Heat of Vaporization by Measurement Using DSC/TGA versus Estimation Using Detailed Hydrocarbon Analysis

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Heat of vaporization by measurement using DSC/TGA versus estimation using detailed hydrocarbon analysis

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Introduction

One important property in assessing the knock resistance of ethanol–gasoline blends is heat of vaporization (HOV). Both estimation and direct measurement of the HOV have been problematic due to several factors.

Measurement of HOV can be done using vapor pressure versus temperature data and applying the Clausius-Clapeyron (CP) equation.[1] While this is an effective approach for pure liquids, measurement for mixtures of components yields an unrealistically low value. For ethanol–gasoline mixtures, the HOV calculated from the CP equation gives HOV in kilojoules per mole (kJ/mol), which is then divided by the molecular weight of the fuel to determine HOV. For mixtures, the vapor pressure is dominated by the most volatile components in the mixture, which comprises only a small percentage of the total fuel. These components have a much lower molecular weight than the total fuel itself, so dividing by this value gives a low result for the HOV.

Measuring HOV is straight-forward for single and dual-component mixtures using differential scanning calorimetry (DSC) or DSC coupled with thermogravimetric analysis (TGA). Multi-component mixtures such as gasoline add much more complexity to the measurement.[2] Additionally, the volatility of gasoline makes these measurements challenging due to sample loss prior to analysis. Some techniques used to try to minimize sample loss include: chilling the sample prior to transfer to the test vessel, using a screen on top of the test vessel to slow evaporation of the sample, and designing special vessels that can be opened in the instrument prior to analysis.[3] We have found that even with special care, a significant amount of the sample can be lost prior to the analysis.

The HOV can also be estimated or calculated from a detailed hydrocarbon analysis (DHA). ASTM D6729 was used to separate and identify the components of the base gasoline fuels. Once identified, the HOV for each component was multiplied by the mol% present in the sample and then summed to give a total HOV for the sample.

Experimental

In this work, two different approaches were taken toward determination of the HOV. One was direct measurement by DSC/TGA. The other was by estimating the HOV by DHA. Samples used for this work were ethanol blends ranging from E10 to E50 in three different gasoline blendstocks and one natural gasoline (NG). Gasoline blend stocks used included a conventional wintertime blendstock for oxygenate blending (cBOB), a summer blendstock from an ozone non-attainment area (sCBOB), and a California reformulated blendstock (CARBOB). Samples were prepared gravimetrically on the bench scale by splash blending the components after they had been stored overnight in the freezer to mitigate evaporative loss of the volatile components. The accuracy of the blend level was measured using ASTM D5501.

For DSC/TGA, a TA Instruments (New Castle, DE) Q600 SDT was used for sample measurements. Samples were stored on dry ice prior to transfer to the platinum sample pans via a gas-tight microliter (µL) syringe. After transfer of 25 µL of sample to the pan, the pan was immediately covered with a 120-mesh screen (to reduce rapid evaporation of the sample), the instrument furnace was closed, and the heat flow measurement was started. After 0.1 minute (min), the nitrogen flow was turned on at 100 milliliters (mL)/min, and the sample was held isothermally at room temperature (23°C) for the duration of the test. The total heat flow in milliwatts was then adjusted for the zero heat flow by subtracting out the heat flow recorded when the sample had completely evaporated (100% weight loss) and dividing by the total mass of the sample.

For DHA, ASTM D6729 was used, which utilizes a gas chromatograph equipped with a flame ionization detector and a cryogenic oven cooling valve. Individual components were identified by comparison to a certified standard obtained from Separation Systems (Gulf Breeze, FL). An Excel spreadsheet was generated from the DHA that contained the identification and mol% of each component present. Any component under 0.05 mol% was eliminated from the list: less than 5% of the total sample was eliminated. Using the method of Reid, Prausnitz, and Poling[4] the HOV of each individual component was predicted at given temperatures. The resulting predicted HOV was multiplied by the mol% present in the sample, which were then summed to get a total HOV for the sample:

$$\frac{HOV}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456}$$

where HOV is the heat of vaporization, R is the gas constant (0.008314 kJ/mol K), T_c is the critical temperature, T is the desired temperature, T_r is the reduced temperature (T/T_c), and ω is the accentric factor for the individual compound. The API databook[5] was used for the critical temperature and accentric factors of the individual components. Any values not found in the API databook were taken from Yaw's Handbook of Thermodynamic and Physical Properties of Chemical Compounds.[6]

For ethanol blends, the mol% ethanol was determined by ASTM D5501. The HOV was then adjusted to account for the amount of ethanol present in each sample.

