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Multiple headspace extraction–gas chromatographic method for the study of process kinetics

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Abstract

A multiple headspace extraction gas chromatographic technique to automate the study of process kinetics that involves volatile species was developed in this study. The technique was demonstrated by using it to study methanol formation in kraft black liquor samples under an isothermal temperature of 70 °C. The results indicate that methanol formation in kraft black liquors under isothermal conditions follows an exponential decay function. The present method is very simple, efficient and fully automated. It can be easily applied to study slow kinetic processes, such as reaction or adsorption and desorption, involving volatile species in any environmental and industrial samples with complicated matrices. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of process kinetics, such as chemical reaction kinetics and adsorption and desorption physical kinetics in multiphase systems, is an important subject in chemical engineering, chemistry and environmental sciences. Obtaining time-dependent information on concentrations of the species involved in the process is the key to kinetic study. If rapid and on-line or in-line concentration analysis capability, such as in-situ and time-resolved spectrophotometry, is not available, kinetic study is achieved by conducting replica experiments and terminating (or quenching) the process (or the experiment) at various process times. The concen-

trations of species of interest are then analyzed using an off-line analytical method. Despite advances in analytical chemistry, this primitive method is still the predominant technique today for process kinetics study. The primitive method suffers from the need for time-consuming replica experimentation; it also suffers from the poor repeatability of the experimental process, sampling in a nonuniform sample, and the analytical method. Especially for very slow kinetic processes where the changes in the species concentration are very small and within the experimental error range, the primitive method will fail for kinetic study.

Multiple headspace extraction gas chromatography (MHE–GC) was initially developed to achieve measurement automation in the study of the vapor–liquid equilibrium (VLE) process by Suzuki et al. [1], McAuliffe [2], Kolb and Ettre [3,4] and Chai and Zhu [5]. The successful experimental demonstration

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of MHE–GC for VLE studies was achieved by Chai and Zhu [5]. Based on the success achieved [5], the time sequence of the multiple extractions in MHE–GC can be used for the study of kinetics of processes that involve volatile species under infinite dilution. The advantages of using MHE–GC to study kinetics are obvious. It eliminates replica experimentation required in the primitive method. The headspace sampler provides a well-controlled environment, e.g., temperature and pressure, for the kinetics process to take place. Furthermore, headspace GC measurement is accurate and automated.

The objective of the present study is to develop and demonstrate an MHE–GC method that can be used for the study of process kinetics such as chemical reactions, adsorption and desorption processes in multiphase systems and diffusion processes through membranes. The developed method is demonstrated through the study of the kinetics of methanol formation in a spent pulping liquor through wood lignin demethylation.

2. Methodology

In the study of VLE of a solution system with solute under infinite dilution using MHE–GC, each headspace extraction of the solution system should be carried out under VLE conditions as described by Kolb and Ettre [4]. As shown in Fig. 1a, the solute

mass vented out of the sample vial through each headspace extraction can be expressed as a certain fraction of the solute vapor in the headspace before venting [5], i.e., $m_{EX, \text{solute}} = \varphi C_G V_G$ (φ is volumetric flow fraction for each extraction, $\varphi = 1 - \rho$, with ideal gas law assumption, and ρ is the ratio of headspace pressures before and after venting). Then the sum of the GC signal peak areas of the solute from the first $n - 1$ extractions is linearly proportional to the GC peak area, A , from the n th extraction [5]:

$$\sum_1^{n-1} A_i = a + bA_n \quad (1)$$

where $i = 1, 2, \dots, n \geq 2$, and a and b are constants and can be determined from regression. For a system that has a source or sink of the solute, such as solute formation or reduction due to chemical reactions taking place in the system, or adsorption or desorption of the solute by a solid-phase present in the system, the mass conservation of the solute will be modified by adding a source or sink term. Specifically, solute mass in the sample vial after the n th extraction can be expressed as:

$$\begin{aligned} m_n &= C_{Gn}V_G + C_{Ln}V_L \\ &= m_0 + V_G \sum_0^{n-1} \Delta C_{Gi} + V_L \sum_0^{n-1} \Delta C_{Li} - \varphi V_G \sum_1^{n-1} C_{Gi} \end{aligned} \quad (2)$$

