

Novel Testing System for Evaluating the Thermal Stability of Polyol Ester Lubricants

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This paper reports the development of a novel testing system for evaluating the thermal stability of polyol ester lubricants. The thermal degradation of three pentaerythritol tetrapelargonate based lubricants in the temperature range of 180–220 °C was studied using the developed comprehensive system. The system includes (1) a high-temperature quartz crystal microbalance for the real-time, in situ measurement of the solid residual deposition on metal surfaces and the viscosity change of thermally stressed liquid phase; (2) an on-line gas chromatograph for monitoring the volatiles generation in real time; and (3) an off-line gel permeation chromatograph for determining the molecular weight distribution of the liquid-phase products. The results indicate that the strategy can provide an integrated picture of the thermal stability of lubricants by providing quantitative, real-time, in situ information on gas-, liquid-, and solid-phase products during the thermal decomposition of the lubricants.

Introduction

Polyol ester based lubricants represent one of the most important types of synthetic lubricants.¹ Their high thermal stability and good lubricating properties have resulted in a wide range of applications from the textile industry to gas turbine motors.^{2,3} However, the trend of advanced technologies toward increased operating temperatures results in a critical need for the exploration of lubricants for extreme environments. Under elevated temperatures, thermal breakdown of the lubricants occurs, accompanied by the generation of unwanted degradation products. In addition to the toxic volatiles and viscous liquids with higher-molecular-weight constituents, a more troublesome aspect of the breakdown is the formation of a varnish or char. These organic residues that are very difficult to remove from hot machine surfaces.^{1,4} These problems have prompted studies to understand the degradation mechanisms of lubricants and to develop predictive methodologies for describing the thermal stability of lubricants.^{1,3,5–12}

Traditionally, the thermal stabilities of liquid organic materials have been evaluated by (1) the rate and extent of weight loss at a specific temperature and (2) the value of the smoke point.² Along with the significant developments in analytical techniques, a number of new approaches, such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and chromatographic and spectroscopic techniques, have been applied to study the thermal properties of lubricants. Generally, TGA is used to profile weight loss due to chemical and physical phenomena occurring in the materials.^{10,11} DSC measurements provide relevant information on the

maximum utilization temperature of the materials.^{11,12} Chromatographic and spectroscopic techniques, such as gel permeation chromatography (GPC), gas chromatography/mass spectrometry (GC/MS), and FT-IR and NMR spectroscopies, have been used to determine the constituents of degraded products in both volatile and liquid phases.^{3,5–8} However, because of the lack of a sensitive evaluation tool for measuring small amounts of deposits while materials are thermally stressed, previous experimental tests were generally conducted under accelerated test conditions. Under such accelerated test conditions, the temperature or oxygen concentration exceeds the value expected in a real material system.¹³ In addition, the mass deposition rate is commonly determined after the test, resulting in only an estimated average deposition rate over the duration of a test.^{4,14}

The quartz crystal microbalance (QCM) has proven to be a novel analytical method for the in situ measurement of deposition and adsorption of quantities ranging from the sub microgram level down to the nanogram level.¹⁵ The high sensitivity and the simple relationship between mass and frequency make the QCM an excellent tool for the study of mass deposition on surfaces. The QCM was originally used for microgravimetric studies in a vacuum system.¹⁶ The later development of the QCM theories has enabled its use as a microweighing device in gas and liquid phases.^{17,18} However, although the QCM has recently been successfully used to investigate solid deposition on metal surfaces for a series of jet fuels heated to temperatures of 125–200 °C,^{19,20} there are a limited number of studies at extreme conditions (e.g., high viscosity of liquid and elevated temperatures) because of the challenges associated with QCM operation.

Because the degradation of a lubricant at elevated temperatures is a very complex process accompanied by the generation of products in the gas, liquid, and solid phases, it is critical to develop a systematic method for evaluating the process in real time. Therefore, the

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purpose of the present study was to design a comprehensive approach to provide a dynamic picture of the generation of degraded products in gas, liquid, and solid phases while the lubricant is thermally stressed. This paper presents the development of a novel testing system that uses a QCM, combined with an on-line gas chromatograph and an off-line gel permeation column, to conduct in situ, real-time evaluation of the thermal degradation of lubricants. The challenge in this research is to operate the QCM at elevated temperatures in a highly viscous liquid phase. Experiments have been performed that demonstrate the capability of the system in monitoring the thermal stability of three polyol ester lubricants heated to the temperature range of 180–220 °C. The unique combination of the analytical techniques presents an ideal system for the systematic study of the thermal degradation of lubricants. The information obtained from this novel system will provide a foundation for a new class of lubricants and enable predictions of their thermal stability.

2. QCM Theory

A QCM sensor consists of a thin wafer of quartz, each of the two major faces of which have been partially predeposited with metal film electrodes. Because of the piezoelectric properties of the quartz, a voltage applied across the electrodes leads to a shear deformation of the quartz crystal. The fundamental frequency of a quartz crystal resonator is dependent on its own material properties and the properties of the associated metal electrodes. The fundamental frequency shift can occur because of contributions from (1) the mass loading on the electrode surfaces, (2) the properties (i.e., density and viscosity) of the fluid in contact with the crystal, (3) the temperature and pressure of the crystal environment, and (4) the surface roughness of the electrodes. The total frequency shift observed when a crystal is immersed in a fluid can be written in general form^{21,22} as

$$\Delta F = F - F_0 = \Delta F_m + \Delta F_\eta + \Delta F_T + \Delta F_P + \Delta F_r \quad (1)$$

where F is the measured frequency of quartz, F_0 is the unperturbed fundamental resonant frequency, ΔF_m reflects the mass loading, ΔF_η is caused by the density and viscosity of the fluid, ΔF_T is the temperature effect, ΔF_P relates to the pressure, and ΔF_r results from the roughness of the crystal electrode surface.