Results and Discussion

Figure 1 shows the DSC/TGA heat flow versus time for the ethanol blends in CARBOB. It can be seen that there is an initial high heat flow as the more volatile components rapidly evaporate, which slows down as the ethanol and associated components come off concurrently, matching the flattening that is observed in the distillation curve for ethanol blends.[7] Once all of the ethanol has evaporated, there is a rapid drop in the heat flow curve.
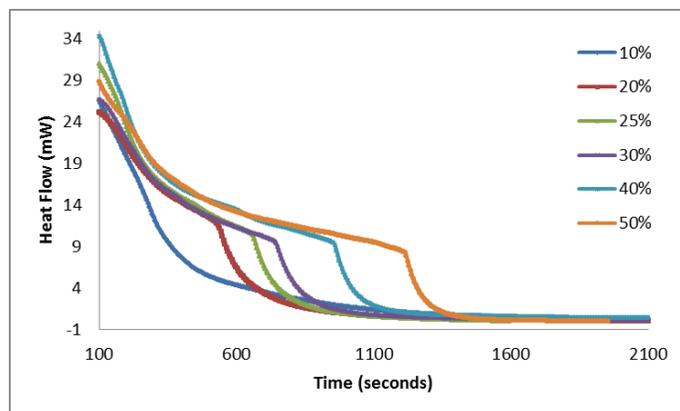

Figure 1: Heat flow versus time for DSC/TGA of ethanol blends (E10-E50) in CARBOB

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The HOV was calculated by estimating the area under the heat flow curve using the trapezoid method. This value was then divided by the total sample mass for each sample to obtain the HOV. As would be expected, as the ethanol level increases, the HOV also increases because the HOV for ethanol (920 kJ/mol)[8] is much higher than that for hydrocarbons (typically about 350 kJ/mol).[9] This measurement could also be used to calculate the HOV as a function of the fraction of the sample evaporated.

While this measurement provides useful information, it suffers from loss of sample prior to starting the analysis. In our laboratory, we measured the time it took for addition of the sample to the pan (via gas-tight syringe), placing the screen on the pan, and closing the furnace of the instrument. On average, this took anywhere from 30 to 45 seconds. Sample loss from the pan was measured by adding the sample to a pan on a balance, placing the screen on top, and taking a weight reading every 10 seconds. In general, about 20-25% of the sample was lost after one minute. We also tried using a different kind of pan, one typically used in DSC instruments in which a lid having a laser-drilled hole can be crimped on top. Sample losses due to evaporation were reduced using the pinhole pan; however, losses were still approximately 15%.

To reduce the amount of sample loss from the pans prior to analysis, we plan to utilize larger sample pans and also use the pinhole lids. The mass of sample lost should be unchanged but will be a smaller percentage of the starting mass. The lids will not crimp on the pans, which should reduce the time it takes to load the sample into the instrument. Currently, placing the screen on top of the pan can be tricky, and sometimes the screen can be dropped. With the lids, there is a lip that fits perfectly into the top of the pan. The rate of evaporation should also be reduced as the lid only contains a 75-μm laser-drilled hole in the top.

sCBOB was also analyzed in triplicate to assess the repeatability of the measurement by DSC/TGA. The coefficient of variation was 2.8%, demonstrating that this technique is precise for the direct measurement of HOV.

Comparison of the HOV calculated by DHA and the measurement by DSC/TGA can be seen in Figure 2. Because of the sample loss associated with the DSC/TGA measurement, the HOV was consistently lower than the HOV calculated by DHA. There is also error associated with the DHA calculation. Most of this error occurs in the uncertainty of the ethanol concentration which is measured by ASTM D5501. The precision of this method can contribute a somewhat large error (±10%) in the HOV as the ethanol is a high-concentration single compound that contributes considerably to the total calculated HOV. Additional error can occur during DHA measurements from the mis-assignment of minor compounds that co-elute or elute close enough to be improperly identified by retention time.
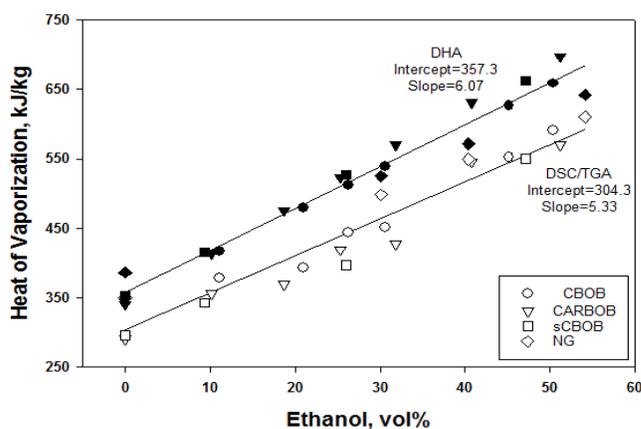

Figure 2: HOV as measured by DSC/TGA and calculated with DHA

Conclusions

A simple and fairly accurate way to measure HOV can be performed using DSC/TGA. This method suffers from sample loss due to the volatility of gasoline during loading of the sample into the instrument. We are currently investigating ways to reduce the sample load time as well as sample loss prior to starting the measurement. A lid with a small pinhole opening should help seal the pan better than the screens that are currently being used. Using a larger pan will also allow us to increase the size of the sample from 25 μL to about 50 μL. Results for the additional pinhole lid/pan combination will be presented. Additionally, results on HOV versus fraction evaporated will be discussed.

Using DHA to calculate HOV yielded higher HOV results, as can be expected due to the loss of the sample when performing the DSC/TGA measurement. While the error associated with the DHA-based HOV calculation is lower than with the DSC/TGA, improvements to the way in which the test is performed could significantly reduce the error in the measurement. Accounting for this lost portion of the sample could help to align the values obtained by both methods.

Acknowledgement

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