VOLATILE ORGANIC COMPOUNDS (VOCs) IN KRAFT MILL STREAMS

Part II
Protocol Development to Measure the Contents and Henry's Constants of VOC's in Kraft Mill Streams

Part III
Vapor-Liquid Equilibrium Partitioning of Methanol in Black Liquors

Project F01708
Reports 2 and 3

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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J.Y. Zhu, X.S. Chai, and B. Dhasmana

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Part II: Protocol Development to Measure the Contents and Henry's Constants of VOC's in Kraft Mill Streams

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ABSTRACT

VOC emission in kraft mills has been an environmental concern. The VOC content and the vapor-liquid phase equilibrium are the two factors that dictate VOC emission. The present report document the measurement protocol to develop a database that describes the contents and the VLE behaviors of VOC's in various kraft mill streams using a commercial headspace gas chromatographic system with the methods described in Part I of this report. The methods are indirect, rapid, automated, and do not require modification of the sample matrix. Validation experiments with VOC-water mixtures indicate that the methods are accurate. Preliminary results of various mill streams are also obtained using the developed protocol.
INTRODUCTION

The new toxic and permit provisions of the 1990 clean air amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. Many VOC's are now on the list of hazardous air pollutants. Several studies on VOC emissions at kraft mills have been conducted. Venketesh et al. [1] reported a millwide VOC prediction using a process simulation technique. The 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 [2] indicated that the VOC content and the thermodynamic vapor-liquid phase equilibrium behavior of VOC's are two of the key factors that affect the release of VOC's during mill operations. Therefore, a database that quantifies the contents and the VLE behaviors of VOC's in kraft mill streams is very important for understanding VOC emissions and emission predictions using computer simulation models [3]. Unfortunately, limited experimental techniques are available for the determination of the contents and VLE behaviors of VOC's in kraft mill streams due to their corrosive nature.

Recently, Gunshefki and Cloutier [4] developed a method for measuring methanol contents in black liquor. However, the method involves a series of sample pretreatment. It is, therefore, very complicated, time-consuming, and less accurate. There are many methods available to study vapor-liquid phase equilibrium [5-7]; however, most available methods are complicated to implement and involve calibration. Much research on vapor-liquid phase equilibrium has been conducted using headspace (HS) GC systems [8-12] that provide direct vapor phase analysis. However, traditional HSGC methods require the direct
analysis of solute content in the sample stream, not suitable for mill stream VLE studies.
Furthermore, most of the existing indirect HSGC methods have either practical difficulties
to implement or complicated calibration procedures.

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 kraft mill streams using a commercial headspace gas
chromatography system. The detail protocols for these measurements and the applications
for the mill samples are also presented.

METHODOLOGY

Quantification of VOC Contents

The method is schematically described in Fig. 1. The method has been discussed in
our previous study [13]. We use two sample vials filled with the same volume of sample
solution. We then add a small amount of concentrated solution of known concentration into
one of the vials. After a phase equilibrium is established within each vial, we conduct
headspace GC analysis for each sample vial. Because of a very low concentration, the
solute VLE partitioning coefficients in these two vials agree with Henry’s Law, i.e.,

\[ H_e = \frac{C^l_i}{C^v_i} = \frac{C^g_2}{C^g_1} \]  

(1)

where \( C^l_i \) and \( C^v_i \) are the solute concentrations in the liquid and vapor phases at equilibrium
in vial \( i \), respectively.
The amount of solutes in the vapor phase at equilibrium state in these two vials can be described as:

\[ C_1^V V_g^0 = C_0 V_i^0 - C_i V_i^0, \]  
\[ C_2^V V_g^0 = C_0 V_i^0 + C_s V_s - C_i V_i^0, \]

where \( C_0 \) and \( C_s \) are the concentrations of the solute in the sample and in the standard solution, respectively. The \( V_i^0, V_s \), and \( V_g^0 \) are the volumes of the sample, standard solution, and headspace, respectively.

![Schematic diagram describing the present indirect HSGC method for VOC content measurements.](image)

Fig. 1. Schematic diagram describing the present indirect HSGC method for VOC content measurements.