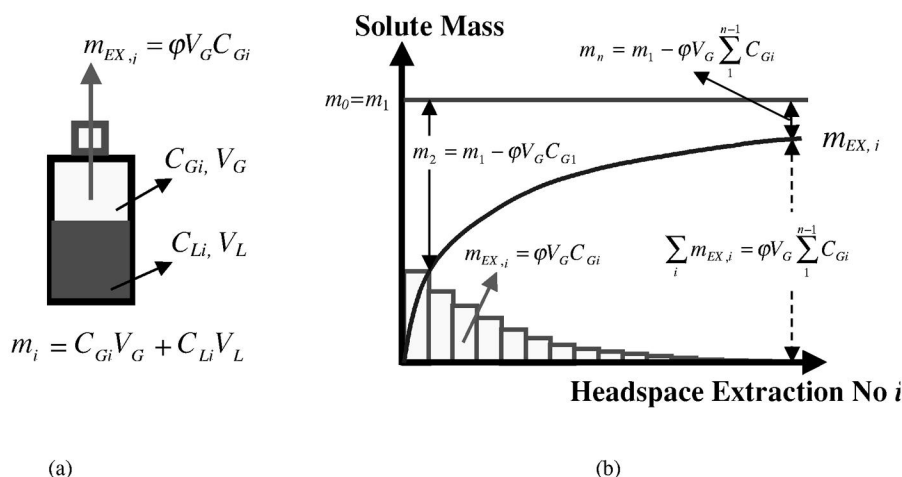


Fig. 1. A schematic diagram that shows the principle of MHE–GC technique.

where m_n is solute mass remaining in the vial after the n th extraction, C_G and C_L are solute concentrations in the vapor and liquid phase, respectively, V_G and V_L are the volumes of the vapor (headspace) and liquid, respectively, and ΔC_{Gi} and ΔC_{Li} are changes of the solute concentration in the vapor and liquid phase due to the source or sink, respectively.

When the rate of change of the solute due to the source or sink in the system is much slower than the rate of equilibrium, i.e., VLE, of the solute in the system and the increase of the solute due to the source did not affect the solute infinite dilution assumption, Henry's law still holds approximately. Furthermore, one can determine that the ratio between the changes of the concentration of the solute in the vapor (ΔC_{Gi}) and liquid phase (ΔC_{Li}) is also equal to the dimensionless Henry's constant, i.e., $H_c = \Delta C_{Gi}/\Delta C_{Li}$. Then, a modified form of Eq. (1) can be obtained from Eq. (2) as follows:

$$\sum_1^{n-1} A_i = a - b \sum_0^{n-1} \Delta A_i + bA_n \quad (3)$$

where ΔA_i is the change of GC signal peak area due to the change of solute concentration in the vapor phase (headspace), ΔC_{Gi} , with

$$a = \frac{fm_0}{\varphi V_G} \quad (4a)$$

and

$$\begin{aligned} b &= -\frac{1}{\varphi} \cdot \left(1 + \frac{1}{H_c} \cdot \frac{V_L}{V_G}\right) \\ &= -\frac{1}{\varphi} \cdot \left(1 + \frac{1}{\beta H_c}\right) \end{aligned} \quad (4b)$$

as derived by Chai and Zhu [5], where m_0 is the solute initial mass, $\beta = V_G/V_L$ is called phase ratio [4], and f is a calibration constant between the GC peak area and the vapor phase solute concentration, i.e., $A = fC_G$.

Eqs. (2) or (3) can be used to obtain the time-dependent changes of the total solute mass and its concentrations in the vapor and liquid phases, respectively.

$$\begin{aligned} \Delta m(t_n) &= \sum_0^{n-1} \Delta m_i = V_G \sum_0^{n-1} \Delta C_{Gi} + V_L \sum_0^{n-1} \Delta C_{Li} \\ &= \frac{m_0}{a} \cdot \left(\sum_1^{n-1} A_i - bA_n - a\right) \end{aligned} \quad (5a)$$

$$\begin{aligned} \Delta C_G(t_n) &= \sum_0^{n-1} \Delta C_{Gi} = \frac{1}{f} \sum_0^{n-1} \Delta A_i \\ &= \frac{-1}{fb} \cdot \left(\sum_1^{n-1} A_i - bA_n - a\right) \end{aligned} \quad (5b)$$

$$\begin{aligned} \Delta C_L(t_n) &= \sum_0^{n-1} \Delta C_{Li} = \frac{1}{H_c} \sum_0^{n-1} \Delta C_{Gi} \\ &= \frac{-1}{H_c fb} \cdot \left(\sum_1^{n-1} A_i - bA_n - a\right) \end{aligned} \quad (5c)$$

where t_n is time and

$$t_n = n \Delta t \quad (5d)$$

For the present kinetic study, a and b can be calculated using Eq. (4) for the given initial mass m_0 and dimensionless Henry's constant H_c of the solute in the sample system with f and φ obtained through calibration following the procedure described by Chai and Zhu [5]. If the ratio of headspace pressures before and after extraction, ρ , is known, then $\varphi = 1 - \rho$, and calibration for φ is not needed.

