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The Vapor-Liquid Equilibrium of Methanol in Black Liquors

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# THE VAPOR-LIQUID EQUILIBRIUM OF METHANOL IN BLACK LIQUORS

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## ABSTRACT

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We applied an indirect headspace gas chromatographic method to study the vapor-liquid phase equilibrium of methanol in weak black liquors to obtain empirical correlation of Henry's constant of methanol for emission predictions in kraft mills. We used six samples from four kraft mills and five samples collected from our laboratory batch pulping processes under known pulping conditions. The 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. 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.

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## INTRODUCTION

The emission of volatile organic compounds (VOC's) in pulp and paper mills has been an environmental concern. The VOC content and vapor liquid phase equilibrium (VLE) in mill streams are the two key factors that dictate VOC emissions. The VLE partitioning approach has been used in computer models to describe the VOC emission in various mill processes [1-3]. 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, and the understanding of the subject is very limited. A previous study by NCASI [4] indicated that using existing VLE data obtained in a methanol-water mixture can overpredict VOC emissions. Therefore, the objective of the present research is to obtain VOC VLE data in mill process streams for computer predictions.

Methanol accounts for 90% of the VOC emission at kraft mills. Black liquor deviates from water the most and is very difficult to analysis due to its corrosive nature. Furthermore, black liquor evaporation is an process during which methanol can be regenerated and released. Therefore, this study is focused on the VLE data of methanol in black liquors. The objective of the study is to obtain an empirical correlation of the VLE behavior of methanol in mill black liquors.

## 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.

## Measurement Method

There are many methods available for VLE studies. The headspace gas chromatographic method (HSGC) has the advantage of giving direct analysis of the vapor phase of the solute and has been used for VLE studies. The traditional HSGC method [5,6] for VLE study requires the direct analysis of both the liquid and vapor phases through error-producing calibration procedures. We use the indirect HSGC method that we developed for VLE studies [7] in this research. The method is accurate, rapid, and automated.

## Apparatus and Operation

All measurements were carried out using a HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard). A detailed description and the basic operation principles of the headspace sampler can be found in our previous study [8]. 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. 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 [7]. 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.

## RESULTS AND DISCUSSIONS

The total solids content of all the black liquors used in this study is below 20%. Therefore, we can 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 processes, an organic sulfur compound, dimethyl sulfide (DMS), and  $\alpha$ -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 [6] 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 a single measurement is about 15% as shown in Fig. 1. However, the relative standard deviation was 8.8%, within the error margin from our precision analysis [7]. 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. 2. 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. 2. The results show that the overall slope of the data of all of 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 I. 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 of the six data sets is only 15%. More data and black liquor samples are required to further validate this argument.

$$\text{Log}_{10}(H_c) = \frac{a}{T} + b \quad (1)$$

Figure 2 shows that 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 [7]. The results in Fig. 2 indicate that using the Henry's constants of methanol in a water mixture for VOC computer models could overpredict mill VOC emissions.

### ***Effect of Ionic Strength***

Black liquor contains a large quantity of inorganic salts. The inorganic salts cause a variation in 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 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 an increase in ionic strength as shown in Fig. 3. 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. 3, 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. 2.

### ***Effect of pH***

We took a 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 for ionic strength.

### ***Effect of Total Solids Content***

To explain the significant variation in Henry's constant in different black liquors as shown in Fig. 2, 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. 4, the Henry's constant of methanol decreases linearly with an increase in 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. 4 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. 4, with the consideration of the data scattering. We use the following equation to express this relation,

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

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. 4. 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,

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

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  $\alpha$ -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. 3. 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. 5, 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. 5 are all measured at a liquor temperature of 70°C. Figure 5 indicates that the methanol Henry's constant in black liquors decreases with an increase in 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 or organic solids content on methanol Henry's constant is rather complicated. Weak black liquor contains a large quantity of soap [9], i.e., resin acids and fatty acids, that is proportional to the solid content of the liquor in general. These acids act as surfactants, or soap, in the liquor that can affect methanol Henry's constant significantly [10]. The understanding on the subject is very limited [10]. Further study of 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.

## ACKNOWLEDGEMENT

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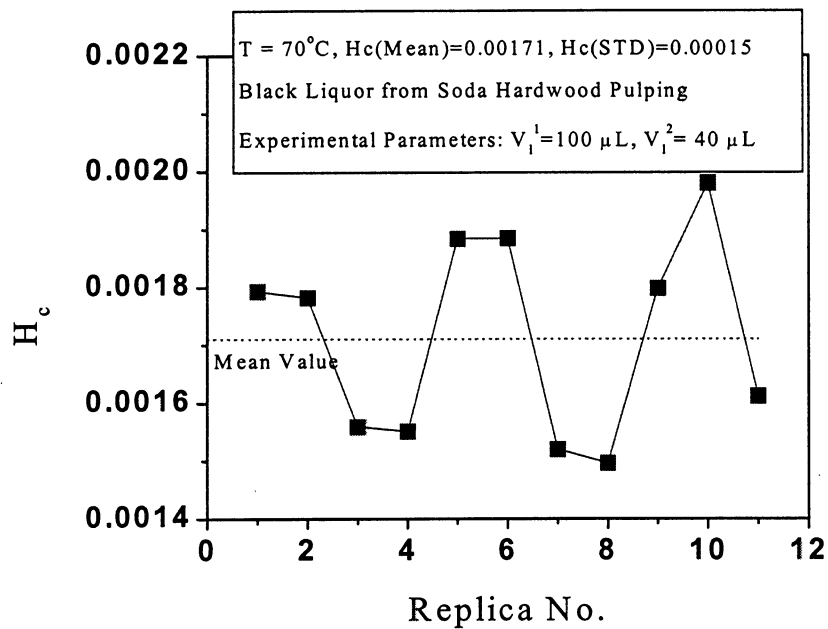


