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in a Kraft Mill Multiple-Effect Evaporator

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THE FORMATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN A KRAFT MILL MULTIPLE-EFFECT EVAPORATOR

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ABSTRACT

The air emission of volatile organic compounds (VOCs), including sulfur and nonsulfur compounds, is an environmental problem in many countries. This paper studies the formation and evaporation of VOCs during black liquor evaporation in a multiple-effect evaporator in a kraft mill. Mill sampling was conducted and the liquor was analyzed for VOC concentrations. An empirical model was developed for the prediction of VOC partitioning between the liquor and vapor phase. Future condensate sampling is needed to further validate the model.

INTRODUCTION

The release of volatile organic compounds (VOCs) in kraft mills, including sulfur and nonsulfur compounds, has been an environmental concern. In the US, the US EPA Cluster Rule limits nonsulfur VOC air emissions from kraft mills. The air emission of sulfur-containing VOCs is a public relations issue and therefore regulated in many European countries. VOCs are primarily formed in the wood pulping processes. Much research on the formation of VOC in pulping has been conducted [1-9]. Sulfur-containing VOCs can also be released in the kraft chemical recovery cycle during black liquor evaporation and combustion due to the reduction of pH of the process streams and chemical reactions. Recently, it was indicated by many mills that a significant amount of methanol (a nonsulfur-containing VOC), the major component of VOCs, can also be formed in black liquor evaporation. Laboratory study of methanol formation in evaporation cannot simulate the methanol formation process in mill evaporators. Therefore, a mill sampling study is needed to quantify the formation and partitioning of VOCs between the liquor and vapor phase in evaporation for air emission predictions.

APPROACH - MILL SAMPLING

In this initial study, only the liquor phase was conducted. It turns out that the sampling in the condensate is necessary to validate the model for the prediction of VOC formation and partitioning between the liquor and vapor phase. Therefore, the model developed in the following section only provides some qualitative information.

The black liquor samples were collected from various stages of a multiple-effect evaporator in a kraft mill. Figure 1 shows the schematic diagram of the evaporator process stream. The sample bottles were filled without headspace and shipped to our laboratory for analysis.

ANALYTICAL METHODS

Determination of VOC concentration in black liquor is very difficult because black liquor has a very complex sample matrix of dissolved lignin, inorganic salts, etc. Traditional analytical methods for VOC analysis in black liquors requires solvent extraction [10] or other sample pretreatment procedures [11], which are very complicated, time-consuming, and inaccurate. Headspace gas chromatography (HSGC) was developed specifically for volatile species analysis. Direct species analysis of VOCs in the liquid phase is not necessary and, therefore, HSGC can be used. In the past several years, we have devoted a lot of research effort to develop several HSGC methods for species analysis in black liquors [12-15]. In this section, we will briefly discuss two methods that were used in the present study.

Nonsulfur-Containing VOC Measurements

We have developed an indirect HSGC method specifically to analyze methanol and other nonsulfur-containing VOCs in black liquors [13]. The method was initially developed by Drozd and Novak [16] for aqueous-solution analysis. It is based on the thermodynamic VLE and material balance of the VOC to be determined. Two sample vials, both filled with the same volume of sample solution, were used. A very small amount of concentrated analyte solution was then added to one of the vials. The volume of the solution added is very small compared to the volume of the original solution and, therefore, can be ignored. After phase equilibrium was established within each vial, HSGC analysis of each sample was conducted. It can be assumed that the analyte concentrations in these two sample vials are very low or the analyte is under infinite dilution (which is valid for most VOCs in pulp and paper mill streams even after the standard addition). Therefore, the analyte VLE partitioning in these two vials follows Henry's law, which connects the two independent headspace measurements as shown. Together with the material balance equation of the analyte, the following mathematical expression of the analyte concentration in the original sample can be obtained [13, 16]:

$$C_0 = \frac{C_S V_S}{(A_2 / A_1 - 1) \cdot V_{L0}} = \frac{C_S V_S}{(r_A - 1) \cdot V_{L0}} \quad (1)$$

C_0 is the concentration of the analyte to be determined, V_{L0} is the initial sample volume in the testing vial, and V_S and C_S are the volume and analyte concentration of the solution used for spiking (added to the testing vial) through the standard addition. r_A is the ratio of the GC signal peak areas A_2 and A_1 of the two HSGC measurements. Calibration is not needed with Eq. (2) for VOC analysis.

