 / C_g^2\right)}{C_g^1 / C_g^2\left(V_t - V_l^1\right) - V_l^1 / V_l^2\left(V_t - V_l^2\right)}. \tag{10}$$

The solute concentration in the vapor phase C_g is proportional to the peak area from GC measurement. Thus, we have

$$C_g^1 / C_g^2 = A_1 / A_2. \tag{11}$$

Substituting Eqn. (11) into (10), the dimensionless Henry's constant *Hc* can be determined

$$H_c = \frac{V_l^1\left(1 - A_1 / A_2\right)}{A_1 / A_2\left(V_t - V_l^1\right) - V_l^1 / V_l^2\left(V_t - V_l^2\right)} = \frac{V_l^1(1 - r)}{r\left(V_t - V_l^1\right) - x\left(V_t - V_l^2\right)}, \tag{12}$$

where $r = A_1 / A_2$, and $x = V_l^1 / V_l^2$.

The approach that we took to derive the present indirect HSGC method is very similar to that of the Equilibrium Partitioning in Closed Systems (EPICS) method developed by Lincoff and Gossett [12]. However, the present method differs from the EPICS method significantly. It overcomes all the shortcomings of the EPICS method and has the following advantages: (1) it does not require that one know the solute concentration to determine the VLE partitioning coefficient of the solution, which has significant importance for any industrial, environmental, and practical application; (2) it does not need to assume that the solute is under infinite dilution; therefore, the method is not only applicable to measure the Henry's constant, but also to measure the partitioning coefficient *K* of a solute in any solution; and (3) it has high precision even for determining a very small Henry's constant (*Hc<0.1*).

EXPERIMENTAL

Chemicals

We used methanol, methyl ethyl ketone (MEK), and acetone to mix with deionized water to make standard solutions of methanol-water, MEK-water, and acetone-water to validate the present methods.

We conducted measurements of VOC contents and VLE partitioning in various mill streams from four separate Kraft mills (Mills A, B, C, and D) to demonstrate the applicability of the present methods.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatography (Hewlett-Packard). A detailed description and the basic operation principles of the headspace sampler can be found in Dhasmana et al. [13]. GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow (He): 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: 25 minutes gentle shaking for equilibration of the sample, vial pressurization time: 0.2 min, sample loop fill time: 1.0 min., and loop equilibration time: 0.05 min.

Temperature of the Headspace Sampler

For VOC content measurements, we set the temperature of the headspace sampler at 70°C to avoid water vaporization and obtain a good sensitivity as sufficient methanol will be present in the vapor phase at this temperature. The temperature was varied from 45-80°C for vapor-liquid partitioning measurements, close to the range of operating temperatures of most mill streams.

RESULTS AND DISCUSSION

VOC Content Measurements

Technique Validation

The experimental technique is validated using a set of standard VOC-water (methanol-water, MEK-water, and acetone-water) solutions with known concentrations. The present method measures the VOC concentration of the standard solutions according to Eqn. (7). The ranges of the concentrations of these three standard solutions are 100-2000, 10-100, and 1-10 ppm, respectively. The combination of these three concentration ranges covers trace species concentration over three orders of magnitude within the infinite dilution assumption limit. The comparison between the standard and the measured data is excellent. A perfect correlation between the standard and the measured is shown in Fig. 3. The repeatability of the method was demonstrated by using a standard methanol-water solution (methanol concentration = 800 ppm). A relative standard deviation of measured liquid methanol content is about 2.0% for the five measurements conducted, indicating that the repeatability of the technique is excellent.

Measurements of the VOC content in black liquor samples is very difficult because it has a complex composition such as dissolved solids and it is corrosive. We were able to separate various volatile species in black liquor using the GC system and the conditions stated previously [13]. We measured methanol contents in four black liquor samples from Mills A and B using the present method. Our data agree with the results obtained using the NCASI method [3] as shown in Table 1, indicating the applicability of the present method.

Measurements in Various Mill Streams

We measured methanol and MEK contents in various Kraft mill streams from Mill C using the present method. The results are shown in Table II. Mill C is a unbleached Kraft paper mill. For this particular mill, the data indicate: (1) the weak wash stream in the recovery cycle does not contain methanol; (2) the shower water and filtrate streams in the washers contain a significant amount of methanol; (3) the blow tank condensate stream from the digester also has a high content of methanol as indicated by the measurement of the sample from the hot water tank; (4) the white water from the paper-machine head tank for the present unbleached mill contains some methanol; (5) weak black liquor has a significant amount of methanol; and (6) MEK concentrations in various streams are in the order of a several hundred of ppb, and they do not have a direct correlation with the concentrations of methanol. The measured methanol contents in various streams are reasonable with practical knowledge. Similar conclusions can be drawn from the measurements of VOC concentrations of various streams in another unbleached Mill D as shown in Table III . The absolute concentrations of VOC's in mill streams depend on various factors such as water dilution, mill operating conditions, and VOC formation during pulping.