Fig. 1. Measured methanol Henry's constant from 11 replicas in a black liquor.

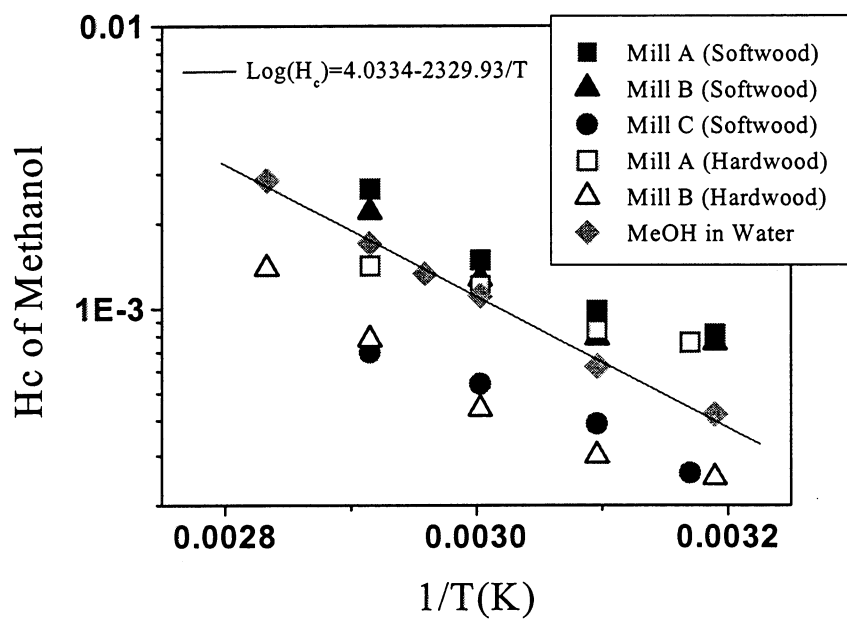


Fig. 2 Effect of temperature on the Henry's constant of methanol in various black liquors.



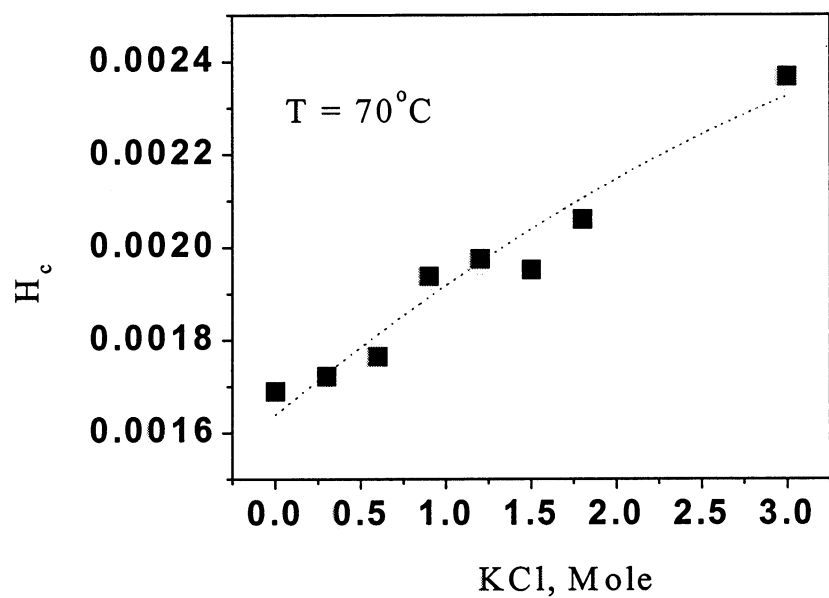


Fig. 3. Effect of ionic strength temperature on the Henry's constant of methanol in a methanol-water mixture.

