MEASUREMENTS OF VAPOR PRESSURES OF COAL TARS USING THE NON-ISOTHERMAL KNUDSEN EFFUSION METHOD

Vahur Oja and Eric M. Suuberg
Division of Engineering
Brown University, Providence, RI, 02912

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INTRODUCTION

Vapor pressures of high molecular weight thermal decomposition products of coals (i.e., tars) are sometimes an important parameter in modeling the combustion behavior of the coals. The extent to which the tars can vaporize, before retrograde reactions reincorporate them into a char, plays a key role in determining the flux of combustibles to the flame front. This is reflected in various pyrolysis models [1-8]. There has been a lively debate in the coal pyrolysis literature concerning what values to assume for the vapor pressures of coal tars, since there have never been actual measurements of this property. What relevant data have been available have come from highly hydrogenated coal liquids [9] or from pure model compounds, and uncertainties of an order of magnitude have not been uncommon. The significance is that models of the coal pyrolysis tar yield are quite sensitive to this input parameter. Comparisons of the behavior of various proposed correlations are offered elsewhere [5,10].

In this study, the vapor pressures of primary coal tars have been examined using the Knudsen Effusion method, modified for application to mixtures containing components with a wide range of volatilities. The Knudsen effusion technique was selected because of the thermally labile nature of the primary tars (those that have not undergone secondary cracking). This requires that the vapor pressures be determined at temperatures well below those of pyrolysis, i.e., below 250 °C. This, in turn, means that the vapor pressures will be very low, because the tars have molecular weights of several hundred dalton.

EXPERIMENTAL

The Knudsen Effusion Technique for Vapor Pressure Measurement

The vapor pressures of actual coal tars and model "tars", consisting of mixtures of PAH, are measured, using a molecular effusion/TGA technique. The various so-called "effusion" methods are based on the molecular effusion of a vapor from a surface, or through an orifice [11]. Of these methods, that which has been selected for use here, is the Knudsen method [12,13], in which a substance of interest effuses through a small pinhole of known area, in an otherwise sealed container or cell. The Knudsen method is used for the measurement of low vapor pressures in the range from 1 to 10^{-6} torr, under molecular flow conditions. This ideally requires that pressures inside and outside the sample cell are low enough that the frequency of collisions of vapor molecules with gas phase species are low in comparison with the frequency of collisions with the cell. The measurement of vapor pressure involves determining the rate of loss of molecules of the evaporating substance from the effusion cell under these conditions. Measurements are typically made under isothermal conditions, with weight loss from the cell being recorded as a function of time, generally in a TGA-type apparatus. We have, however, modified the technique for non-isothermal operation, as described further below.

The basic theory of the effusion method has been often reviewed in the literature [12-14]. The theory of method is actually based upon the basic kinetic theory of gases. From these classical results, Knudsen derived an expression for the slow isothermal flow out of a cell with a small hole in it. The vapor pressure of a material in the cell can be calculated from Knudsen's original effusion rate result:

$$P_1 - P_2 = \frac{G}{t} \frac{w_1 + w_2}{\sqrt{\rho}}$$

where P_1 is the pressure of saturated vapor inside the cell, P_2 is the pressure outside of the effusion cell, w_1 is the resistance of hole in the cell, w_2 is the resistance of cell containing the

sample, G is the mass lost by effusion, t is the effusion time, ρ is the density of the vapor at the temperature of experiment. The relation simplifies upon applying several simplifying assumptions, including the ideal gas law, that the pinhole leak is the main flow resistance, and assuming $P_1 >> P_2$, yielding:

$$P = \frac{m}{t\,A_0}\left(\frac{2\pi R T}{M}\right)^{1/2}$$

The above result is called the ideal Knudsen equation, in which P is the desired vapor pressure, m the mass loss during the effusion time interval , A_0 is orifice area, M the substance molecular weight , t the effusion time, and T the absolute temperature of the experiment. It is further assumed when applying this equation to the effusion process that the equilibrium vapor pressure of the effusing species obtains within the cell, that the orifice walls do not intercept and return into the cell an appreciable fraction of molecular current entering the hole, that there is no back flux into the orifice exit and the number of intermolecular collisions in the vapor phase occurring within the orifice is negligible.

In our implementation, the mass loss rate was continuously recorded, using a Cahn 2000 recording electrobalance. The cell containing the pinhole leak was suspended on one arm of the balance, which has nominal sensitivity in the μg level. The backpressure in the TGA system was maintained at 10^{-7} torr, which has been noted to be sufficient so as to provide accuracy in the 10^{-6} torr range of vapor pressures. The cell itself was maintained inside of a black capsule within the TGA, and was in close proximity to a thermocouple within the capsule. This was necessary in order to achieve the 0.1°K accuracy in temperature measurement required in vapor pressure work at low temperatures. The temperature measurement issue will be further discussed below.

