Experimental test of the Sydney Young equation for the presentation of distillation curves

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A B S T R A C T

The distillation (or boiling) curve of a complex fluid is a critically important indicator of the bulk behavior or response of the fluid. For this reason, the distillation curve, usually presented graphically as boiling temperature against volume fraction distilled, is often cited as a primary design and testing criterion for liquid fuels, lubricants and other important industrial fluids. Clearly, the boiling temperatures that is measured near ambient conditions during the course of a distillation curve determination depend upon the local atmospheric pressure. For this reason, the user community is accustomed to data presented with an adjustment of the temperatures to those that would be observed at a standard atmospheric pressure of 101.325 kPa, or standard atmospheric pressure of 1 atm. Typically, this is done with a simplified Sydney Young equation. This correction makes little difference to measurements done consistently in a particular laboratory, or when the atmospheric pressure varies little. The correction can be quite large when measurements are done in laboratories at different elevations, however. In this paper, we describe an evaluation of this correction. Specifically, we performed measurements of the distillation curve of a binary mixture of \((n\text{-decane} + n\text{-tetradecane})\) at three elevations (and, therefore three different values of atmospheric pressures, \((70.06, 82.73, \text{and } 101.00)\) kPa). Comparisons are made between the raw and adjusted values, and recommendations are presented as to when the equation might be inadequate.

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1. Introduction

One of the most important and informative measurable parameters that is measured for complex fluid mixtures is the distillation (or boiling) curve [1]. The distillation curve is a graphical depiction of the boiling temperature of a fluid mixture plotted against the volume fraction distilled [2,3]. Since the direct measurement of (vapor + liquid) equilibrium on a complex, multicomponent mixture is impossible, the distillation curve provides the only practical metric of volatility. This volume fraction is usually expressed as a cumulative per cent of the total volume. One most often thinks of distillation curves in the context of petrochemicals and petroleum refining, but such curves are of great value in assessing the properties of any complex mixture. The most common implementation of distillation curve measurement is found in the ASTM D-86 standard [4]. Commercial instruments that are available to perform this test have varying degrees of sophistication, automation, and convenience to the operator. In the ASTM D-86 test, the data obtained are the initial boiling temperature (IBT), the temperature at volume fractions of \((10, 20, 30, 40, 50, 60, 70, 80, \text{and } 90)\) per cent, and then the final boiling temperature (FBT). There are significant disadvantages associated with the ASTM D-86 test, and these have been well documented [5].

Clearly, the boiling temperatures that are measured during the course of a distillation curve determination are dependent upon the local atmospheric pressure. Since the atmospheric pressure not only varies diurnally, but also with elevation, this is an important consideration [6,7]. The usual technique that is applied to correct the observed temperature for variations in the atmospheric pressure is the application of the Sydney Young (SY) equation [8]. This equation was developed during the course of Young’s work on distillation separations and (vapor + liquid) equilibrium measurements [9,10]. Young advocated the measurement of atmospheric pressure multiple times during long distillations, or when performing distillations in unsettled weather, since the effect of the pressure variations on the observed temperatures is so significant. A simplified SY equation is specified in the above standard, ASTM D-86:

\[
C_c = K_1(760 - (P/\text{Torr})) \{273 + (t_f/\circ C)\},
\]

\[
C_c = K_2(101.3 - (P_k/\text{Torr})) \{273 + (t_f/\circ C)\},
\]

where \(C_c\) is the correction applied to the observed temperature, \(K_1\) and \(K_2\) are constants, \(P\) is the measured ambient pressure in Torr, \(P_k\) is the measured ambient pressure in kPa, and \(t_f\) is the measured
temperature in °C. The constant $K_1$ is fixed at 0.00012, and $K_2$ is fixed at 0.0009 in ASTM D-86 method. We note that fixing $K$ as a constant is a simplification of the original form of the SY equation, in which this constant was provided in a table as a material dependent quantity. The variability of $K$ can be large. For example, in a series of $n$-alkanes, the constant $K_1$ decreases linearly with increasing chain length (methane: 0.000135 and n-tetradecane: 0.000104). Increasing molecular complexity will generally cause a decrease, as will the replacement of a hydrogen atom with a halogen. Intermolecular association among moieties on a molecule will generally lower the constant, although the addition of –OH to a moiety introduces considerable irregularity into the variation [8].

Although most of the literature on the application of ASTM D-86 suggests application of the above equation in every case, one set of guidelines recommends against using the SY equation adjustment for more than a 5 K adjustment [11]. Clearly, this recommendation poses problems for many laboratory locations. Our location at 1655 m elevation results in a typical atmospheric pressure between (81 and 83) kPa which in turn results in a SY equation adjustment of approximately 7 K in distillation temperature for typical hydrocarbon fluids. The literature is silent on what to do in such cases.

