Factors affecting the partitioning of methanol vapor–liquid phases in black liquors

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ABSTRACT

Using headspace gas chromatography, we examined the partitioning of methanol vapor–liquid phases 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 provide a wide representation of black liquors from kraft and soda pulping of both hardwoods and softwoods. The results showed that temperature and total solids content are two major factors affecting the Henry's constant (H_C) of methanol in black liquor. Linear regression analysis indicates that the methanol H_C in black liquors increases exponentially with the inverse of temperature (in degrees Kelvin) and decreases linearly with the total solids content.

Application:

A method for estimationg and predicting methanol emissions in kraft mills.

THE NEW TOXICITY AND PERMIT provisions of recent amendments to the 1990 Clean Air Act require pulp and paper mills to provide information on emissions of volatile organic compounds (VOCs). Many VOCs are now classified as hazardous air pollutants (HAPs).

Several studies on VOC emissions at kraft mills have been conducted. Venkatesh *et al. (1)* reported on a process simulation technique for predicting millwide emissions of VOCs. NCASI (National Council of the Paper Industry for Air and Stream Improvement) conducted a series of studies on VOC emissions at kraft mills. The NCASI studies indicated that the release of VOCs during mill operations is determined by several factors *(2)*:

- The VOC content in mill streams
- The fundamental thermodynamic vapor–liquid phase equilibrium behavior of the VOCs in mill streams
- The mass transfer associated with specific mill processes
- The mill operating conditions (wood species, pulping chemicals used, water reuse in operation, etc.)

Some of these factors pertain to unit operating conditions and specific mill processes, such as mass transfer in a unit operation. It is very difficult to generalize for these specific situations. However, the thermodynamic behavior of the VOCs should not depend on the characteristics of specific unit operations. Thus it is important to understand the thermodynamic behavior of vapor–liquid phase equilibrium (VLE) of VOCs, with the ultimate goal of developing predictive computer models for VOC emissions *(1, 3)*.

Unfortunately, few studies have been conducted on the VLE behavior of VOCs in mill streams. Indeed, the understanding of the subject is very limited. A previous study by NCASI *(4)* indicated that the use of existing VLE data obtained in VOC–water mixtures overstates VOC emissions. Clearly, there is a need to develop a VLE database of VOCs in kraft mill streams that can be used by computer models to accurately predict VOC emissions.

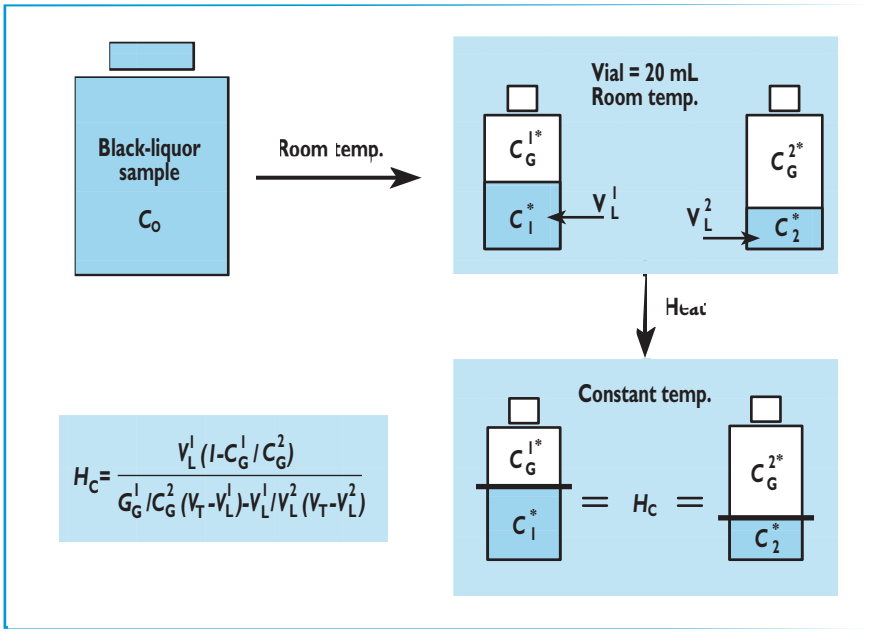
Because VOC concentrations in various kraft mill streams are very low, Henry's law best describes the VLE partitioning behavior of VOCs. Methanol, the dominant species of VOCs in black liquors, accounts for more than 90% of the VOC emission in kraft mills *(2)*, and black liquor is one of the most difficult streams to analyze. In this work, we focus our research on the measurement of the Henry's constant of methanol in a wide range of black liquor samples. The objective of this study was to understand the major factors that affect the VLE partitioning of methanol in various black liquor samples.