Volatile Organic Sulfur Compounds Measurements

We also developed a full evaporation (FE) HSGC technique for volatile organic sulfur compound analysis in black liquor [14] based on the pioneer work of Markelov and Guzowski [17]. It uses a very small sample size to achieve a near-complete transfer of analytes from a condensed matrix into a vapor phase in a very short period of time; therefore, it does not require sample pretreatment. It should be pointed out that complete evaporation of the condensed analyte is not necessary; only a near-complete transfer of the analyte into the vapor phase is required.

In the case of near-complete evaporation, material balance within the sample vial of the analyte can be expressed,

$$C_G \approx M_0/V_G \quad (2)$$

where C_G is the equilibrium concentration of the analyte in the vapor phase (headspace) of volume V_G and M_0 is the initial mass of the analyte in the sample. Therefore, the effect of sample matrix-dependent parameters is eliminated in Eq. (2).

Some special precautions were taken for the analysis of methyl mercaptan. Please refer to our previous publication [14] for details.

EMPIRICAL MODEL TO ESTIMATE VOCs

In this section, we will develop an empirical model to estimate the amounts of VOCs formed and evaporated (condensed) throughout different stages of a multiple-effect evaporator in a kraft mill. We assume that VOC loss due to evaporation is proportional to water loss with a proportionality coefficient k . Then, VOC remaining can be expressed as

$$m_i = m_i^0 - k\Delta m_w + \Delta m_i^G \quad (3)$$

where Δm_w is the water loss and Δm_i^G is formation of species i during black liquor evaporation.

By definition of solids content

$$S = \frac{m_s}{m_s + m_w} \quad (4a)$$

and

$$S^0 = \frac{m_s}{m_s + m_w^0} \quad (4b)$$

Water loss can be expressed as

$$\Delta m_w = m_w^0 - m_w = \frac{S - S^0}{S} \cdot \frac{1}{1 - S^0} \cdot m_w^0 \quad (5)$$

Because most VOCs have a boiling point that is lower than that of water, one can expect that the rates of vaporization of VOCs are much faster than the vaporization of water. As the vaporization proceeds, there will be fewer VOCs present in the liquor. To some extent, the amount of VOC lost will no longer be controlled by the vaporization process, but by the

VOC formation process. Therefore, the proportionality coefficient k is not a constant; rather, it varies with the extent of liquor evaporation process, i.e., time and temperature. Because $S - S^0$ is related to evaporation time and temperature, we assume that the k has the following functionality:

$$k = \xi' \left(\frac{1}{S - S^0} \right)^\tau \quad (6)$$

Eq. (6) indicates that k is inversely proportional to the extent of liquor evaporation. It should be pointed out that k in Eq. (6) is the averaged proportionality coefficient over the period when the liquor is concentrated from solids content S^0 to S .

The amount of VOC formed is also related to temperature and reaction time during evaporation. Furthermore, it can be approximated by an exponential decay function according to kinetics. We assume the following expression for methanol formation

$$\Delta m_i^G = \eta' [1 - \exp(-\alpha(S - S^0))] \quad (7)$$

Substitute Eqs. (5) – (6) into Eq. (3), and we have

$$\frac{m_i}{m_i^0} = 1 - \xi' \cdot \frac{(S - S^0)^{1-\tau}}{S} \cdot \frac{1}{1 - S^0} \cdot \frac{m_w^0}{m_i^0} + \frac{\eta'}{m_i^0} [1 - \exp(-\alpha t)] \quad (8)$$

or simply

$$\frac{m_i}{m_i^0} = 1 - \xi \cdot \frac{(S - S^0)^{1-\tau}}{S} + \eta \cdot [1 - \exp(-\alpha(S - S^0))] \quad (9)$$

RESULTS

Concentrations of methanol, MM, DMS, and MEK in the black liquor samples were analyzed. Figures 1 and 2 show the results of methanol, MEK, MM, and DMS in the black liquor samples collected at various stages of a multiple-effect evaporator. The data clearly show that the VOCs in the liquor decrease rapidly initially due to the removal of VOCs with water through evaporation; however, after further liquor concentration, the VOCs in the liquor remain at a constant level and even have a slight increase at high solids of about 40%. This indicates that VOC formation is occurring.