Henry's Constant Measurements

Technique Validation

We found from mathematical precision analysis [11] that the present method can be very accurate by properly choosing the two key experimental parameters, i.e., the solution volume ratio x and the volume of the sample V_l^1 or V_l^2. We applied the present method to measure the methanol Henry's constant in a methanol-water mixture. The Henry's constant of methanol in water under a temperature range of 45-80°C is very small (<0.005); therefore, it is a good precision test of the present method. The data obtained using the present indirect HSGC method show excellent agreement with those in the literature [14-18] as shown in Fig. 4. A linear regression analysis shows that the logarithm of all the data fit to a straight line with the inverse of temperature very well. The linear relationship agrees with thermodynamic theory, i.e., the Henry's constant is related to the partial molar excess enthalpy, which is a weak function of temperature. The data demonstrate the validity and the accuracy of the present method.

Measurements in Black Liquors

We applied the present method to measure Henry's constant of methanol in black liquor. Both softwood and hardwood black liquor samples from Mill B were used in this study. Fig. 5 shows the effect of temperature on the methanol Henry's constant in black liquors along with the data obtained in the methanol-water mixture. The results indicate that the logarithm of Henry's constant in the two black liquor samples decreases linearly with the inverse of temperature. It appears that the slops of the three sets of data presented are the same; the differences are within the error margin. However, the variation in the measured Henry's constant among these three types of samples is very significant. It is obvious that there is a significant variation in the composition, ionic strength, solid contents, etc., among these samples, which may cause the large variation in the Henry's constant.

CONCLUSIONS

The present study reported on the development of indirect methods for measuring VOC concentration and vapor-liquid phase equilibrium partitioning coefficients in mill streams using a commercial headspace gas chromatography system. The methods are rapid, automated, and accurate, and do not require calibration and modification of the sample matrix. The method can also be applied to various industrial and environmental streams. Preliminary measurements of VOC content and Henry's constant of methanol in Kraft mill streams using the methods developed were conducted. Significant variation in the measured data was observed, indicating the complicated nature of the behaviors of VOC in Kraft mill streams.

PART II: VLE BEHAVIORS OF METHANOL IN BLACK LIQUORS

INTRODUCTION

The vapor-liquid phase equilibrium partitioning is one of the key factors that dictates VOC emission at Kraft mills. The VLE partitioning approach has been used in computer models to describe the VOC emission in various mill processes [1, 19]. This type of computer model can provide a predictive tool for mills to qualitatively determine VOC emissions when processes change. Unfortunately, few studies have been conducted on the VLE behavior of VOC's in mill streams. The understanding of the subject is very limited. A previous study by NCASI [20] indicated that using existing VLE data obtained in VOC-water mixtures overpredict VOC emission. Therefore, it is important to develop a VLE database of VOC's in Kraft mill streams that can be used as an input of computer models for accurate prediction of VOC emissions.

As we discussed previously, the VOC contents in various Kraft mill streams are very low; therefore, Henry's Law best describes the VLE partitioning behavior of VOC's. Because methanol is the major species that accounts for more than 90% of the VOC emission in Kraft mills [2] and black liquor is one of the most difficult stream to analysis, we focus our research on the measurements of Henry's constant of methanol in various black liquor samples using the method developed. We try to understand the major factors that affect the VLE partitioning of methanol in various black liquor samples. Black liquor has a very complex composition, which contains dissolved lignin and other humic material; therefore, the understanding of the effects of various composition parameters on the VLE partitioning behavior of methanol in black liquor is not trivial and deserves detailed study in the future.

EXPERIMENTAL

Black Liquors

Weak black liquor samples collected during various pulping stages of five pulping processes in our laboratory were used to understand the effect of pulping processes on the Henry's constant of methanol in black liquors. These black liquor samples are obtained under known pulping conditions such as wood species, sulfidity, active alkali concentration, etc. Six other black liquor samples from four kraft mills (mills A, B, C, and D) were also used for the present study. These samples have a good representation of black liquors yielded from different wood species and pulping processes.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard). The GC conditions were described in Part I of this study. The basic principles of the headspace sampler can be found in Chai et al. [13]. The measurement procedure was as follows: pipette 0.05 and 10 mL of sample solution into two 20 mL vials, then close the vials and put into the oven of the Headspace Sampler. The vial is gently shaken for a certain length of time until VLE phase equilibrium within the vial is achieved according to our previous study [11]. The vial is then pressurized by helium to create a pressure head to fill the sample loop. The vapor in the sample loop is finally injected into the GC column and analyzed. The peak areas of the GC analysis were recorded by a personal computer for the calculation of Henry's constant using Eqn. (12) in Part I of this study.

RESULTS AND DISCUSIONS

The total solids content of all the black liquors used in this study is below 20%. Therefore, we treat them as aqueous solutions, which is a good assumption for weak black liquors in most mill processes except in evaporators. Black liquor has a very complex composition, which contains both inorganic and organic species. For volatile organic compounds, methanol is a dominating species in black liquors; however, in sulfide-involved kraft pulping process, an organic sulfur compound, dimethyl sulfide (DMS), and α-pinene in the softwood pulping are also significant. The effects of multicomponents on methanol VLE partition are very complicated. In this study, we only examine the effects of several important parameters, *i.e.,* temperature, ionic strength, and solids content, on the Henry's constant of methanol in black liquors. We leave the work of understanding the effects of various composition parameters on methanol Henry's constant in black liquor for future investigations.