To demonstrate that reaction kinetics can be studied by the present method, we will apply Eq. (5) to study methanol formation in a pulping spent liquor under an isothermal condition. Pulping spent liquor, called black liquor because of its color, is a caustic wood lignin solution with a typical pH around 13 and a total dissolved solids about 15% that contains inorganic salts, lignin, hemicellulose, and other organic compounds, such as methanol, methyl mercaptan, and dimethyl sulfide. A typical wood lignin molecular contains one or two methoxyl groups (OCH_3) depending on the wood species. Methanol can be formed through the lignin demethylation reaction with hydroxide ion (OH^-), according to Sarkanen et al. [6]. The activation energy of the wood lignin demethylation reaction is low, and therefore reaction can take place even under normal black liquor storage temperatures (about 60–90 °C) in kraft pulp mills. Because of the very slow reaction and the inhomogeneous nature of black liquor, a kinetic study of methanol formation in spent pulping liquor under liquor storage conditions is very difficult using the primitive method which requires replicate experiments.

3. Experimental

3.1. Chemicals

Methanol of analytical grade obtained from a commercial source was used as solute and deionized water was used as solvent to prepare the standard aqueous methanol solution for calibration to obtain f and φ . A weak black liquor derived from kraft pulping of loblolly pine in a kraft mill was used for the study of methanol formation kinetics. The total solids content of the liquor was 15.2%.

3.2. Apparatus and operation

All measurements were carried out using an HP-7694 automatic headspace sampler and an HP-6890 capillary gas chromatograph (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA) equipped with an HP ChemStation for data acquisition and analysis. The GC sample vial serves as the reactor for the study of methanol formation reaction kinetics in the black liquor sample being tested. The headspace sampler provides an isothermal environment for the reactor. Compressed air is used for vial pressurization to create a pressure head within the vial for sample transfer. The sample loop is open to the atmosphere during sample transfer to fill the sample loop. At the completion of the sample transfer process, the vial pressure reaches the atmosphere pressure. The specific headspace sampler operation conditions are: vial pressurization time of 0.2 min at pressure of 1.2 atm, sample-loop fill time of 1.0 min, and loop equilibration time of 0.05 min (1 atm = 101 325 Pa). GC conditions are: HP-5 capillary column at 30 °C and carrier gas helium flow-rate of 3.8 ml/min. A flame ionization detection (FID) system was employed with hydrogen and air-flow-rates of 35 and 400 ml/min, respectively.

The measurement procedure was as follows: pipette 50 μ l of sample solution into a sample vial. The headspace sampler then heats the sample in the vial to a desired temperature with strong shaking for three min to achieve vapor–liquid equilibrium within the vial. At equilibrium, the vial is pressurized by compressed air, and the headspace is partially withdrawn to fill the sample loop and vented to the atmosphere so that the vial pressure returns to its initial level. The sample is injected into the GC

column for analysis. The GC signal as peak area A is recorded. This procedure is repeated several times automatically for multiple headspace extraction analysis and can be programmed by the HP ChemStation.

The sample size was fixed at 50 μ l for both the calibration and reaction experiments and the volume of the sample vial was 21.6 ml, which gives a phase ratio $\beta = 431$. For demonstration purposes, all the experiments were conducted only at 70 °C.

4. Results and discussion

4.1. Determination of a and b

A standard aqueous methanol solution with a known methanol concentration of 800 mg/l was used to calibrate f and φ according to the procedure described by Chai and Zhu [5]. The Henry's constant of methanol in the solution was obtained from literature [7] measured by an indirect headspace GC method. The result was 277.3 kPa, or $H_c = 0.00175$, at 70 °C. A multiple headspace extraction experiment was carried out using the standard aqueous methanol solution. The measured peak areas were used for linear regression according to Eq. (1) to obtain a and b from which $f = 353$ (l/mg) and $\varphi = 0.354$ were calculated using Eq. (4). The value of f and φ only varies with the experimental conditions and is independent of the sample system; therefore, it can be used to calculate the values of a and b of black liquor sample systems from Eq. (4).

A black liquor with methanol concentration of 736 mg/l was first measured using a headspace GC method [8]. According to Zhu et al. [9], the Henry's constant of methanol in the liquor was measured to be 433.6 kPa, or $H_c = 0.00273$, which is different from that in the aqueous solution mainly due to the dissolved inorganic salts and other organic materials in the liquor [9]. Therefore, a and b for the black liquor sample at temperature 70 °C was calculated to be 1702.8 and 5.2257, respectively.