The crystal can be used effectively as a microbalance because a small change in mass on the surface of the crystal results in a proportional shift in resonant frequency. This relationship was first described by Sauerbrey with the equation¹⁶

$$\Delta F_m = -2nF_0^2 \Delta m / (\mu_q \rho_q)^{1/2} \quad (2)$$

where Δm is the loaded mass per unit surface area; μ_q and ρ_q are the quartz shear stiffness and mass density, respectively; and n is the number of sides of the crystal in contact with liquid or coated by a mass layer.

The effect of viscosity, ΔF_η , describes the interaction of the vibrating crystal with a viscous medium. This interaction leads to a decrease in frequency that is proportional to the square root of the product of the viscosity, η , and density, ρ , of the fluid in which the resonator is immersed. For a Newtonian fluid, the

Table 1. General Properties of Lubricants

lubricant	viscosity ^a (cP)	flash point ^b (°C)	specific gravity
EM	62.3	275	0.9650
AF	60.2	282	0.9600
ST	87.7	>93.9	0.9615

^a Determined using a dynamic stress rheometer at 25 °C. ^b From producers.

frequency shift can be expressed by¹⁸

$$\Delta F_\eta = -nF_0^{3/2} (\rho\eta/\pi\mu_q\rho_q)^{1/2} \quad (3)$$

The third term of eq 1, ΔF_T , expresses the contribution of temperature to the overall frequency change. The absolute temperature limit for the QCM measurements is the Curie point of quartz (573 °C), the point at which the piezoelectric properties disappear.²³ Above 400 °C, the temperature dependence of the quartz resonator frequency becomes significant; hence, the precision of the mass measurement is reduced at high temperatures. Two different approaches can be utilized to compensate for the effect of temperature: (1) using two QCM crystals, a shielded reference crystal and a working crystal, and (2) modeling.^{24,25} In the present work, surface mass measurements were made only during the constant-temperature (± 0.1 °C) portion of an experimental run. The contribution from temperature is negligible at a fixed temperature. In addition, because the experiments were conducted at ambient pressure and polished crystals were used, the frequency shifts caused by the effects of pressure (ΔF_P) and roughness (ΔF_r) can be neglected.²⁶

If the product of the viscosity and density of the fluid is constant, the change in resonant frequency, ΔF , can be used directly to calculate mass accumulation by rewriting eq 2 as

$$\Delta m = -[2.21 \times 10^5 \text{ g}/(\text{cm}^2 \text{ s})] \Delta F / F_0^2 \quad (4)$$

If the fluid properties change during the experimental run, the measurement of the resonant frequency alone cannot distinguish changes in the deposited mass on the surface from changes in liquid properties. An independent measurement is required to resolve or separate responses due to surface mass accumulation from changes in liquid properties. The motional resistance of the crystal, R , arising primarily from losses caused by viscous coupling to the adjacent liquid, is a convenient measure of crystal damping. The motional resistance is proportional to $(\rho\eta)^{1/2}$, and the relationship can be written as^{27,28}

$$R = \frac{\pi n}{8K^2 C_0} \left(\frac{\rho\eta}{\pi F_0 \mu_q \rho_q} \right)^{1/2} \quad (5)$$

where K is the quartz electromechanical coupling coefficient and C_0 is the static capacitance of the device.

3. Experimental Section

3.1. Materials. Three commercial-grade pentaerythritol tetrapelargonate based lubricants, EM, AF, and ST, were obtained from three lubricant manufacturing companies. In initial degradation studies, the lubricants were used without any further purification. The general properties of the lubricants are listed in Table 1. These

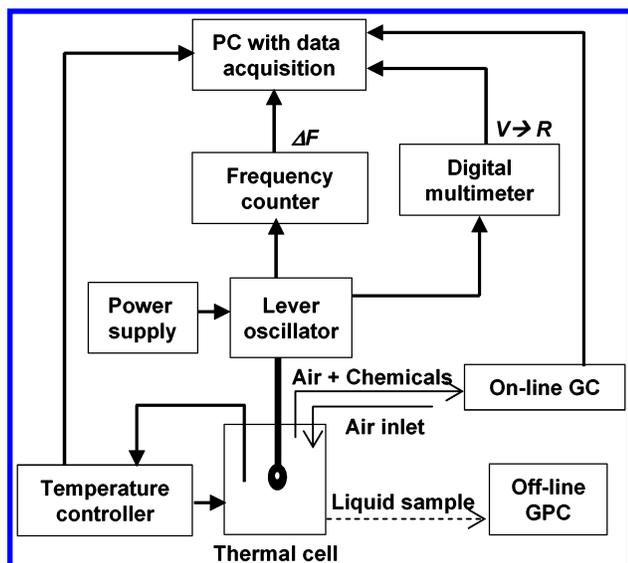


Figure 1. Integrated QCM surface and bulk experimental system.