Measurement Uncertainty

Precision analysis of the present measurement method [11] indicated that the potential measurement error of the present method was less than 10% for the experimental parameters used. Measurement uncertainty can occur in applying the present method to black liquor samples due to the inhomogeneous nature of black liquors. It is difficult to obtain uniform and representative samples during experiments. We determined the actual experimental uncertainty by analyzing the Henry's constants of methanol in the soda hardwood liquor obtained in our laboratory from 11 replica measurements. We found the maximum error for single measurement is about 15% as shown in Fig. 6. However, the relative standard deviation was 8.8%, within the error margin from our precision analysis [11]. We conducted triplicate experiments and averaged the measurements; therefore, the actual measurement uncertainty of the data presented in the paper is less than 8.8%.

Effect of Temperature

From basic thermodynamics, we know that the VLE partitioning behavior of any solute is strongly dependent on temperature. The operating temperature of weak black liquor in Kraft mills varies significantly. We measured the Henry's constants of five black liquors from four different kraft mills in a temperature range of 40-70°C. Our measurement results indicate that the Henry's constant of methanol in all the black liquors examined increases exponentially with temperature. We found that the Logarithm of Henry's constant of methanol in all the black liquors fits to a linear line with the inverse of temperature in Kelvin very well as shown in Fig. 7. This linear relationship in Eqn. (1) agrees with the basic thermodynamic theory very well, i.e, the Henry's constant is related to the partial molar excess enthalpy, which is a function of temperature.

For comparison purposes, we also plotted the Henry's constants of methanol in a water mixture in Fig. 7. The results show that the overall slope of the data of all the five black liquor samples is very close to the slope of the methanol-water mixture data. Because of the limited data points in each individual data set of the black liquor samples and the data scattering caused by the measurement uncertainty, linear regression analysis shows that there are some variations among the slopes of each individual data set as listed in Table IV. The slopes of the data of the black liquor samples are slightly lower than that of the methanol-water mixture solution. However, the relative standard deviation of the slopes of all the six data sets is only 15%. More data and black liquor samples are required to further validate this argument.

$$Log_{10}(H_c) = \frac{a}{T} + b \qquad (1)$$

Figure 7 shows there is a significant variation in the intercepts among the linear lines. The variations in the compositions of the black liquors such as the solids contents, the wood species, the pulping conditions, and other parameters could contribute to the differences in the Henry's constants. The data also show that the Henry's constants of methanol in most of the black liquor samples are smaller than those in the methanol-water mixture under the same temperature. This behavior can be explained as due to the multicomposition of black liquors, in particular the dissolved solids, which could have a strong affinity to organic compound molecules [21]. The results in Fig. 7 indicate that using the Henry's constants of methanol in water mixture for VOC computer models could overpredict mill VOC emissions.

Effect of Ionic Strength

Black liquor contains a large quantity lot of inorganic salts. The inorganic salts cause a variation of ionic strength among various black liquors. Basic thermodynamic principles indicate that ionic strength has an adverse effect on the solubility of most solutes. Therefore, it is important to understand the effect of ionic strength on the methanol Henry's constant. We added different amounts of potassium chloride into several methanol-water mixtures to obtain the solutions with different ionic strengths. We then measured the methanol Henry's constants in these solutions. We found that the Henry's constant increases with the increase of ionic strength as shown in Fig. 8. We analyzed the sodium and potassium contents in all of the five liquors from mills A, B, and C and found that the ionic strength calculated based on the measured sodium and potassium varies from 0.89-1.5 mol/L. The variation of ionic strength among these five liquors only accounts for 10% of the variation in Henry's constant according to Fig. 8, indicating that ionic strength is not a major factor that contributes to the significant variation of Henry's constant in the different black liquors shown in Fig. 7.

Effect of pH

We took the similar approach to study the effect of pH on the Henry's constant of methanol. A different amount of sodium hydroxide was added into several methanol-water mixtures. Measurements show that the effect of pH on the measured methanol constant is not significant after correction of ionic strength.

Effect of Total Solids Content

To explain the significant variation in Henry's constant in different black liquors as shown in Fig. 7, we measured methanol Henry's constant in 11 black liquor samples at three different temperatures. Six samples were obtained from four kraft mills of unknown pulping conditions, and the other five samples were collected from our laboratory under known pulping conditions. These 11 samples represent black liquors yielded from hardwood and softwood, kraft and soda pulping processes. We found from our measurements that the methanol Henry's constants in these black liquors correlate with the total solids content well, even though the black liquors are completely different in terms of wood species, pulping conditions, etc. As shown in Fig. 9, the Henry's constant of methanol decreases linearly with the increase of solids content in the sample. As we discussed previously, the measurement errors of our experiments are less than 8.8% with triplicate averaging; therefore, the scattering of the data in Fig. 9 is partly due to measurement uncertainty and partly due to the real variation in Henry's constant caused by the variation in the composition matrix of black liquors and other parameters such as ionic strength that affect Henry's constant.

Linear regression analysis indicates that there is not much difference among the slopes of the three sets of data presented in Fig. 9 with the consideration of the data scattering. We use the following equation to express this relation,

$$H_c = cS + d, \qquad (2)$$

where S is the total solids content of the liquor. Constants *c* and *d* are listed in Table II for the plots shown in Fig. 9. The standard deviation of the three slopes listed in Table II is less than 15%.

By combining Eqns. (1) and (2), we can correlate methanol Henry's constant in black liquors using the following equation,

$$H_c = m \cdot \exp(\frac{A}{T}) + B \cdot S + C. \qquad (3)$$

More data are required for linear regression analysis to obtain good empirical correlation of Henry's constant of methanol in various black liquors.