The Non-Isothermal Knudsen Effusion Technique

One modification of the Knudsen effusion technique was required in order to apply it to materials as complicated as coal tars. Very complex mixtures, which contain materials exhibiting a wide variety of vapor pressures, cannot be conveniently studied by the traditional Knudsen effusion methods involving increasing temperature in isothermal steps. Typically, mixtures of components exhibiting a wide range of volatility are examined by a non-isothermal distillation procedure, for example ASTM D86, D216, D447, D850 and D 1078. The difficulties in applying these methods have led to various alternative methods, including the well-known "simulated distillation" as performed by gas chromatograph, and thermogravimetric methods [15]. These ordinary distillation techniques are not, however, acceptable in our case. Here, as noted above, the temperatures that would be typically involved in an ambient pressure , or mild vacuum, distillation would still be unacceptably high. We are forced to work at the high vacuums of the Knudsen effusion method in order to keep temperatures below those for decomposition of the tars. In contrast to the ASTM-type procedures, however, the pressure outside of the cell is of no consequence, provided that it is below the vapor pressure of the sample by at least an order of magnitude, and as long as the situation in the pinhole leak approximates collisionless flow.

The non-isothermal Knudsen effusion method was developed in response to the above need. The method allows a very wide range of temperatures to be scanned quickly, and with modest amounts of mass loss. The latter is important in the case of a mixture, in which the properties of the sample will change with mass loss. Reliable measurements using the Knudsen effusion method require particular attention to the problem of the measuring and controlling the temperature of the Knudsen cell. Most discrepancies between the results of the different workers using the Knudsen or related techniques are the result of insufficient attention to temperature measurement. As the sample must receive heat purely by radiation (since the cell is operated in a high vacuum) a long time is required to reach thermal equilibrium in an isothermal experiment. In our case, the main thermal lag is associated with heating of the five gram capsule which surrounds the sample cell. However, the sample cell has a view factor of the capsule which approaches one. Together with the fact that the effusion cell has a much smaller mass, 0.15 grams, it thus tracks the capsule temperature well. Thus a long equilibration time, associated with changing the capsule temperature in isothermal experiments, is avoided if an experiment is carried out non-isothermally.

RESULTS AND DISCUSSION

The performance of the non-isothermal technique was checked using anthracene and naphthacene, since the vapor pressures of these compounds have earlier successfully measured by us, using the standard isothermal Knudsen effusion method. Figure 1 shows the non-isothermal measurement

results for anthracene at heating and cooling rates of 5 °C/min. It is apparent that there is a significant deviation of the results from the isothermal technique data. The fact that the heating data under-predict, and the cooling data over-predict, the real vapor pressures might be anticipated. This performance suggests that the cell temperature is lagging the surrounding capsule temperature, and that the heat transfer limitation has shifted to the capsule-cell transport process. For this reason, it is logical to expect that by decreasing the rate at which the capsule is driven in temperature, this limitation can be minimized. This is borne out by the results obtained at 0.8 °C/min heating rate, shown in Figure 2. There is in this case good agreement between the results obtained from the non-isothermal and isothermal techniques.

Figure 3 shows the results of the isothermal technique applied to naphthacene, in "cooling" mode. As seen in Figure 3, there is again good agreement between the results of isothermal and non-isothermal methods. Thus the reliability of the non-isothermal method appears to be established.

The results of the first application of the non-isothermal method to coal tars is shown in Figure 4. The results were applied to a fresh coal tar in this case. The tar was produced by the pyrolysis of a Bruceton "standard" Pittsburgh No. 8 high volatile bituminous coal, in a fluidized bed at approximately 550°C. The Bruceton coal has the following elemental composition: C-80.4%, H-5.3%, O-6.7%, N-1.6%, S-1.0%, ash 4.6%, all on a dry basis. The tar was collected in THF, and carefully dried prior to measurement.

In the vapor pressure experiments, the temperature of the tar sample was continually raised from an initial value of 60 °C to a final temperature of 220 °C, at a rate of 0.5 °C/min. Because the tar changes in composition during evaporative loss of its components, the ability to quickly scan the whole temperature space of interest is of great importance. The results of Figure 4 show that the tars evaporate in a "distillation-like" fashion. More volatile species are lost earlier in the process, leaving behind a progressively less volatile residue. The experiments of Figure 4 involved tracking the vapor pressure during both heatup and cooldown cycles. It can be seen that the trace of each heatup cycle (at a progressively higher total level of mass loss) tracks well the immediately preceding cooldown curve. This is not surprising, because during cooldown, the rates of mass loss fall quite low, and until the temperature is again raised to considerably higher values, little further mass loss occurs. Thus there should be little change in vapor pressure attributable to mass loss during the cooldown and early part of the next heatup cycle.