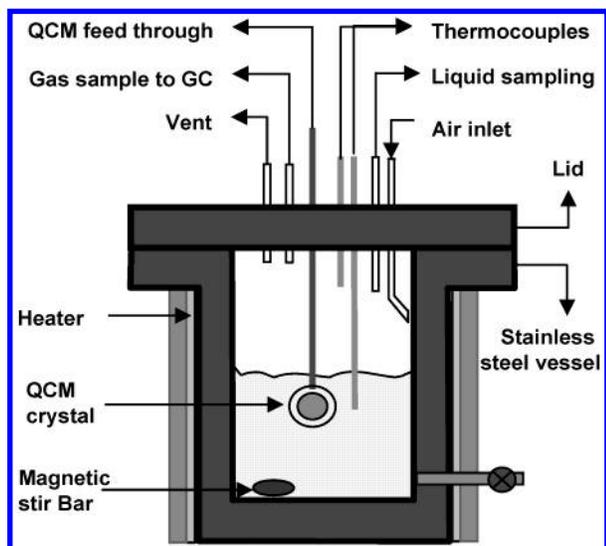


Figure 2. Schematic diagram of thermal cell.

lubricants were selected because of the different responses to thermal stress they each exhibit in actual textile manufacturing processes.

3.2. System Description. The experimental system shown in Figure 1 was designed for evaluating the thermal behavior of lubricants by providing information on the volatilization of liquid components to the gas phase, the degradation of the liquid phase, and the deposition of solid residues on metal surfaces when the lubricants are heated. The system includes four major parts: (1) a thermal cell for heating lubricants, (2) a high-temperature QCM system for the real-time, in situ monitoring of the solid residual deposition and the associated viscosity change of degraded liquid lubricants, (3) an on-line GC analytical system for determining the real-time gas-phase constituents, and (4) an off-line GPC system for measuring the molecular weight distribution of the liquid-phase products. Detailed descriptions about each part of the system are provided in the following paragraphs.

The thermal cell (shown in Figure 2) is a 215-mL stainless steel vessel (6-cm i.d. and 7.6-cm height) with a thick stainless steel lid on it. A custom-built QCM electrical feedthrough, a liquid-phase sampling port,

three gas-phase inlet and outlet ports, and two thermocouple probes (one is immersed in the liquid phase, and the second is suspended in the gas phase) are mounted on the lid. A Teflon O-ring is used to seal the thermal cell. The thermal cell is heated with a custom-made heater that is regulated by a temperature controller (Barnant Company) via the thermocouple that is immersed in the liquid. The temperature of liquid inside the thermal cell can be within ± 0.1 °C over the experimental temperature range (180–220 °C).

The quartz crystal is mounted to the QCM feedthrough and driven by an oscillator circuit. The crystals used are 5-MHz AT-cut wafers with polished gold electrodes (International Crystal Manufacturing Co. Inc.). The crystal dimensions are 1.36 cm for the blank diameter and 0.66 cm for the electrode diameter. A Lever oscillator (International Crystal Manufacturing Co. Inc.) utilized to drive the quartz crystals is specially designed for QCM operation in viscous liquids.²⁹ The oscillator has two outputs: (1) a frequency output that is read by an Agilent 225-MHz universal frequency counter (model 5313A) and (2) a dc voltage signal, proportional to motional resistance, R , that is measured by a digital multimeter (model 34401A, Agilent Technologies). The in situ, real-time mass accumulation and viscosity change of the lubricant can be obtained simultaneously from the resonant frequency and dc voltage.

An HP 5890 gas chromatograph system equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors is used to detect permanent gases (CO, CO₂, N₂, and O₂) and organic gases (paraffin, olefin, etc.), respectively. A 10-port Valco valve is used for on-line sample injection through two 250- μ L sample loops. A 60/80 Carboxen-1000 column and a HayeSep-Q column (Supelco) are utilized to separate the permanent gases and organic gases, respectively. Helium is used as the GC carrier gas. The Scotty Standard Gases (permanent gases CO, CO₂, N₂, and O₂; paraffins C1–C6; olefins C2–C6) obtained from Supelco and liquid standards (pentane, hexane, heptanes, and octane) are employed for calibrating the GC system.

A Waters Breeze liquid chromatograph (GPC) was used to evaluate the molecular weight distribution of the liquid-phase products. The unit is combined with an ultraviolet (UV) absorbance detector and a differential refractive index (RI) detector. The GPC columns used were Styragel HR0.5 (effective molecular weight range = 0–1000) and Styragel HR2 (effective molecular weight range = 500–20000) obtained from Waters. The temperature of columns was maintained at 30 °C. The degraded lubricant samples dissolved in tetrahydrofuran (THF) at known mass concentrations were injected in 100- μ L quantities after filtration. The molecular weights were calculated from column calibrations performed under the above conditions using a series of poly(ethylene glycol) standards with molecular weights ranging from 106 to 4042 (Waters).

3.3. Experimental Protocol. In a typical run, the thermal cell was filled with 136 mL of lubricant. The QCM crystal was suspended vertically in the lubricant to minimize gravitational effects on the deposition (Figure 2). A magnetic stir bar and stirrer were used to minimize spatial temperature gradients. Because of the importance of oxygen in the thermal degradation of lubricants and the fact that lubricants are utilized in an air environment in actual textile processes, pre-heated dry air was continuously fed into the cell at a

constant flow rate of 21.0 mL/min. The air that exited through the outlet port together with the volatile components was sent directly to the GC injection valve. The heater was turned on after the thermal cell was sealed. At this point, computer data acquisition was initiated. The computer monitored the quartz crystal frequency, the dc voltage signal of the crystal damping, and the temperatures in both the liquid and gas phases at 5-s intervals. The GC analysis was carried out approximately once per hour. The volatile component profiles and their variation with heating temperature and heating duration were obtained from the GC data. The thermal degradation tests were conducted at ambient pressure and constant temperatures of 180, 200, and 220 °C. The experimental runs were performed for 10–23 h. Independent runs were carried out under exactly the same conditions as above to collect degraded liquid and gas samples for GPC and GC/MS analyses. The liquid samples were collected after specified heating periods. The gas samples were collected by cooling and condensing the exiting overhead gases with dry ice.