We can derive the initial solute concentration in the sample solution from Eqns. (2) and (3),

\[ C_0 = \frac{C_s V_s}{(C_g^2 / C_g^1 - 1)V_i^0} \]
\[
C_0 = \frac{C_s V_s}{(C^2_g / C^1_g - 1)V^0_i},
\]

where we assume that the total volume of the solution in the vials remains the same because of \( V^0_i \gg V_s \).

The ratio of the solute concentration in the vapor, \( C^2_g / C^1_g \), is proportional to the ratio of the peak areas, \( A_2 \) and \( A_1 \), measured from GC analysis. Thus, we can rewrite Eqn. (4) as,

\[
C_0 = \frac{C_s V_s}{(A_2 / A_1 - 1)V^0_i}. \tag{5}
\]

**Determination of VOC Henry's Constant**

The indirect HS-GC method for measuring VLE Henry’s constant is schematically shown in Fig. 2. The method has been discussed in great detail in our previous study [14]. We used two vials filled with the same sample solution but significant volume difference. We then conducted headspace GC analysis for each vial when the phase equilibrium was established within the vials. Because the two vials contain the same dilute solution, the solute VLE partitioning coefficients in these two vials agree with Henry’s Law as shown in Eqn. (1). We can express the total moles, \( M_i \), of the solute in these two vials as follows,

\[
M_i = C^0_i V^1_i = C^1_i V^1_i + C^1_g V^1_g = C^1_g \left[ \left( V^1_i / H_c \right) + V^1_g \right], \tag{6}
\]

and

\[
M_2 = C^0_i V^2_i = C^2_i V^2_i + C^2_g V^2_g = C^2_g \left[ \left( V^2_i / H_c \right) + V^2_g \right], \tag{7}
\]

where \( C_g \) is the concentration of solute in the vapor phase, and \( V_g \) is the vapor volume in the vial.
Fig. 2. Schematic diagram describing the present indirect HSGC method for VLE partitioning Henry's constant measurements.

We can derive the dimensionless Henry's constant $H_c$ from Eqns. (6) and (7),

$$H_c = \frac{V_i^1 (1 - C_i^1 / C_g^2)}{C_i^1 / C_g^2 (V_t - V_i^1) - V_i^1 / V_i^2 (V_t - V_i^2)} = \frac{V_i^1 (1 - A_1 / A_2)}{A_1 / A_2 (V_t - V_i^1) - V_i^1 / V_i^2 (V_t - V_i^2)}$$

MEASUREMENT PROTOCOLS

I. Liquid VOC Content Measurement.

This measurement protocol is used to simultaneously determine liquid contents of methanol, MEK, and acetone in sample solution.

Apparatus

1. A gas chromatograph, HP 6890 (Hewlett-Packard) equipped with a single or dual column instrument with flame ionization detector (FID). A HP-5 capillary column (Hewlett-Packard) operated at 30°C with an injection port temperature of 250°C and a detector temperature of 250°C is used for species separation. GC conditions: helium carrier
gas flow rate: 3.8 ml/min, and hydrogen gas and compress air flow rates for the FID: 35 and 400 ml/min, respectively.

2. An automatic Headspace Sampler, HP-7694 (Hewlett-Packard). Headspace conditions: thermo equilibration time 25 min with gentle shaking, injection time: 1.0 min, vial pressurization time: 0.3-0.5 min, and sample loop fill time: 0.2 min. In headspace sampling, the solid, liquid, or gaseous sample is placed in a vial and sealed by a septum with a crimper. The sampling operation is controlled by a personal computer and automated.


Reagents

Standard mix solvent of methanol, acetone, and MEK. Preparation: Add about 9 ml of methanol into a 10-ml dried volumetric flask. Pipette 0.1 ml of MEK and 0.1 ml of Acetone into the volumetric flask, respectively, then fill methanol to the mark of 10 ml of the flask. The volume of the headspace in the volumetric flask should be as small as possible to avoid the vaporization of the solutes from the solvent. The concentrations of methanol, acetone, and MEK are 24.5, 0.135, and 0.111 mole/L, respectively.