Black liquor has a very complex composition, containing dissolved lignin and other humic material. Understanding the effects of various compositional parameters on the VLE partitioning behavior of methanol in black liquor is beyond the scope of this work. However, it is not trivial and deserves detailed study in the future.

EXPERIMENTAL

Black liquors

Weak black liquor samples collected during various stages of five pulping processes in our laboratory were used to characterize the effect of pulping variables on the Henry's constant (H_C) of methanol in black liquors. These black liquor samples were obtained under known pulping conditions (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 provide a wide representation of black liquors yielded from different wood species and pulping processes.



1. Schematic diagram representing the indirect HSGC method for measuring Henry's constant (C represents concentration at a nonequilibrium state)*

Apparatus and operation

All measurements were carried out using an automatic headspace sampler (Model HP-7694) and a capillary gas chromatograph (Model HP-6890, Hewlett-Packard). The GC conditions were described in a previous study *(5)*. The basic principles of the headspace sampler can be found in Chai *et al. (5)*. The measurement procedure was as follows: pipette 0.05 mL of sample solution into one 20 mL vial and a 10 mL sample into another vial; then close the vials and put them into the oven of the headspace sampler. The vial is gently shaken until vapor–liquid phase equilibrium is achieved, as described in a 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 H_C using the method developed in a previous study *(6)*.

Methodology

There are many methods available to study vapor–liquid phase equilibrium. 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. The traditional direct HSGC method *(7–10)* for VLE study requires direct determination of the concentrations of the solute in both the liquid and vapor phases using tedious and error-producing calibration procedures. Lincoff and Gossett *(11, 12)* developed an indirect HSGC method to determine H_C using equilibrium partitioning in closed systems (EPICS). Recently Ettre *et al. (13)* developed a similar indirect method, the phase-variation method (PRV), to measure H_C. Both of these methods are based on mass conservation and equilibrium headspace. The present method is very similar to the EPICS *(11, 12)* and PRV *(13)* methods, taking the advantages of both methods into account, as described in a previous article *(6)*. The pros and cons of the EPICS and PRV methods—and the detailed mathematical precision analysis of the present method—can be found in a previous study *(6)*. We provide only a brief derivation of our indirect HSGC method here.

The present indirect HSGC method uses two sample vials, each filled with the same sample solution but with a significant variation in volume, as shown in **Fig. 1**. We conducted a headspace analysis of each sample after establishing a phase equilibrium within each vial. The solute of the two systems has the same VLE H_C (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 as follows:

$$M_1 = C_L^0 V_L^1 = C_L^1 V_L^1 + C_G^1 V_G^1 = C_G^1[(V_L^1/H_C) + V_G^1] \quad (1)$$

$$M_2 = C_L^0 V_L^2 = C_L^2 V_L^2 + C_G^2 V_G^2 = C_G^2[(V_L^2/H_C) + V_G^2] \quad (2)$$

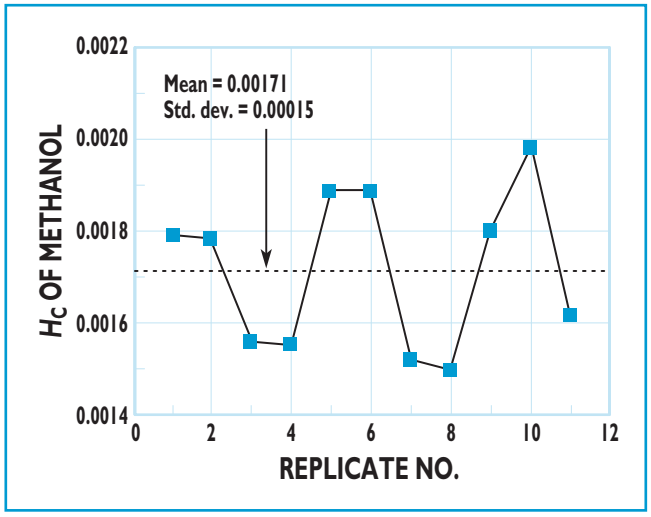
where

V_G = vapor volume in the vial
V_L = liquid volume in the vial
C_G = concentration of solute in the vapor phase
C_L = concentration of solute in the liquid phase
H_C = dimensionless Henry's constant