4. Results and Discussion

4.1. Deposition of Solid Residues on the Metal Surface.

In this section, the reliability of the QCM technique under extreme conditions (i.e., higher viscosity and elevated temperature) and the QCM system used in the present work are discussed, and then the QCM responses indicating thermal degradation of lubricant are described. The rate and extent of mass accumulation results obtained from QCM data are also presented and discussed.

4.1.1. Reliability of the QCM Technique under Extreme Conditions.

The accuracy, resolution, and reproducibility of the QCM sensor in quantifying mass accumulation in jet fuel fluids at elevated temperatures were established by Klavetter et al. and Zabarnick and Grinstead.^{19,30} Klavetter et al. compared the deposit thickness calculated from the QCM data with the thickness independently determined from ion sputtering/Auger data. The percent differences of the deposit thicknesses determined by the two methods ranged from 13 to 17%. The resolution of the QCM for measurement of the solid deposits was reported to be 0.1–0.3 $\mu\text{g}/\text{cm}^2$ during the thermal stressing of jet fuel fluids. The reproducibility of the mass deposition measurements on fuels was limited to $\pm 20\%$ for the QCM technique.

The temperature control is the major parameter in determining the resolution associated with mass accumulation on the QCM. As described in QCM theory, the large temperature dependence of the crystal resonant frequency at elevated temperatures results in a reduced precision of the mass measurement at higher temperatures. The temperature dependence of the resonant frequency in air for the crystals used in the present work was tested. At room temperature (25 ± 0.1 °C), the fluctuation of the resonant frequency in air is less than ± 1 Hz. In the temperature range of 180–220 °C (temperatures used in the present experiments), the average frequency shift is 49.6 Hz per degree. Thus, the temperature fluctuation of ± 0.1 °C in air will result in a ± 4.96 Hz fluctuation of frequency. However, in the actual lubricant degradation tests carried out at constant temperatures of 180–220 °C (± 0.1 °C), the maximum frequency fluctuation of ± 15 Hz was measured. This frequency fluctuation results in a limit of the resolution for mass accumulation measurements esti-

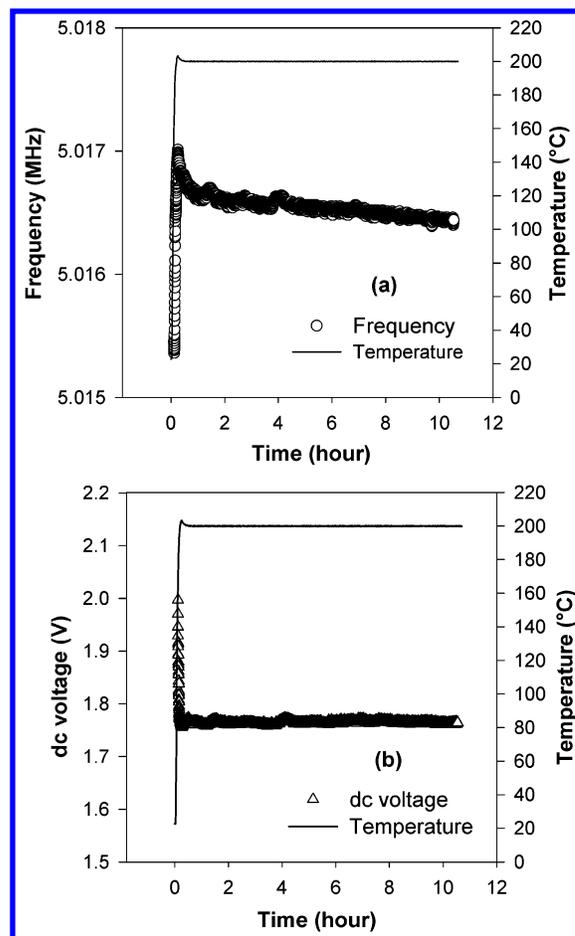


Figure 3. QCM responses to the thermal degradation of a lubricant (EM, 200 °C): (a) frequency, (b) voltage.

mated at ± 0.133 $\mu\text{g}/\text{cm}^2$. This value is comparable to the results given by previous studies described above.^{19,30} In addition to the fluctuation of the temperature, the effects of the possible surrounding electric fields and the inappropriate installation and insufficient cleaning of the quartz crystal are also potential sources of a reduction in the precision of the measurement. For most of the runs in the present work, good reproducibility was obtained. The reduced reproducibility of some runs could be attributed to poor electrode surface conditions of the quartz crystals.