Several significant VOC's such as α-pinene from softwood and sulfur compounds from kraft cooking will not be formed in a soda hardwood pulping process; therefore, the effect of these major species can be eliminated in the study of the methanol Henry's constant in soda hardwood black liquors. To obtain a better understanding of the effect of total solids content on methanol Henry's constant, we measured Henry's constants of several black liquor samples collected from a soda pulping process of a hardwood at various pulping stages in our laboratory. The total solids content in the cooking liquors included both inorganic and organic compounds. The inorganic chemicals were mainly alkali and various sodium and potassium salts. Their effects on methanol Henry's constant should be similar to those of potassium chloride as shown in Fig. 8. The chemical in the starting cooking liquor was sodium hydroxide that was consumed to form other salts during pulping. The total solids content increase in the process was mainly caused by dissolved lignin from wood chips. As shown in Fig. 10, the methanol Henry's constant decreases linearly with time (or solids content as shown) as the pulping process proceeds. It should be clarified that the methanol Henry's constants shown in Fig. 10 are all measured at a liquor temperature of 70°C. Fig. 10 indicates that the methanol Henry's constant in black liquors decreases with the increase of dissolved lignin in the liquor. The data scatter is mainly due to experimental uncertainty and nonrepresentative sample collection in the experiments. The effect of dissolved lignin, mainly humic materials, on methanol Henry's constant is rather complicated, and the understanding on the subject is very limited [21]. It is unclear whether the decrease of Henry's constant is very slow when the solids content is very low. Further study on the subject is required.

SUMMARY

We conducted measurements of Henry's constant of methanol in various black liquors using the HSGC method that we developed. The results indicate that the Henry's constant of methanol in black liquor is mainly affected by temperature and the total solids content. Linear regression analysis indicates that the methanol Henry's constant in black liquors increases exponentially with the inverse of temperature in Kelvin and decreases linearly with the total solids content. More experimental data are required to better correlate Henry's constant of methanol in various black liquors with major parameters such as temperature and solids content.

REFERENCES

1. Venketesh, V., Lapp, W., and Parr, J., 1996 TAPPI International Environmental Conference and Exhibits 31 (1996).
2. Jain, A., TAPPI Minimum Effluent Mills Symposium (1996).
3. Gunshefki, M. and Cloutier, S., NCASI Technical Memo (1994).
4. Mackay, D. and Shiu, W.Y., J. Phys. Chem. Ref. Data, 10 (1981) 1175.
5. Turner, L.H., Chiew, Y.C., Ahlert, R.C., and Kosson, D.S., AIChE J., 42 (1996) 1772.
6. Sherman, S.R., Trampe, D.B., Bush, D.M., Schiller, M., Eckert, C.A., Dallas, A.J., Li, J., and Carr, P.W., Ind. Eng. Chem. Res., 35 (1996) 1044.
7. Ioffe, B.V. and Vitenbery, A.G., "Head-Space Analysis and Related Methods in Gas Chromatography," John Wiley & Sons, Inc., New York, (1984).
8. Hussam, A. and Carr, P.W., Anal. Chem. 57:793 (1985).
9. Kolb, B., Welter, C., and Bichler, C., Chromatographia 34:235 (1992).
10. Jones, W., Egoville, M.J., Strolle, E.O., and Dellamonien, E.S., J. Chromatogr. 455 (1988) 45.
11. Chai, X.-S. and Zhu, J.Y., (1997), submitted to J. Chromatogr. A.
12. Lincoff, A.H. and Gossett, J.M., In Gas Transfer at Water Surfaces, Brutsaert, W. and Jirka, G.H., Eds. Reidel: Dordrecht, Holland, p.17, (1984).
13. Chai, X.-S., Dhasmana, B., and Zhu, J.Y., (1997), accepted for publication by J. Pulp & Paper Sci.
14. Hofstee, M.T., Kwantes, A., and Rijnders, C.W.A., Symp. Dist. Brighton, 105 (1960).
15. Pividal, K.A., Birtigh, A., and Sandler, S.I., J. Chem. Eng. Data, 37 (1992) 484.
16. Dallas, A.J., Ph.D. Dissertation, University of Minnesota, Minneapolis, MN (1993).
17. Kooner, Z.S., Putela, R.C., and Fenby, D.V., Aust. J. Chem., 33 (1980) 9.
18. Lebert, A. and Richon, D.J., J. Agric. Food Chem. 32 (1984) 1156.
19. Gu, Y., Edwards, L., Haynes, J., and Euhus, L., Application of Modular Computer Simulation to Aid Development of Pulp and Paper Mill Closure Technology: VOC Prediction. Submitted to Tappi J., (1997).
20. NCASI, Technical Bulletin No. 678, (1994).
21. Anderson, M.A., Environ. Sci. Tech., 26:2186 (1992).