Least-squares fit of the analyzed data were conducted to get the parameters in Eq. (7) for the prediction of VOC formation and evaporation. The results are listed in Table 1. The comparisons of predicted and measured data are shown in Figs. 3-6. The measured VOCs in the liquor agree with those predicted. The prediction indicates that a significant amount of VOCs was formed during evaporation, i.e., about 65, 85, 40, and 80% of the initial methanol, MEK, MM, and DMS were formed when the liquor was concentrated from 18 to about 50% in solids.

Table 1: List of parameters of Eq. (7) for various VOCs.

	ξ	τ	η	α
Methanol	9.5	0.35	0.90	9.8
MEK	9.6	0.35	0.90	9.0
MM	6.0	0.35	0.36	43
DMS	7.5	0.35	0.88	11

SUMMARY

An empirical model has been developed for the prediction of methanol formation and partitioning between the vent and the liquor phase in kraft mill multiple evaporators. However, only the data analyzed in the liquor were used for model validation. Methanol data from the samples collected in the vents or condensate are needed to validate the model for accurate prediction of methanol formation and emission during black liquor evaporation.

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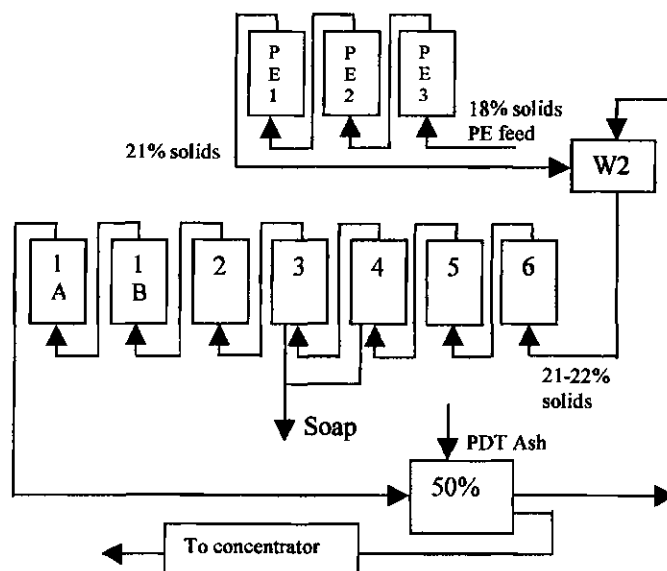


Fig. 1 A schematic diagram of the multiple-effect evaporator.

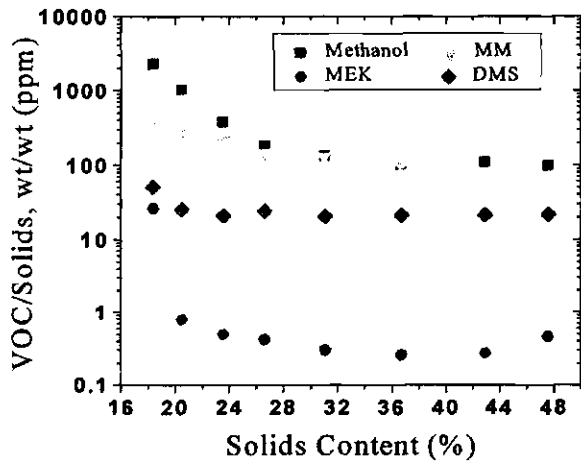


Fig. 2 VOC remaining in the liquor/mass solids

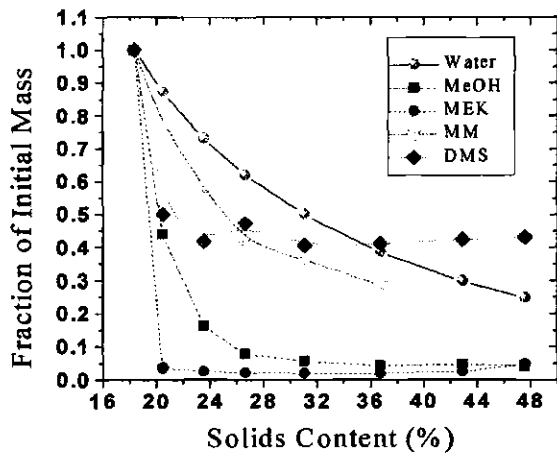


Fig. 3 Fraction of VOC remaining in the liquor.