Procedure

1. Pipette 10 ml of sample solution into three 20-ml vials, then close the vials.
2. Pipette 10 ml of sample solution into another three 20-ml vials. Add 10 µl of standard solvent by microsyringe into each vial, then close the vial.
3. Put the vials into the headspace Sampler for equilibration and then measure by the GC.
4. Triplicate run the samples in step 1, determine the peak areas at retention times of 2.24, 2.50, and 3.23 min for methanol, acetone, and MEK, respectively. Then calculate the average peak areas $A_{1,MeOH}$, $A_{1,acetone}$, and $A_{1,MEK}$.
5. Triplicate run the samples in step 2, determine the peak areas at retention times of 2.24, 2.50, and 3.23 min for methanol, acetone, and MEK, respectively. Then calculate the average peak areas \( \overline{A}_{2,\text{MeOH}} \), \( \overline{A}_{2,\text{acetone}} \) and \( \overline{A}_{2,\text{MEK}} \).

**Calculation**

Use the following equation to calculate the concentrations:

\[
C_{0,i} = \frac{C_{s,i}V_i}{\left(\frac{\overline{A}_{2,i}}{\overline{A}_{1,i}} - 1\right)V_i^0}
\]

where \( C_{0,i}, C_{s,i} \) and \( V_i^0, V_i \) are \( i \) component concentrations and the volumes of the original testing sample and the standard solution in mole/L, respectively; \( \overline{A}_{1,i} \) and \( \overline{A}_{2,i} \) are the averaged GC peak areas of component \( i \) in the vapor phase measured before and after standard addition, respectively.

**II. VLE Measurement.**

This protocol is used to determine Henry’s constant of VOC’s in the sample solution.

**Apparatus**

The system and operating conditions of gas chromatography are the same as that mentioned in Protocol I. The operating conditions of the headspace Sampler are also the same as above, except the time of equilibration will be determined by the sample volume used in the experiment. The suggested sample volumes \( (a \text{ and } b) \) and equilibrium time in the headspace Sampler are listed in Table I.
Procedure

1. Pipette $a$ ml of sample solution into three 20-ml vials, then close the vials.

2. Pipette $b$ ml of sample solution into another three 20-ml vials, then close the vials.

3. Put the vials into the Headspace Sampler for equilibration and then measure by the GC.

4. Triplicate run the samples in step 1, determine the peak area at the retention time of the solute as indicated in Protocol I. Then calculate the average peak areas $\overline{A}_{1i}$.

5. Triplicate run the samples in step 2, determine the peak areas at the retention time of the solute. Then calculate the average peak areas $\overline{A}_{2i}$.

Table I. Suggested sample volumes and equilibration time in headspace sampler.

<table>
<thead>
<tr>
<th>Henry's constant</th>
<th>$V_1$, ml</th>
<th>$V_2$, ml</th>
<th>Equilibration time*, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.1</td>
<td>0.01</td>
<td>5</td>
</tr>
<tr>
<td>0.01</td>
<td>1</td>
<td>0.1</td>
<td>15</td>
</tr>
<tr>
<td>0.1</td>
<td>10</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>9</td>
<td>25</td>
</tr>
</tbody>
</table>

*For the samples with humic matters or particles, HSGC analysis should be conducted immediately after adding sample solution into the vial.

Calculation

Use the following equation to calculate results:

$$H_c = \frac{V_1(1 - \frac{A_{1i}}{A_{2i}})}{\frac{A_{1i}}{A_{2i}} - \frac{V_1}{V_2}(V_i - V_1)/V_2(V_i - V_2)}$$

where $H_c$ is the Henry's law constant (dimensionless). $\overline{A}_{1i}$, $\overline{A}_{2i}$ and $V_1$, $V_2$ are the average GC peak area of the $i$ component measured and the sample volume (in ml) in vial 1 and 2, respectively.
APPLICATIONS

Measurement of Liquid VOC Contents in Mill Streams.