4.1.2. QCM Responses to the Thermal Degradation of Lubricants.

The profiles of QCM frequency and damping voltage combined with temperature for a typical experimental run are shown in Figure 3a and b, respectively. This particular run is for lubricant EM at 200 °C for 10 h. In these plots, zero on the time axis is defined as the moment when the heater is turned on. In the first 30 min, the temperature rapidly rises to slightly higher than the set point and then stabilizes at the set point. The temperature stays constant within ± 0.1 °C for the 10-h test period. According to eq 5, a higher viscosity results in a higher motional resistance. Because of the high viscosity of the lubricant at lower temperatures in the initial heating period, the resonator immersed in the lubricant ceased to vibrate. The resonators utilized in the present work provided valid data when the lubricant temperature reached a value of approximately 150 °C. The measured QCM frequency and damping voltage closely follow the temperature profile as the frequency of quartz and the viscosity of the lubricant are extremely sensitive to small changes

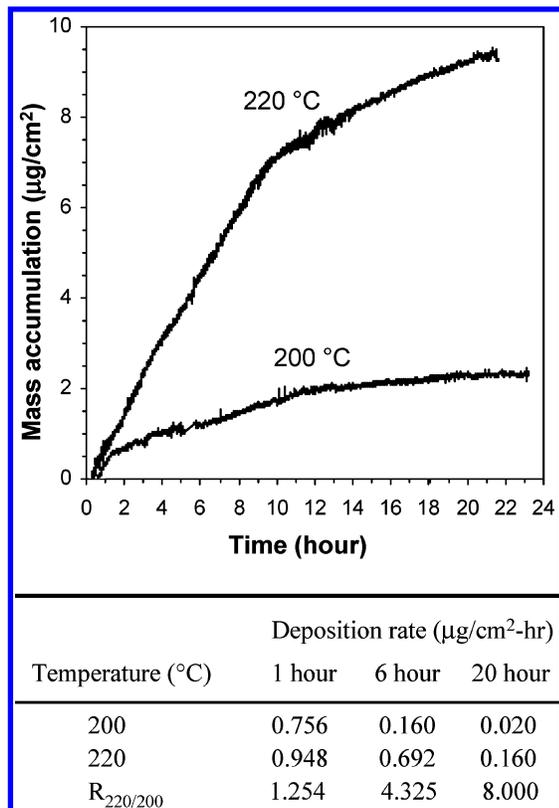


Figure 4. Mass accumulation of EM at 200 and 220 °C.

in temperature. The QCM frequency increases in the initial temperature-rising period and peaks when the associated temperature overshoots. In the constant-temperature portion of the experiment, the QCM frequency decreases. The measured damping voltage decreases as the temperature increases because of the reduced viscosity of the liquid lubricant at higher temperatures. The damping voltage remains relatively constant in the constant-temperature period of the run. This corresponds to a condition in which the product of the viscosity and density of the lubricant remains relatively constant (eq 5). Therefore, the mass accumulation on the electrode surfaces can be related to the frequency change through eq 4. It should be pointed out that the data shown in subsequent plots include only data for the constant-temperature period of the experiment. The major limit of the system comes from the viscosity of the liquid medium in which the crystal resonator can be oscillated. This limit can be improved by improving the crystal figuration and the circuit oscillator.

4.1.3. Measurement of Solid Residue Deposition.

Previous investigations have proposed mechanisms related to the thermal degradation of oils (ester lubricants, mineral oils, fuels, etc.) in the presence of oxygen.^{1,3,4,8} It is generally agreed that the primary oxidation products formed in the system undergo further polymerization to form high-molecular-weight oxypolymeric compounds that form deposits.⁸ However, the studies related to the solid residue deposition either were limited in deposit-forming tendency or utilized accelerated test conditions.^{4,31} In this study, the in situ accumulation of mass was measured for the three lubricants to determine the effect of temperature on mass deposition and demonstrate the capability of the QCM system to quantitatively evaluate lubricant thermal stability. Figure 4 shows the time-dependent mass

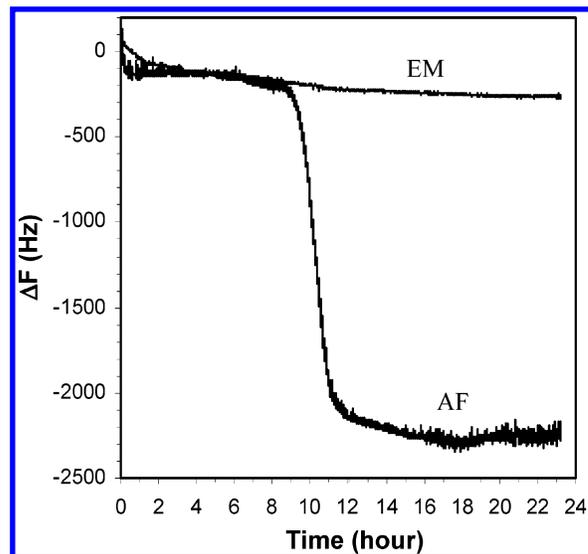


Figure 5. Time-dependent frequency change of QCM in EM and AF at 200 °C.

accumulation (calculated by using eq 4) on the crystal electrodes obtained at isothermal conditions for lubricant EM heated at 200 and 220 °C. The time zero here is defined as the time at which the temperature of the lubricant reached the desired set-point value. The deposition rates were calculated at 1, 6, and 20 h from the slopes of associated mass accumulation data and are listed in Figure 4 as well. The term $R_{220/200}$ is defined as the ratio of deposition rates at 220 and 200 °C. It is found that the higher temperature greatly enhanced the deposition of residues on the metal surfaces. The deposition rate decreases with the heating time at both heating temperatures of 200 and 220 °C; the decrease is more pronounced at 200 °C. The data shown in Figure 4 represent the averages of three runs at each temperature. The error is less than $\pm 10\%$ for data after 2 h of heating. The reduced reproducibility observed in the initial stages is attributed to the overheating and/or the initially interfacial stabilization between the crystal surfaces and the liquid lubricant.