4.2. Multiple headspace extraction measurements during methanol formation

Figs. 2 and 3 show the time-dependent GC detector signal peak areas of methanol obtained from

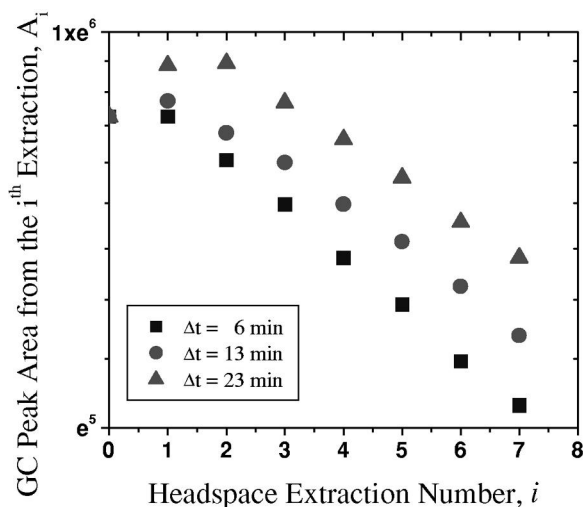


Fig. 2. A typical relationship between the GC signal peak area and the headspace extraction number in multiple headspace measurements for the system with solute mass formation.

multiple headspace measurements in the black liquor sample being tested. The first data point in Fig. 2 is a calculated imaginary GC peak area, i.e., A_0 . It would be the peak area from the first headspace extraction if there were no methanol formation. Based on VLE, mass balance of methanol, and the assumption that no methanol is formed, A_0 can be expressed as:

$$A_0 = \frac{fC_0H_c}{1 + \beta H_c} \quad (6)$$

For the experimental conditions in the present study, we found $A_0 = 325.9$. The three sets of data shown in the figures were obtained using three different headspace extraction delay times, i.e., 6, 13 and 23 min, respectively. The purpose of using three different headspace extraction delay times is to demonstrate that the VLE rate is much faster than the chemical reaction rate, the key assumption in the derivation of Eq. (5), which will be discussed later in this study. If the testing sample is purely under VLE without a source or sink, the logarithm of the peak area will be linearly proportional to the extraction number [4]. Furthermore, the sum of GC peak areas from the first $(n - 1)$ extractions also will be linearly proportional to the peak area from the n th extraction [5], i.e., Eq. (1). Obviously, because there is methanol formation, the peak area measured after the first extraction, A_1 , will be higher than A_0 , which violates the linear relationship as shown in Fig. 2. For the black liquor sample used in the present study, the two linear relationships still hold approximately after the first couple of extractions even when there is methanol formation, as clearly shown in Figs. 2 and 3. The results suggest that either the methanol formation is so slow that it did not significantly distort the linear relationships or that the changes of the GC peak area due to methanol formation and headspace extraction follow the same functionality, i.e., exponential decay function with extraction number. Therefore, we should be able to obtain a good fit of the methanol formation data using this functionality, i.e., the extraction number-dependent changes of GC peak area can be approximated by an exponential decay function, as will be discussed in the following section.

4.3. Time-dependent methanol formation measurements in a black liquor

We calculated the methanol formation in the black liquor sample under temperature 70 °C from Eq. (5) using the data presented in Figs. 2 and 3. Fig. 4 shows the time-dependent amount of methanol formed in terms of the percentages of the methanol in the original sample. Because the key assumption adopted in the present method is that the VLE rate of

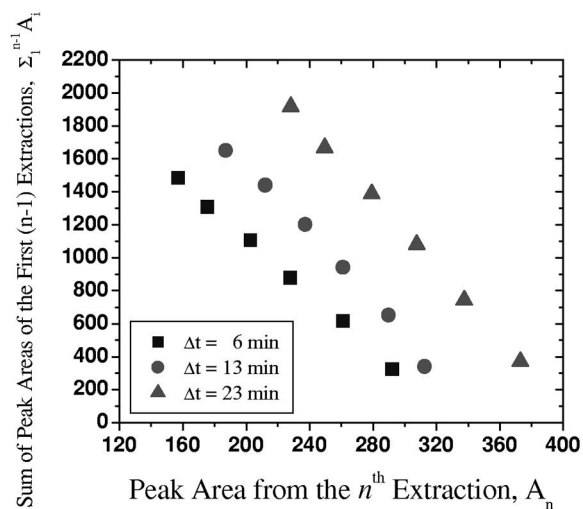


Fig. 3. A typical relationship between the sum of the GC signal peak areas from the first $n - 1$ headspace extractions and the signal from the n th measurement based on the data shown in Fig. 2.