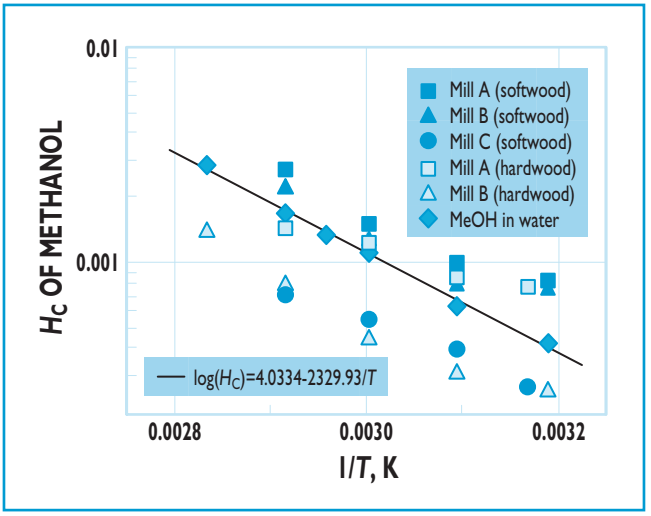
C_G is proportional to the GC peak area A from the GC measurements.

From Eqs. 1 and 2, with the substitution of GC peak area A for C_G, the dimensionless Henry's constant H_C can be determined using Eq. 3.

$$H_C = \frac{V_L^1\left[1-\left(\frac{C_G^1}{C_G^2}\right)\right]}{\left[\left(\frac{C_G^1}{C_G^2}\right)(V_T-V_L^1)\right]-\left[\left(\frac{V_L^1}{V_L^2}\right)(V_T-V_L^2)\right]}$$



2. Methanol Henry's constant (at 70°C) for 11 replicates in black liquor obtained after soda hardwood pulping in the laboratory



3. Effect of temperature on methanol Henry's constant in various mill black liquors and in methanol–water mixture

$$= \frac{V_L^1\left[1-\left(\frac{A_1}{A_2}\right)\right]}{\left[\left(\frac{A_1}{A_2}\right)(V_T-V_L^1)\right]-\left[\left(\frac{V_L^1}{V_L^2}\right)(V_T-V_L^2)\right]}$$

$$= \frac{V_L^1(1-r)}{r(V_T-V_L^1)-x(V_T-V_L^2)} \qquad (3)$$

where

V_T = total volume of the sample vial

$r = C_G^1/C_G^2 = A_1/A_2$

$x = V_L^1/V_L^2$

Sample	Intercept (*b*)	Slope (*a*)	Correlation coefficient (*r*)
Mill A (softwood)	2.8	–1872	0.975
Mill B (softwood)	2.4	–1735	0.949
Mill C (softwood)	1.7	–1659	0.990
Mill A (hardwood)	0.5	–1141	0.984
Mill B (hardwood)	3.1	–2116	0.976
Methanol–water mixture	3.5	–2147	0.998
Mean	…	–1778	…
Standard deviation	…	267	…
Relative std. dev., %	…	15.0	…

I. Fitting parameters of Eq. 4 for mill black liquors and a methanol–water sample

RESULTS AND DISCUSSION

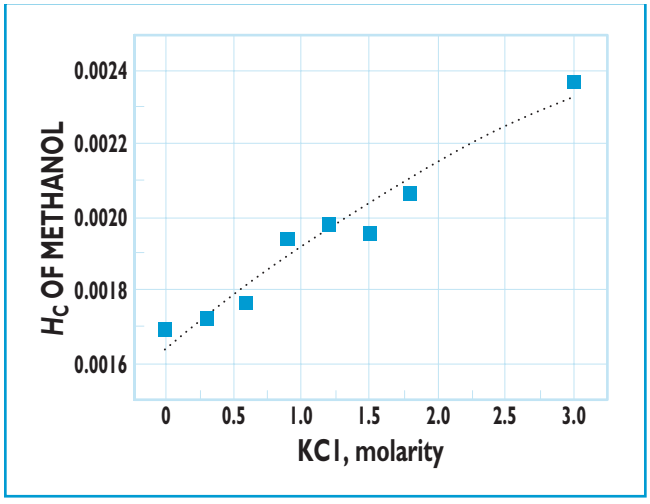
The total solids content of all the black liquors used in this study was less than 20%. Therefore, we treat them as aqueous solutions, which is a good assumption for weak black liquors in most mill processes (except in evaporators). Black liquor has a very complex composition, containing both inorganic and organic species. Methanol is the dominant species of volatile organic compounds in black liquors. However, in the kraft pulping process, dimethyl sulfide (an organic sulfur compound) and α-pinene (a by-product of softwood pulping) are also significant. The effects of multicomponents on the methanol VLE partition are very complicated. In this study, we examine the effects of only a few important parameters—temperature, ionic strength, and solids content—on the H_C of methanol in black liquors. We leave the work of understanding the effects of various compositional parameters on methanol H_C in black liquor for future investigations.