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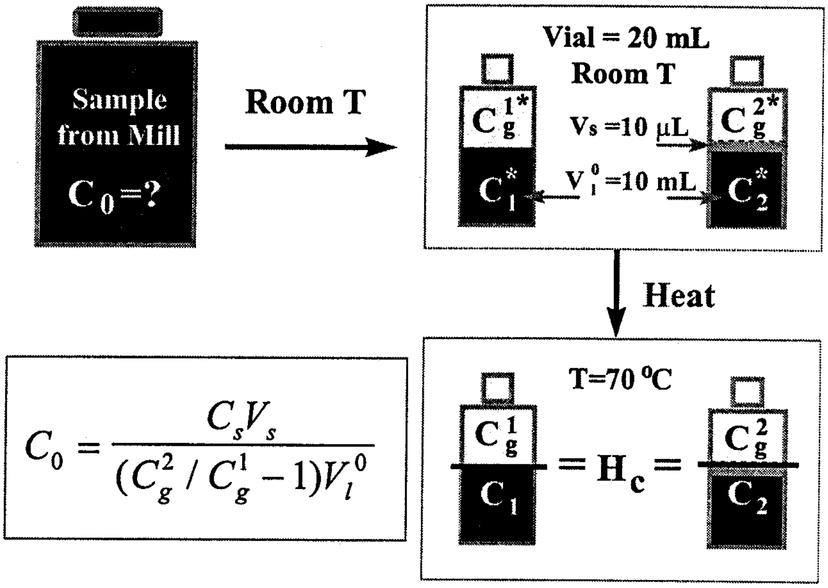

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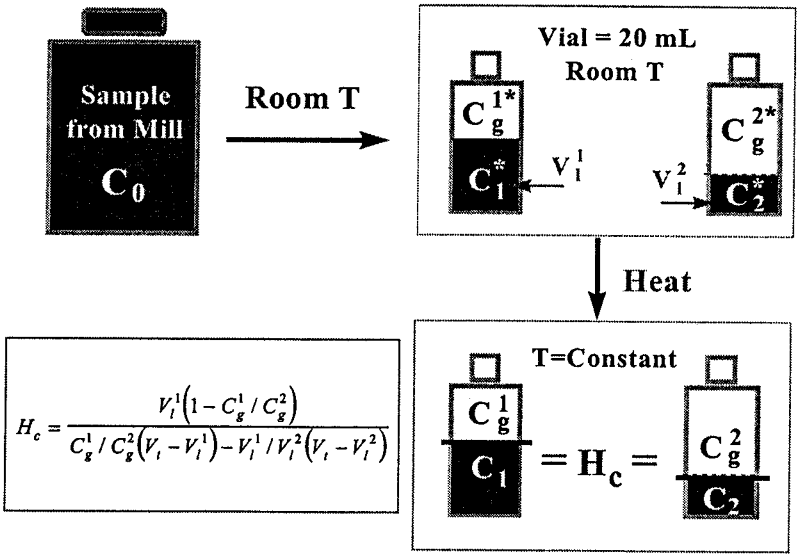

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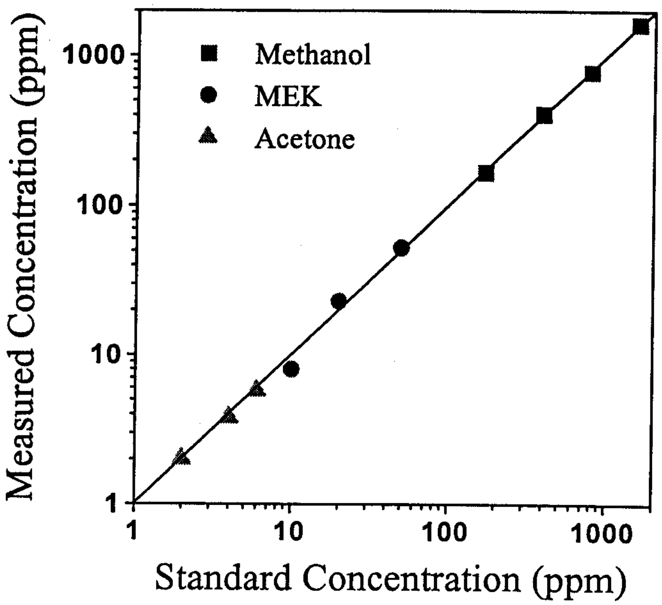

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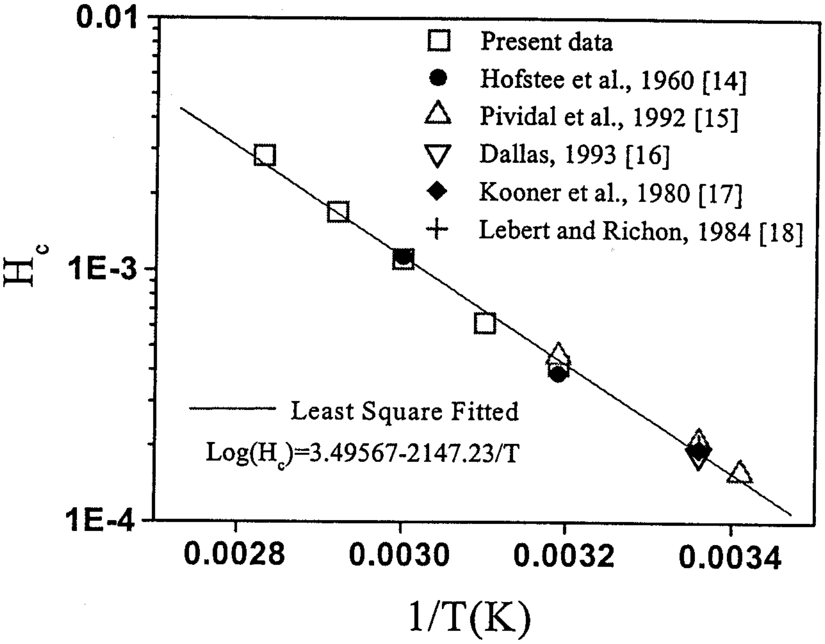