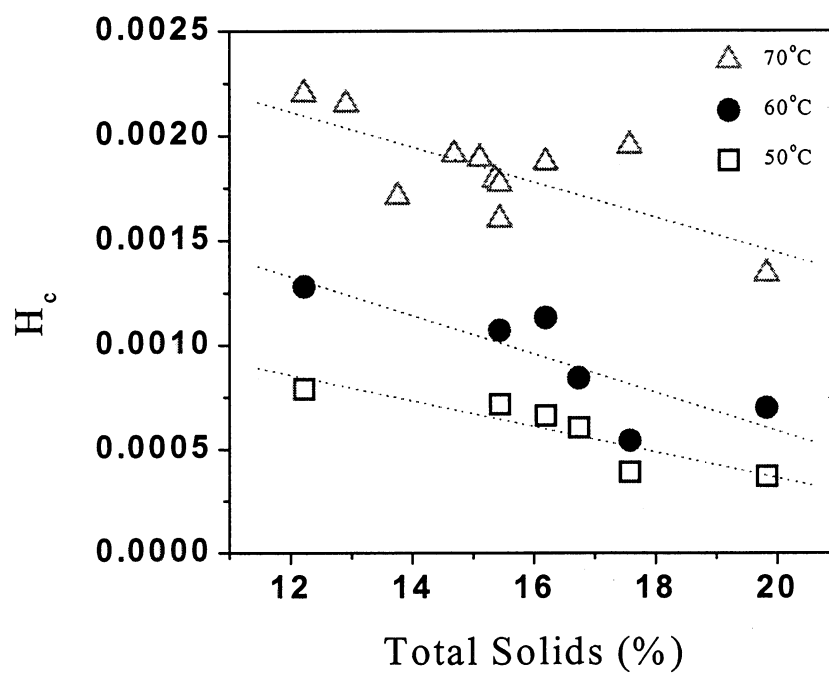


Fig. 4. Effect of total solids content on the Henry's constant of methanol in black liquors at different temperatures.

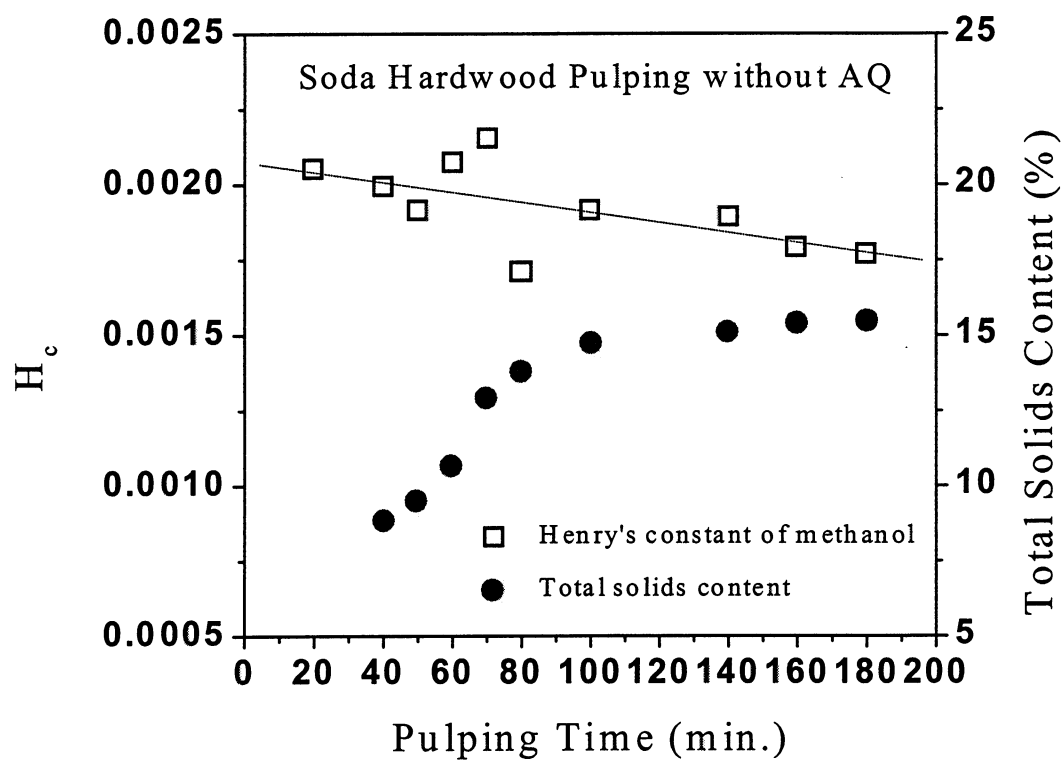


Fig. 5. Measured methanol Henry's constant in different black liquor samples collected at various pulping stages in a laboratory batch pulping process.

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

<b>Sample</b>	<b>Intercept: b</b>	<b>Slope: a</b>
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 [7]	3.4957	-2147.23
<b>MEAN</b>	-	<b>-1778.37</b>
<b>STD</b>	-	<b>266.8</b>
<b>RELATIVE STD</b>	-	<b>15.0%</b>

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

<b>Temperature</b>	<b>Intercept: d</b>	<b>Slope: <math>c \times 10^5</math></b>
50°C	0.0016	-6.1765
60°C	0.0024	-9.2325
70°C	0.0031	-8.3825
<b>MEAN</b>	-	<b>-7.9305</b>
<b>STD</b>	-	<b>1.1693</b>
<b>RELATIVE STD</b>	-	<b>14.7%</b>