Methanol, acetone, and MEK are the major VOC species with lower boiling points in most mill streams. Traditional methods to measure these VOC’s use organic solvents to extract them from the aqueous phase. These methods are time-consuming and less accurate due to a low concentration of these species in mill streams. With the present method (Protocol I), we can measure methanol, acetone, and MEK in various mill streams simultaneously. The measurements are rapid, automated, and accurate as demonstrated in a previous study [13]. Some results of VOC contents in various streams of a kraft mill are shown in Table II.

Measurement of Methanol Henry’s Constant in Black Liquors.

It is known that 90 % of VOC’s in mill streams is methanol. It is therefore important to understand methanol’s thermodynamic behavior in these mill streams. The measurement of methanol Henry’s constant in mill streams is also very difficult because it is very small. We can use the present method (Protocols II) to measure the Henry’s constant of methanol in mill streams with a reasonable accuracy.

Both softwood and hardwood black liquor samples from a mill were used in this study. Fig. 3 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. The variation in the measured Henry’s constant among these three types of samples is very significant. We believe that the significant variations in the composition, ionic strength, solid contents, etc., among these samples, may cause the large
variation in the Henry's constant. We will conduct a detailed study to understand the effect of various parameters on the Henry’s constant in the future.

**CONCLUSIONS**

The present study reported on the methods and protocols to measure the contents and the vapor-liquid phase equilibrium partitioning coefficients of VOC's in mill streams using a commercial headspace gas chromatography system. Both methods are rapid, automated, accurate, and do not require calibration and modification of the sample matrix and can also be easily 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.
Table II. VOC contents measured in various streams from a pulp mill.

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

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Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Part III: Vapor-Liquid Phase Equilibrium Partitioning of Methanol in Black Liquors

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ABSTRACT

In Part III of this report, we report on the behaviors of methanol vapor-liquid partitioning in various weak black liquor samples. 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 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.

Application:
Analysis of VOC content and VLE partitioning in mill and environmental streams.

Keywords:
VOC, Henry's law, vapor-liquid partitioning, headspace, GC, black liquor, mill streams.

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INTRODUCTION

The vapor-liquid phase equilibrium partitioning is one of the key factors that dictates VOC emission at Kraft mills as we discussed in Part I of this study. The VLE partitioning approach has been used in computer models to describe the VOC emission in various mill processes [1, 2]. 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 [3] 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 in Part I of this study, 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 [4] 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 and protocol developed in Parts I and II of this study. The objective of this part of the study is 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 Parts I and II of this study. The basic principles of the headspace sampler can be found in Chai et al. [5]. 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 [6]. 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. (8) in Part II of this study.
RESULTS AND DISCUSSIONS

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 $\alpha$-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 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 [6]. 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 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 the six data sets is only 15%. More data and black liquor samples are required to further validate this argument.
\[ \log_{10}(H_c) = \frac{a}{T} + b \] (1)

Figure 2 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 [7]. The results in Fig. 2 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. 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 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. 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 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. 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,

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

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,

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

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. Fig. 5 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 [7]. 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.
ACKNOWLEDGEMENT

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REFERENCES


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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.

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Table II: List of fitting parameters of Eqn. (2) at different temperatures.
Fig. 1

Black Liquor from Soda Hardwood Pulping

Experimental Parameters: $V_i^1 = 100 \mu L$, $V_i^2 = 40 \mu L$

Fig. 2

$\log(H_c) = 4.0334 - 2329.93/T$

Hc of Methanol vs. $1/T(K)$
Fig. 5

Soda Hardwood Pulping without AQ

- $H_c$
- Total solid content

- Henry's constant of methanol
- Total solids content

Pulping Time (min.)

Total solid content (%)
Table I: List of fitting parameters of Eqn. (1) for various samples.

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

* The values are from Part I of this study

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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Intercept: d</th>
<th>Slope: cxE10^5</th>
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<tbody>
<tr>
<td>50°C</td>
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<tr>
<td>60°C</td>
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<td>70°C</td>
<td>0.0031</td>
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<tr>
<td>MEAN</td>
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<td>-7.9305</td>
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<td>STD</td>
<td>-</td>
<td>1.1693</td>
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<tr>
<td>RELATIVE STD</td>
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<td>14.7%</td>
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</table>