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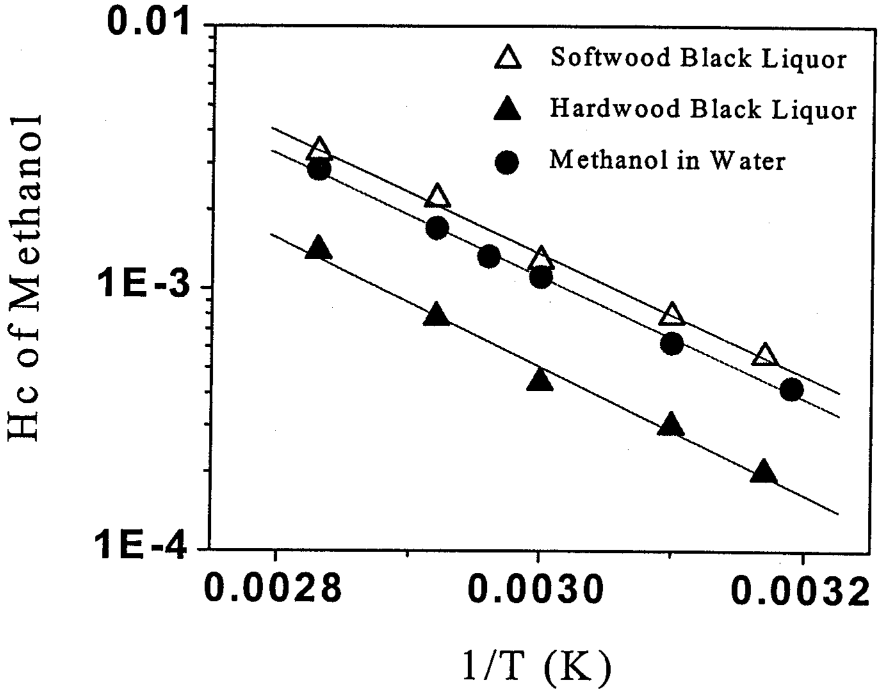

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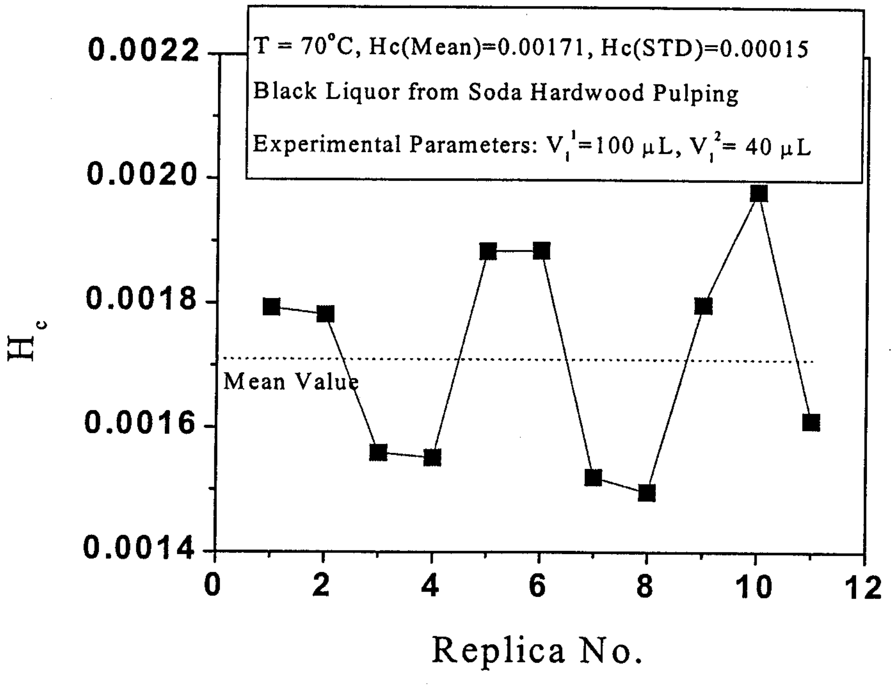