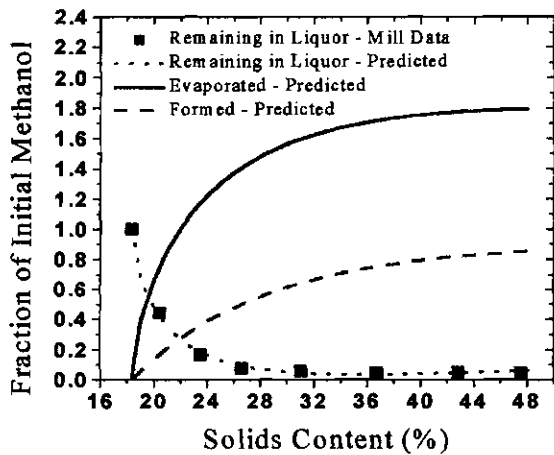


Fig. 4 Fractions of methanol evaporated and formed as of initial amount in the liquor.

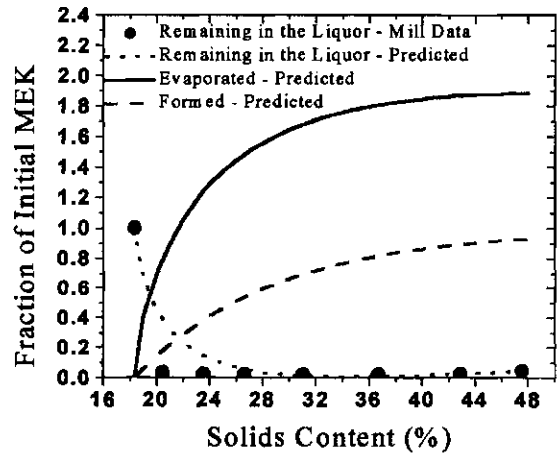


Fig. 5 Fractions of methyl ethyl ketone (MEK) evaporated and formed as of initial amount in the liquor.

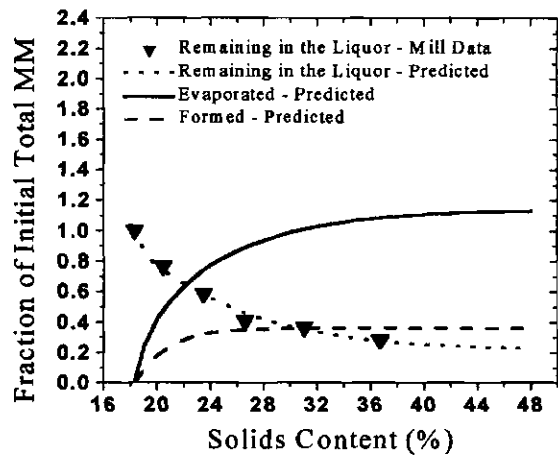


Fig. 6 Fractions of methyl mercaptan (MM) evaporated and formed as of initial amount in the liquor.

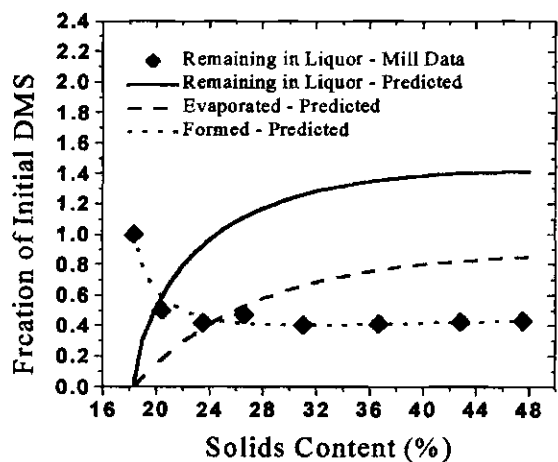


Fig. 7 Fractions of dimethyl sulfide (DMS) evaporated and formed as of initial amount in the liquor.