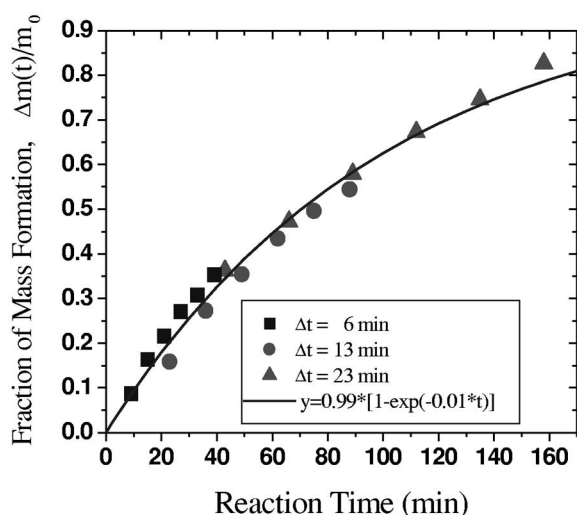


Fig. 4. The measured time-dependent methanol formation in a kraft black liquor as percentages of the methanol in the original sample at temperature 70 °C.

methanol in the sample is much faster than the methanol formation rate in each headspace extraction delay period, Henry's law can be used. It takes less than 2 min to achieve VLE for an aqueous methanol system with a sample size of 50 μl at 70 °C [7]. Therefore, using a headspace extraction delay time of greater than 2 min should be sufficient to obtain valid measurements as long as the methanol VLE will not be disturbed by the amount of methanol formed; in other words, the methanol VLE rate is much faster than the formation rate in the system. Fig. 4 clearly shows that using three different headspace extraction delay times, i.e., 6, 13 and 23 min, yielded the same amount of methanol formation, indicating the validity of the present measurements. Furthermore, the data indicate that the maximum amount of methanol formed during a 2-min time period (required to achieve VLE) is only about 2% in the original sample, too small to affect the methanol VLE. Therefore, the VLE assumption adopted in deriving the present method is valid for the study of methanol formation kinetics in black liquor.

As discussed earlier, the extraction number-dependent changes of GC peak area can be approximated by an exponential decay function:

$$\Delta A_i = q \exp(-pi) \quad (7a)$$

$$\Delta A_i = q \exp(-p \cdot \frac{t}{\Delta t}) = \Delta A(t) \quad (7b)$$

Therefore,

$$\begin{aligned} \sum_0^{n-1} \Delta A_i &= \int_0^t \Delta A(t) \cdot dt \\ &= \frac{q}{p} \Delta t \cdot \left[1 - \exp\left(-p \cdot \frac{t}{\Delta t}\right) \right] \end{aligned} \quad (8)$$

where p and q are constants. According to Eqs. (5a) and (3) the time-dependent methanol formation can be expressed as:

$$\frac{\Delta m(t)}{m_0} = \frac{-b \sum_0^{n-1} \Delta A_i}{a} \quad (9)$$

where $\Delta m(t)$ is the total methanol formation up to time t . Substituting Eq. (8) into Eq. (9), we have

$$\begin{aligned} \frac{\Delta m(t)}{m_0} &= \frac{-bq}{ap} \cdot \Delta t \cdot \left[1 - \exp\left(\frac{p}{\Delta t} \cdot t\right) \right] \\ &= \eta [1 - \exp(-\alpha t)] \end{aligned} \quad (10)$$

Because Eq. (7) is an approximation, we will not use Eq. (10) to predict methanol formation. Rather, we will use Eq. (10) to fit the data presented in Fig. 4 to obtain $\eta = 0.99$, and $\alpha = 0.01$ with t in min. Eq. (10) indicates that methanol formation reaction kinetics follows the traditional exponential decay function quite well for the black liquor sample tested in the present study.

4.4. Confirmation of methanol formation in the experiments

To confirm that methanol was formed through the lignin demethylation reaction, we measured the pH of the black liquor sample before and after the experiments. We found that pH was decreased from 13.6 to 7 for an experiment that lasted for more than 2 h, indicating that at least some hydroxide ions were consumed by the methoxyl groups to form methanol.

5. Conclusions

This study demonstrates a MHE–GC technique for the study of slow process kinetics of a volatile species. The technique can be applied to any system that contains a source or sink of a solute due to chemical reaction, adsorption, or desorption.

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