4.1.4. Evaluation of Lubricant Degradation Using ΔF . According to QCM theory, the resonant frequency shift of a QCM crystal with ideal smooth electrode surfaces under conditions of constant temperature and pressure is caused solely by mass deposition on the electrode surface and changes in the product of the liquid density and viscosity (eq 1). Generally, higher-molecular-weight compounds will be generated as the thermal degradation of a lubricant proceeds. Hence, there is a tendency for increases in both mass deposition and the product of the liquid density and viscosity. Because both mass deposition and crystal damping result in a decrease of resonant frequency (eqs 2 and 3), the frequency shift, ΔF , becomes a convenient comprehensive indicator for evaluating the thermal degradation of lubricants. This is especially meaningful in cases in which detailed quantitative information on the residual deposits and the changes in viscosity are not required. Figure 5 shows the time-dependent frequency shifts of lubricants EM and AF at 200 °C. No significant difference was observed in the first 9 h of heating. However, after 9 h, there was a sudden drop in frequency of the crystal in AF, which distinguishes AF from EM in its response to thermal stressing. Similar phenomena were also observed in the degrada-

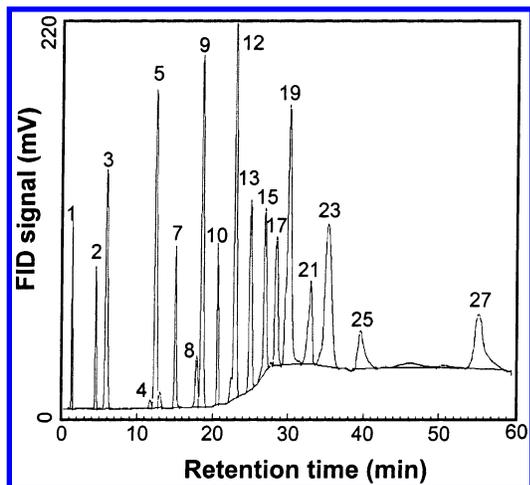


Figure 6. GC chromatogram (FID) of volatiles released from EM heated at 200 °C for 1 h. Peaks 1, 3, 5, 9, 12, and 15 represent methane, ethane, propane, butane, pentane, and hexane, respectively. Peaks 2, 4, and 8 represent ethylene, propylene, and butene, respectively.

tion experiments carried out on AF at different temperatures (180 and 220 °C), but this phenomenon did not occur in the experimental runs for either EM or ST. Studies of the deposit-forming tendency of oils have shown that oil impurity is one of the important parameters controlling the appearance and rate of deposit formation.^{8,31} Although both lubricants consist of the same base component, pentaerythritol tetrapelargonate, the structural characteristics and the trace components in each are different. This is due to the difference in the raw materials and the synthesis processes utilized by different manufacturers. The variation of the impurities between EM and AF is thought to be the major reason for their significantly different QCM resonant frequency responses. The shape of the plot of frequency shift versus heating time for AF agrees well with the S-shaped deposit formation curve of thin film oxidation of mineral oil reported by Tseregounis.⁴ The sharp drop of the QCM frequency response in AF at a heating time around 9 h suggests an induction time for deposit formation. The detailed investigation of these mechanisms is ongoing in our group.

4.2. Generation of Volatiles. GC/MS analyses of the cooled condensed overhead gas samples show that more than 60 organic compounds exist in the volatilized gas phase; these are generated by heating of the lubricants at 200 °C for 7 h in the thermal cell. The following is a summary of the major compounds identified: paraffins with carbon numbers 1–9, aldehydes with carbon numbers 1–9, methyl ketones with carbon numbers 3–9, carboxylic acid with carbon numbers 1–9, and carboxylic acid methyl esters with carbon numbers 4–11. Small amounts of olefin and alcohol are also detected in the GC/MS system.

The on-line GC system enables the real-time composition analysis of the volatilized phase. The time dependence of concentrations of individual components in the overhead gas, and the effect of temperature on the concentration were measured. Figure 6 shows a typical chromatogram that indicates the real-time composition of the overhead gases at the time point of 1 h. As depicted, low-molecular-weight paraffin and olefin (peaks 1–15) are separated well with the column used, whereas peaks 19–27 are mixtures of other polar and nonpolar compounds. A comparison with the chromatograms

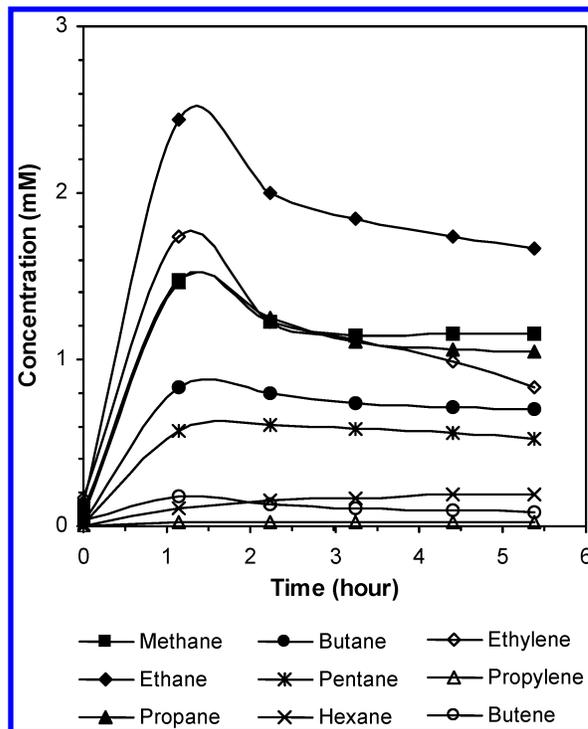


Figure 7. Time-dependent concentrations of compounds volatilized upon heating of EM at 200 °C.

obtained at different heating times indicates that the types of volatilized organics are similar although the generation rates of individual compounds change with heating time.