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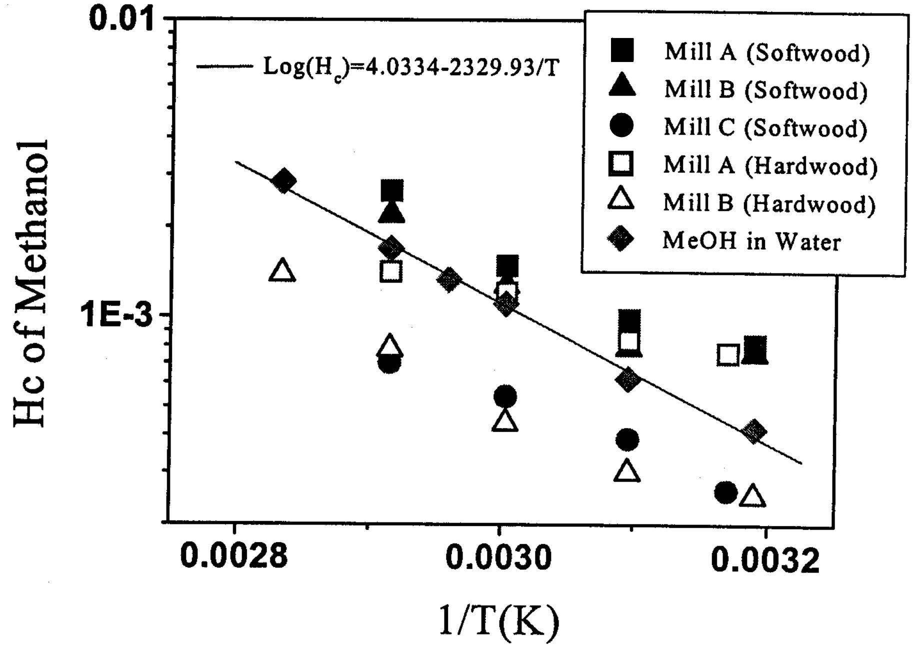

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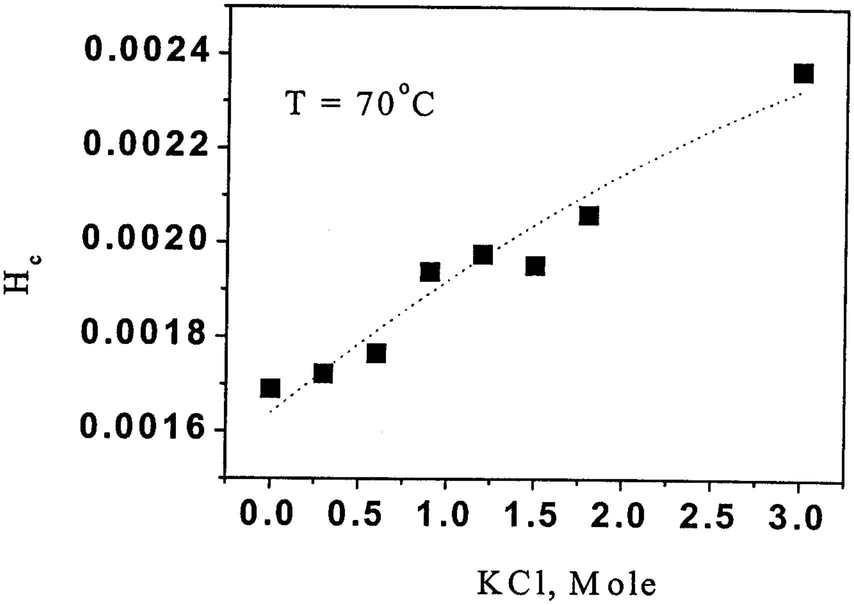

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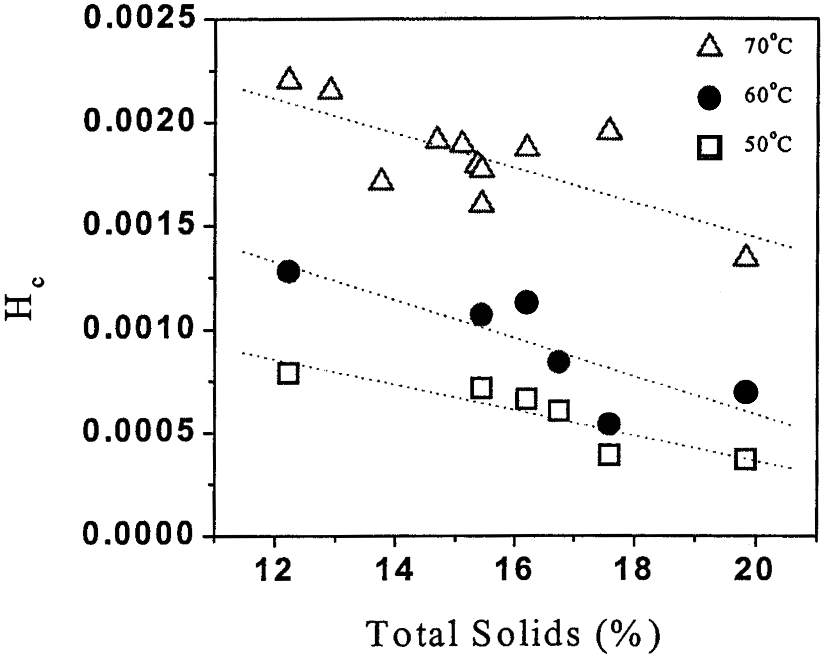