Measurement uncertainty

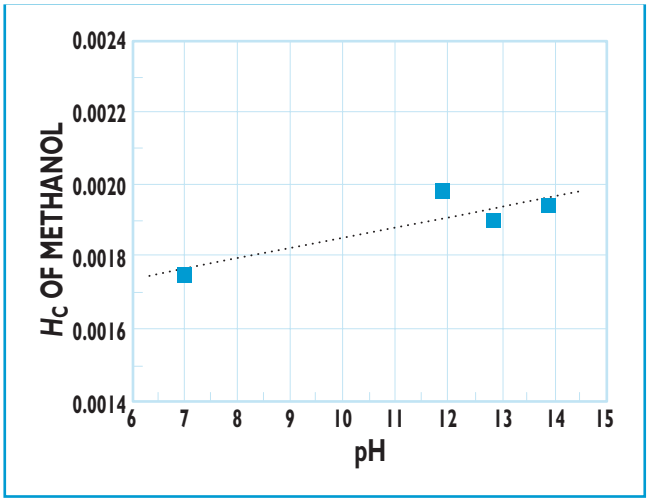
Precision analysis of the present measurement method *(6)* indicated that the potential measurement error was less than 10% for the experimental parameters used. The measurement uncertainty associated with this method can be traced to the nonhomogeneous nature of black liquors and the difficulty of obtaining uniform and representative samples. We determined the actual experimental uncertainty by analyzing the H_C of methanol in the soda hardwood liquor obtained in our laboratory from 11 replicate measurements. The maximum error for a single measurement is about 15%, as shown in **Fig. 2**. However, the relative standard deviation was 8.8%, which is 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 here 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 H_C of five black liquors from four different kraft mills over a tem-



4. Effect of ionic strength on methanol Henry's constant in methanol–water mixture at 70°C



5. Effect of pH on methanol Henry's constant in methanol–water mixture (methanol concentration = 800 mg/L)

Sample	Sodium, mg/kg	Potassium, mg/kg	Total ions gmole/kg	HENRY'S CONSTANT (H_C) at 50°C	at 60°C	at 70°C	pH
Mill A (hardwood)	33,400	2,492	1.516	0.0008	0.0012	0.0014	12.9
Mill A (softwood)	30,230	1,893	1.362	0.0010	0.0015	0.0027	12.9
Mill C (softwood)	27,080	2,265	1.235	0.0004	0.0005	0.0007	11.0
Mill B (hardwood)	20,250	2,966	0.956	0.0003	0.0004	0.0008	12.5
Mill B (softwood)	18,930	2,683	0.892	0.0008	0.0013	0.0022	11.8

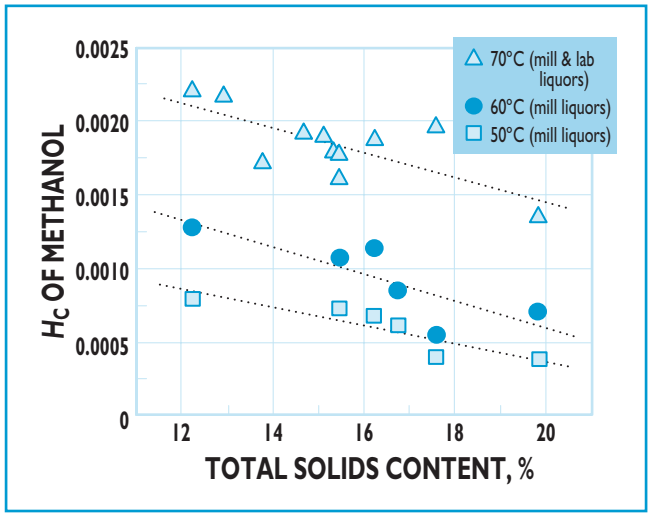
II. Sodium and potassium contents, methanol Henry's constants, and pH of black liquor samples