It can be noted that the vapor pressure remains in the range from about 7×10^{-5} to 7×10^{-3} torr as the temperature of the sample is raised from 60°C to 225°C, as a result of loss of progressively less volatile components. Using an earlier derived correlation for the vapor pressures of coal tars [16]:

$$P\,[\text{torr}] = 4.45 \times 10^{6} \exp(-255\, M^{0.586}/T)$$

if the mid-range of the pressure and temperatures of Figure 4 are taken to be ln P = -7.5 (or P = 5.5×10^{-4} torr) and 1/T = 0.00255 (or T = 392 K), then the value of M would be calculated to be about 430 daltons, which is in good agreement with the measured molecular weight of the middle fractions of the tar, from both present measurements and earlier results [16].

More recently, there has developed a concern about condensation-type reactions influencing the results of the vapor pressure measurements, even at these modest temperatures. Indirect evidence of a problem comes from the decreasing solubility of the tar after the vapor pressure experiments have been carried out. If a non-volatile component were to form during the vapor pressure measurement, then the volume fraction of volatile species would be decreased, and assuming that ideal solution behavior is maintained, the vapor pressure would decrease in proportion to the fraction of non-volatile material. At any given temperature, the shift of vapor pressure with cycling involves many orders of magnitude of pressure. We feel, at this point, that selective distillation of lighter fractions may be the more important effect, because there is an overall upward shift in molecular weight during the experiment, but no evidence of formation of large amounts of condensation products.

The data of Figure 4 allow one to judge that there is little change in the latent heat of vaporization during the experiment. This implies that a relatively narrow range of molecular weight is involved. The tar boiling point curve for an arbitrarily selected pressure of 10^{-4} torr is shown in Figure 5.

CONCLUSIONS

The non-isothermal Knudsen effusion method has been shown to be a useful and reliable method for measuring the vapor pressures of pure components and complex mixtures. It is considerably faster and more convenient than the conventional isothermal Knudsen effusion method.

ACKNOWLEDGMENT

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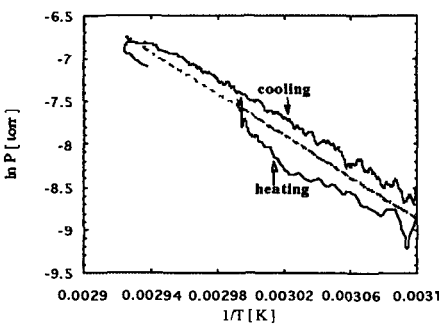

Figure 1. A comparison of vapor pressure results obtained using the non-isothermal and isothermal effusion methods on anthracene. The isothermal data are shown as the dashed line. Heating and cooling rates are 5 °C/min.

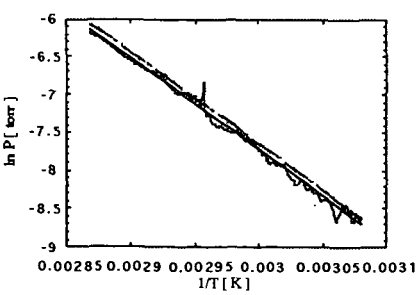

Figure 2. A comparison of the results on anthracene, obtained at 0.8°C/min heating and cooling rates.

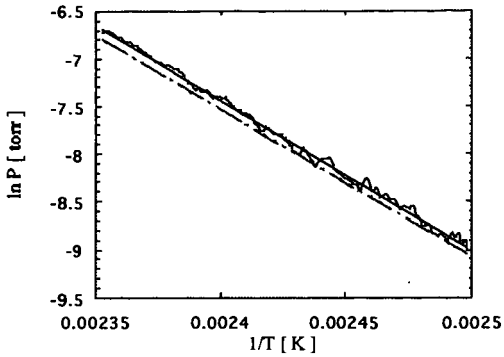

Figure 3. The non-isothermal effusion method applied to measuring the vapor pressure of naphthacene. Cooling rate 0.8°C/min.

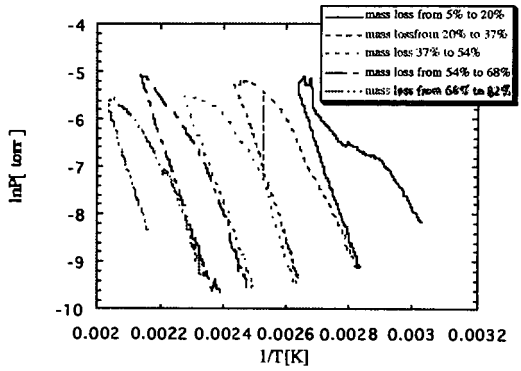

Figure 4. The non-isothermal Knudsen effusion method applied to Bruceton coal tar.

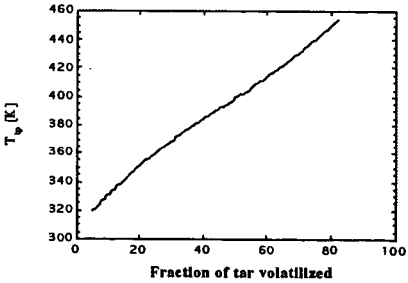

Figure 5. Boiling point distribution of Bruceton coal tar, 0.1 mtorr pressure.