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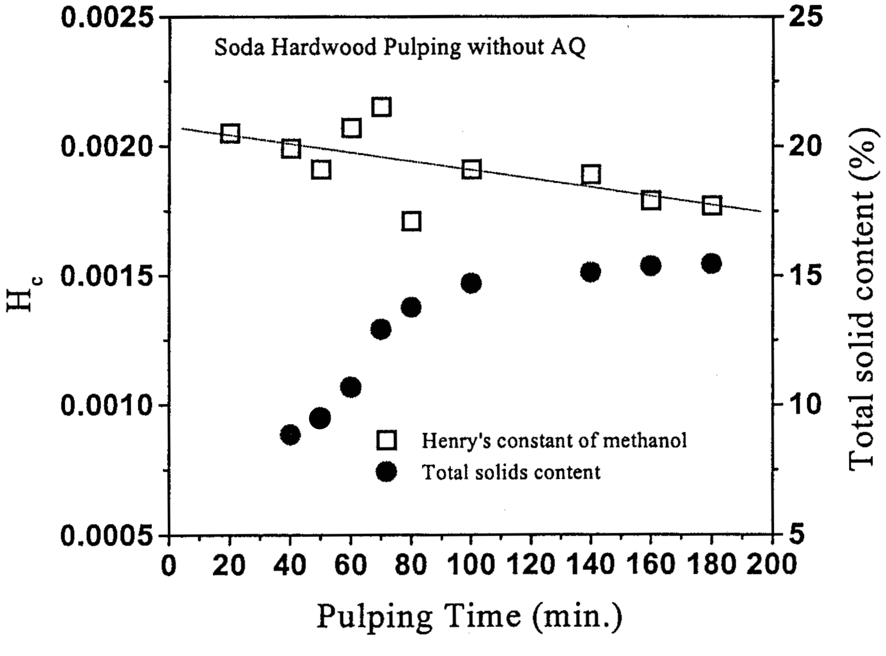

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Table I. Comparisons of measured liquid methanol content in four black liquors using the NCASI method and the present method.

SAMPLE	**Solids Content (%)**	**Methanol Concentration (ppm)**		
		NCASI Method	Present Method	**Difference (%)**
Softwood, Mill A	15.2	775	736	5.0
Hardwood, Mill A	17.1	961	906	5.7
Softwood, Mill B	11.5	434	419	3.5
Hardwood, Mill B	10.8	527	560	-6.3

Table II. Methanol and MEK contents measured in various streams from Mill C.

Sample Number	**Sample Location Description**	**Methanol (ppm)**	**MEK (ppb)**
1	weak wash liquor from recovery cycle	<1	74.5
2	white water from paper-machine head tank	40	0
3	pulp wash shower water first stage digester (D1)	277	165
4	filtrated stream from first washing stage (D1)	251	433
5	filtrated stream from second washing stage (D1)	238	316
6	filtrated stream from first washing stage (D2)	201	583
7	filtrated stream from second washing stage (D2)	172	481
8	condensated stream of blow tank steam in hot water tank	315	251
9	weak black liquor to evaporator	272	307

Table III. VOC contents measured in various streams from Mill D.

Sample Location Description	Label	MeOH	Acetone	MEK
		(ppm)	(ppb)	(ppb)
1st stage showers, 2nd stage filtrate	No. 1 Washer	209.5	494	406
	No. 2 Washer	275.0	484	394
2nd stage showers, 1st stage filtrate	No. 1 Washer	149.8	980	439
	No. 2 Washer	312.7	852	511
3rd stage showers	No. 1 Washer	122.6	683	452
	No. 2 Washer	203.8	715	526
side combined condensate (blow recovery)	No. 1 Washer	178.6	1327	592
	No. 2 Washer	382.6	1113	774
1st stage filtrate	No. 2 Washer	349.0	520	270
3rd stage filtrate	No. 1 Washer	332.2	930	564
combined weak black liquor to recovery		292.4	670	315
evaporator seal tank condensate	No. 2 (M24-0542)	93.1	762	665
	No. 2 (24-0529)	673.1	4138	425
evaporator clean condensate	No. 3	2.0	-	31
	No. 3 (24-0509)	1.7	-	231
evaporator	No. 2	27.1	-	218
evaporator seal tank	No. 1 (M24-0027)	3954.4	11	2706
combined condensate of hotwell	No. 3	659.1	16067	7826
paper-machine condensate	No. 1	3.3	-	59
	No. 2 & No. 3	3.5	-	124
top headbox	No. 1	57.4	323	108
	No. 2	55.3	260	129
base headbox	No. 1	88.8	433	167
	No. 2	64.9	315	158
headbox	No. 3	46.8	-	-
wire pit	No. 1	86.5	375	141
	No. 2	91.8	508	129
	No. 3	90.9	-	-
water reclaim sump	No. 1	13.0	192	62
vacuum dump	No. 2	20.6	-	-
side hill screen drain off	No. 3	65.7	-	-

Table IV: List of fitting parameters of Eqn. (1) for various samples.

Sample	Intercept: b	Slope: a
Mill A, Softwood	2.8356	-1871.83
Mill B, Softwood	2.3504	-1735.11
Mill C, Softwood	1.6990	-1658.92
Mill A, Hardwood	0.4845	-1140.67
Mill B, Hardwood	3.0757	-2116.45
Methanol-Water Mixture*	3.4957	-2147.23
MEAN	-	**-1778.37**
STD	-	**266.8**
RELATIVE STD	-	**15.0%**

* The values are from Part I of this study

Table V: List of fitting parameters of Eqn. (2) at different temperatures.

Temperature	Intercept: d	Slope: cxE10^5
50°C	0.0016	-6.1765
60°C	0.0024	-9.2325
70°C	0.0031	-8.3825
MEAN	-	**-7.9305**
STD	-	**1.1693**
RELATIVE STD	-	**14.7%**