perature range of 40–70°C. Our results indicate that the H_C of methanol in all the black liquors examined increases exponentially with the inverse of temperature. We found that the logarithm of H_C of methanol in all the black liquors fits to a line with the inverse of temperature (in degrees Kelvin). **Table I** lists the regression results along with the correlation coefficients. The linear relationship in Eq. 4 agrees with the van't Hoff equation *(14)* in basic thermodynamic theory for solutes, i.e., H_C is proportional to the partial molar excess enthalpy, which is a function of temperature.

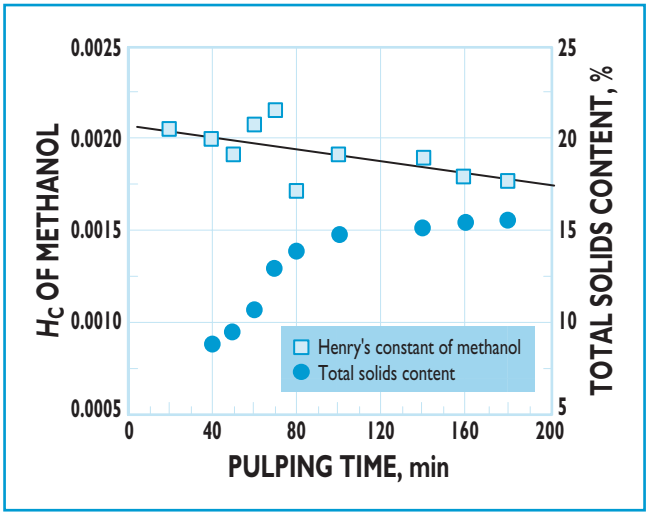
$$\log_{10}(H_C) = \frac{a}{T} + b \qquad (4)$$

For comparative purposes, we also plotted the H_C of methanol in a water mixture in **Fig. 3**. The results in Table I show that the overall slope of the data for the five black liquor samples was very close to the slope of the data for the methanol–water mixture. Nevertheless, linear regression analysis shows that there are some variations among the slopes of each individual data set. The variation is due to (a) the limited number of data points in each of the black liquor samples and (b) the data scattering caused by the measurement uncertainty. The slopes of the data for the mill black liquor samples were slightly lower than that of the methanol–water mixture. However, the relative standard deviation of the slopes of all six data sets was only 15%. More data and black liquor samples are required to further validate this argument.

Table I shows a significant variation among the intercepts for the various regression lines. The variations in the compositions of the black liquors—the solids contents, the wood species, the pulping conditions, and other parameters—could contribute to the differences in the H_C. The data also show that the H_C of methanol in black liquor samples can be smaller or greater than those in the methanol–water mixture at the same temperature. This behavior can be explained by the varied composition of black liquors, in particular, the dissolved solids and resin acids and fatty acids *(15)* that can affect the H_C of methanol. The results in Fig. 3 indicate that using the H_C of methanol in the water mixture for VOC computer models would not accurately predict mill VOC emissions.



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



7. Methanol Henry's constant (at 70°C) and total solids content in black liquor samples collected during soda hardwood pulping (without anthraquinone) in the laboratory

Effect of ionic strength

Black liquor contains a large quantity of inorganic salts that can cause a variation in ionic strength among different 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 H_C. We added different amounts of potassium chloride into several methanol–water mixtures to obtain solutions with different ionic strengths. We then measured the methanol H_C in these solutions. The results in **Fig. 4** show that H_C increases with an increase in ionic strength. After analyzing the sodium and potassium contents in the five liquors from mills A, B, and C, we found that the calculated ionic strength (based on the measured sodium and potassium) varied from 0.9–1.5 mole/L. However, the H_C of methanol in these five black liquors did not correlate to the total sodium and potassium content at several temperatures, as demonstrated by the experimental data shown in **Table II**. According to Fig. 4, the variation of ionic strength between 0.9–1.5 mole/L in water only accounts for 10% of the variation in H_C. This suggests that ionic strength may not be a major factor contributing to the significant variation of H_C in the black liquors shown in Fig. 3.