Figure 7 shows an example of the changes in the concentrations of some paraffins and olefins during heating of lubricant EM at 200 °C. As depicted in Figure 7, the concentrations of paraffins in the gas phase are very low at time zero. As the heating time increases, the concentrations of paraffins increase quickly. After reaching a maximum point of the concentration, the values start to decrease. This phenomenon is more pronounced with smaller paraffin compounds than with larger ones. This indicates that more smaller paraffin were generated at the earlier stage of EM decomposition.

Figure 8 shows the effect of temperature on the real-time concentrations of (a) ethane and (b) olefin ethylene generated by heating EM at three different temperatures. The rate of ethane release increases with increasing heating temperature. The same trends were also found for other paraffins. However, a completely different effect of heating temperature on ethylene concentration was observed, i.e., the rate of generation decreased with increasing heating temperature. The dynamic information obtained from the on-line GC analysis will be useful in investigations of the degradation mechanisms of lubricants.

In addition to the organic gases, CO₂ and CO are also detected by the thermal conductivity detector. Bakunin and Parenago reported that the oxidation process of polyol ester was accompanied by the evolution of H₂ as well as CO₂ and CO.¹ Because helium was used as the carrier gas in our GC experiments, H₂ could not be detected.

4.3. Polymerization of Bulk Lubricant. In addition to the release of volatiles and deposition of solid residues, the molecular weight distribution in the bulk liquid phase also changed when the lubricants were

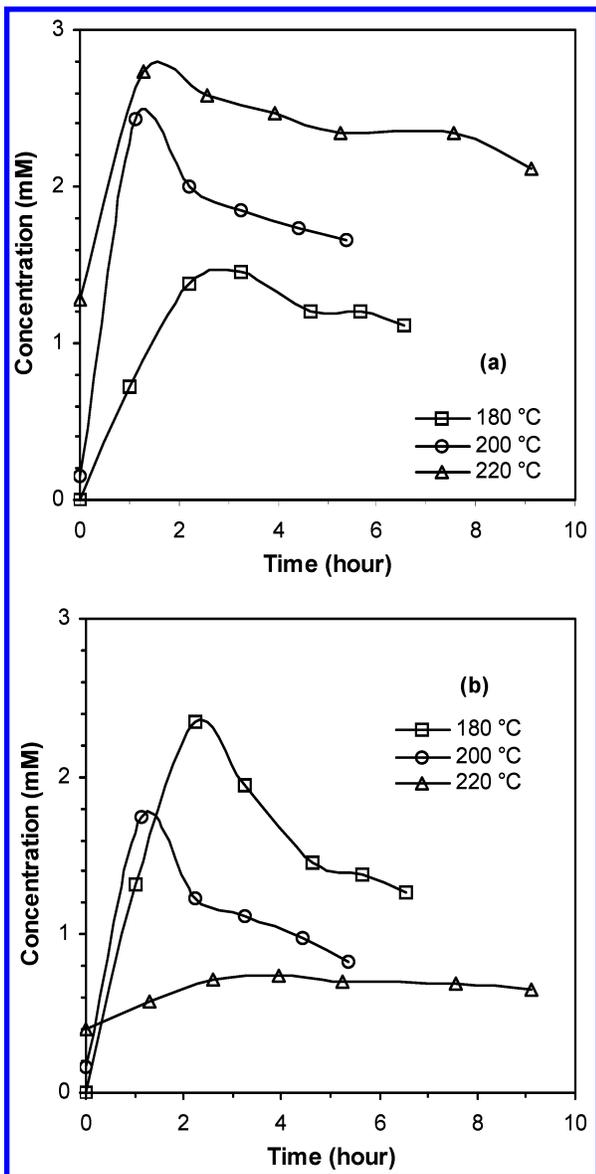


Figure 8. Effect of temperature on the generation of volatilized compounds from EM degradation: (a) ethane, (b) ethylene.

thermally stressed. Figure 9 shows typical chromatograms of EM before heating (original sample) and after 23 h of heating at 200 °C. The primary peak appearing at a retention time of around 14.6 min corresponds to the ester base stock pentaerythritol tetrapelargonate. The small peak emerging earlier than the primary peak in the chromatogram of the original sample represents a trace component with a higher molecular weight included in the original EM. Comparing the chromatogram of heated lubricant to that of original lubricant, one can see that the primary peak has diminished, whereas the higher-molecular-weight peak has grown. To quantify these changes, the percent areas for the primary peak and higher-molecular-weight peak occupied in the sum of these two main peaks were calculated and are plotted versus the heating time in Figure 10. The same method was adopted by Jones and Morales in their work on thermal degradation of gas-turbine engine lubricants.³ The data for the primary peaks are shown in Figure 10a, and those of the higher-molecular-weight peaks are given in Figure 10b. These results indicate that the progressive loss of primary ester and formation of higher-molecular-weight materi-