Temperature	Intercept (*d*)	Slope (*c*), ×10^5	Correlation coefficient (*r*)
50°C	0.0016	–6.2	0.90
60°C	0.0024	–9.2	0.83
70°C	0.0031	–8.4	0.74
Mean	…	–7.9	…
Standard deviation	…	1.2	…
Relative std. dev, %.	…	14.7	…

III. Fitting parameters of Eq. 5 at different temperatures

Effect of pH

We took a similar approach to study the effect of pH on the H_C of methanol. Different amounts of sodium hydroxide were added into several methanol–water mixtures. The effect of pH on the measured methanol H_C in water was not significant after correcting for ionic strength, as shown in **Fig. 5**. This suggests that the pH of the black liquor sample does not significantly affect methanol H_C, as also demonstrated by the experimental data shown in Table II.

Effect of total solids content

To explain the significant variation observed in Fig. 3 for H_C in different black liquors, we measured the methanol H_C 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 from kraft and soda pulping of both hardwood and softwood. We found that the methanol H_C in these black liquors correlates well with the total solids content, even though the black liquors are completely different in terms of wood species, pulping conditions, etc. As shown in **Fig. 6**, the H_C of methanol decreases linearly with an increase in solids content in the black liquor sample. As discussed previously, the measurement errors of our experiments are less than 9% with triplicate averaging; therefore, the scattering of the

data in Fig. 6 is partly due to measurement uncertainty and partly due to the real variation in H_C caused by the variation in the compositional matrix of black liquors and other parameters (e.g., ionic strength) that affect H_C.

Despite the data scattering and real variations in methanol H_C, we conducted linear regression analysis to correlate methanol H_C with solids content at given temperatures. The correlation coefficients are listed in **Table III**. The low correlation coefficients are to be expected, considering (a) that the samples were collected from various mills and laboratory pulping processes and (b) the data scattering caused by measurement uncertainties and real variations. However, the relative standard deviation of the slopes of the three sets of data presented in Fig. 6 was less than 15%. We use the following equation to express the relationship between H_C and solids content:

$$H_C = cS + d \quad (5)$$

where

S = total solids content of the liquor

The constants c and d are listed in Table III for the plots shown in Fig. 6.

By combining Eqs. 4 and 5, we could correlate the methanol H_C in black liquors with liquor temperature and solids content using the following equation:

$$H_C = \left[m \cdot \exp\left(\frac{A}{T}\right)\right] + (B \cdot S) + C \quad (6)$$

where

m = constant coefficient

However, more data are required for linear regression analysis to obtain good empirical correlation of H_C of methanol in various black liquors. The limited available data obtained in the present study prevented such a regression analysis.

Several significant VOCs—such as α-pinene from softwood and sulfur compounds from kraft cooking—are not formed in a soda hardwood pulping process. Therefore, the effect of these major species can be eliminated by studying the methanol H_C in soda hardwood black liquors. To obtain a better understanding of the effect of total solids content on methanol H_C, we measured H_C of several black liquor samples collected from a soda hardwood pulping process 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 H_C should be similar to those of potassium chloride shown in Fig. 4. The chemical in the starting cooking liquor was sodium hydroxide, which was consumed to form other salts during pulping. The increase in total solids content during the process was mainly the result of dissolved lignin from wood chips.

As shown in **Fig. 7**, the methanol H_C decreases linearly with time (or solids content) as the pulping process proceeds. Note that values for methanol H_C in Fig. 7 were measured at a liquor temperature of 70°C. Figure 7 indicates that the methanol H_C 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, mainly humic materials, on the methanol H_C is rather complicated. Weak black liquor contains a large quantity of soap *(15)* (i.e., resin acids and fatty acids) that is generally proportional to the liquor solids content. These acids in the liquor act as surfactants, or soap, which can affect methanol H_C significantly *(16)*. The understanding of this subject is very limited *(16)*, and further study is required.

SUMMARY

We measured the Henry's constant (H_C) of methanol in various black liquors using a headspace gas chromatographic method that we developed. The results indicate that the H_C of methanol in black liquor is mainly affected by temperature and the total solids content. Linear regression analysis indicates that the methanol H_C in black liquors increases exponentially with the inverse of temperature (in degrees Kelvin) and decreases linearly with the total solids content. However, more experimental data are required to better correlate the H_C of methanol in various black liquors with such major parameters as temperature and solids content. **TJ**

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