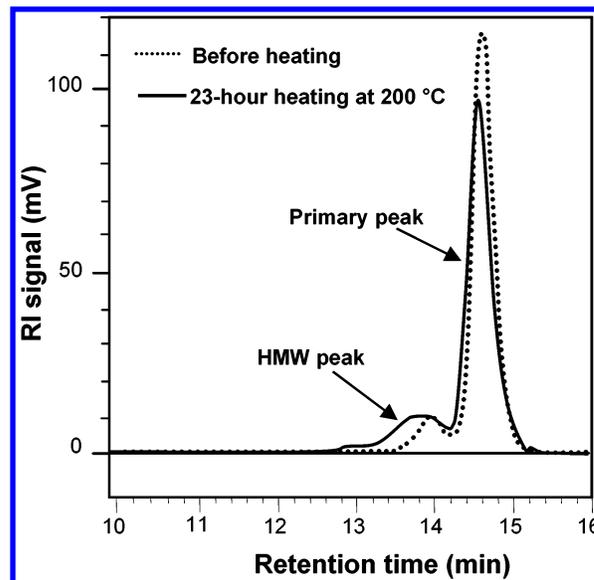


Figure 9. GPC chromatograms of EM. HMW = higher molecular weight.

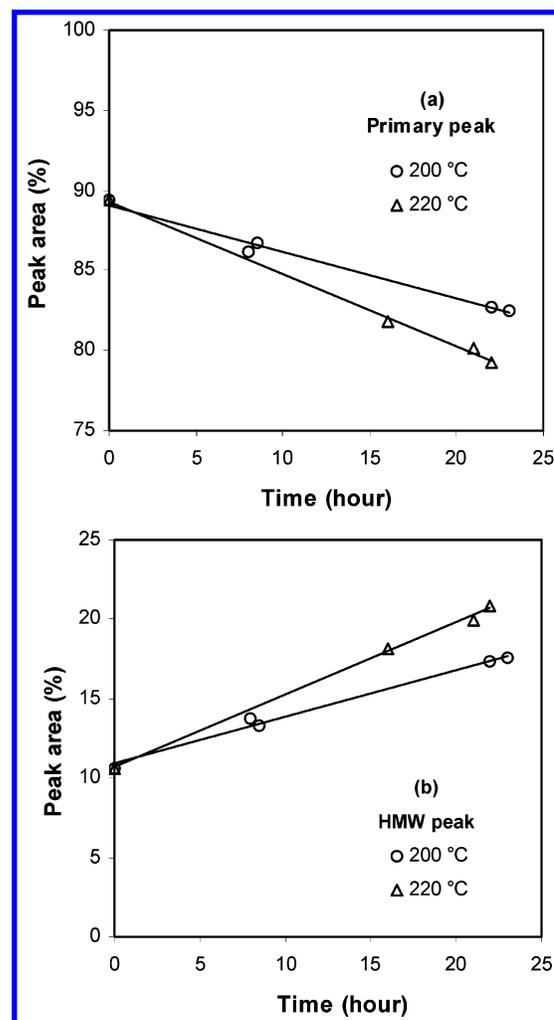


Figure 10. Time dependence of GPC chromatogram area for (a) primary and (b) HMW (higher-molecular-weight) peaks of EM at 200 and 220 °C.

als occurred with heating time. In addition, higher rates of degradation of the base stock ester and of formation of higher-molecular-weight materials were observed at 220 °C. This demonstrates that the higher temperature

accelerates the degradation of EM. This degradation mechanism is in agreement with the results obtained from the QCM deposition and the GC volatiles evolution measurements.

5. Conclusions

The research described herein represents a comprehensive analytical approach that combines a fundamental understanding of interfacial and bulk properties in an effort toward the development of a mechanism for lubricant degradation. The designed experimental testing system is a unique combination of a QCM, an on-line gas chromatograph, and an off-line gel permeation apparatus. The integrated system was successfully utilized to evaluate the thermal behavior of three polyol ester based lubricants at temperatures of 180, 200, and 220 °C. Good reproducibility of the measurements was obtained.

Summarizing the results obtained from an evaluation of the thermal degradation of three polyol ester lubricants leads to the following conclusions regarding the advantages of using the developed system:

(1) The system can simultaneously provide information on the generation of gas-, liquid-, and solid-phase byproducts quantitatively and dynamically from the same set of experiments, especially the QCM and the on-line gas chromatograph, which present the real-time degradation results.

(2) The QCM continuously provides in situ changes in the deposition of the solid residues and in the properties of the bulk lubricant (i.e., the product of viscosity and density) in real time under conditions that are very close to those of the actual lubricant system. These tasks are difficult to achieve using other existing methods.

(3) Furthermore, the frequency shift, ΔF , measured with the QCM can be used as a quick effective indicator for evaluating the extent of lubricant degradation based on the multiple effects of major decomposition factors such as the generation of higher-molecular-weight materials, the deposition of solid residues, and the increase in the bulk lubricant viscosity.

(4) The developed system can be extended to thermal degradation studies for other viscous liquid materials.

The results clearly demonstrate the validity of the developed system as a tool for the systematic evaluation of the thermal stability of polyol ester lubricants. The quantitative dynamic information on the generation of gas-, solid-, and liquid-phase products will provide a foundation on which to evaluate the effects of additives on lubricant performance in extreme environments.

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