In the earlier work on extending measurement of distillation curves, we described a method and apparatus for a composition-explicit distillation curve measurement. The new approach, called the advanced distillation curve approach, addresses many of the shortcomings that are inherent in the classical metrology. It features: (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analyses), (2) the temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for the equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) corrosion assessment of each distillate fraction [5,12–23]. As part of this technique, we apply a modification of the typical (i.e. embodied in ASTM D-86) SY equation that is in fact more aligned with the original equation. Our practice has been to assign an average chain length, determined by a prior chemical analysis, to the mixture under measurement, and use a value of $K$ that is determined by a linear regression of Young’s $K$ data (see Ref. [8]) from this chain length.

Regardless of which version of the SY equation is employed, there can be significant systematic uncertainties associated with its application. These uncertainties stem from the formal approximate nature of the equation itself as well as difficulties with the assignment of the material-dependent constant value. The temperature adjustment that results from application of the equation can range from (0 to 12) K, depending upon location, i.e. elevation, and atmospheric effects. When applied to the classical distillation curve measurement (embodied in ASTM D-86), the uncertainties inherent in this adjustment were historically perceived as being relatively minor compared with the numerous other uncertainties and shortcomings. As we pointed out in earlier work, fluid specifications that include ASTM D-86 distillation curve data are often given in a temperature range that spans 25 K or more; and since the temperatures from ASTM D-86 are not thermodynamic state points, they have little or no theoretical significance. With the introduction of the new distillation curve metrology, however, the reliability of the SY adjustment takes on greater importance, since the temperature data are indeed thermodynamically consistent and are of low uncertainty (0.1 K rather than 25 K or more), and can be modeled with an equation of state.

The advanced distillation curve measurement does not currently provide for measurements at a variety of pressures. Like the classical ASTM D-86 approach, the measurements are done at the local atmospheric pressure. The most convenient avenue to the assessment of the SY adjustment is therefore the measurement of the distillation curve of a well-characterized mixture at multiple elevations and therefore, atmospheric pressure values.

2. Experimental

The advanced distillation curve apparatus and method have been described in detail earlier. The distillation flask is a 500 cm³ round bottomed flask that is placed in a two-part aluminum heating jacket, the lower part of which is contoured to fit the flask. Above the distillation flask, a centering adapter provides access for two thermally tempered J-type thermocouples that enter the distillation head. One thermocouple enters the distillation flask and is submerged in the fluid, to monitor the temperature of the bulk fluid. This temperature is referred to as $T_b$, the subscript signifying its measurement in the kettle. This temperature is a true thermodynamic state point. The other thermocouple is centered at the low point of distillate take-off, which is the typical distillation head placement, as recommended graphically in ASTM D-86. This temperature is referred to as $T_h$, the subscript signifying its measurement in the distillation head. While this temperature is not a true thermodynamic state point, it is important nonetheless because it provides comparability and consistency with a century of historical data on thousands of fluids. Both thermocouples were calibrated in an indium triple point cell traceable to a NIST standard. The other major features of the apparatus, including the level-stabilized receiver, the model predictive temperature controller, the sampling adapter, and the vortex tube chilling of the condenser, are unchanged from the previous reports. The only major difference that was made in the apparatus specifically for this study was the substitution of a portable digital barometer for atmospheric pressure measurement in remote locations. This instrument was calibrated against a NIST standard digital barometer before the measurements were performed. The uncertainty (with a coverage factor $k = 2$) in the temperature measurement of the advanced distillation curve instrument was 0.1 K; the uncertainty in the volume measurement that is used to obtain the distillate volume fraction was 0.05 cm³; and the uncertainty in the pressure measurement, assessed by logging a pressure measurement every 15 s for the duration of a typical distillation, was 0.001 kPa.

To perform a measurement, 200 cm³ of the fluid to be measured is placed in the round-bottomed flask typically with 100 cm³ pipettes, and the thermocouples are placed in the appropriate positions with the aid of a centering adapter. This fluid volume has been chosen for convenience; any volume suitable for the measurement can be used. To test the reliability of the SY temperature adjustment, we used mixtures of ($n$-decane + $n$-tetradecane) (CAS Registry Numbers: 124-18-5 and 629-59-4, respectively) at a mole fraction of 0.5 (50/50, mol/mol). This mixture provides a well-characterized and well-behaved, chemically stable test fluid. These research grade fluids were obtained from a commercial source, and their purities were checked by gas chromatography with mass spectrometric detection (30 m capillary column of 5% phenyl polydimethyl siloxane having a thickness of 1 μm, temperature program from (363 to 498) K, 7 K per minute) [24,25]. The purity was found to be better than 99.99% (mass/mass), and the fluids were used as received. The mixtures were prepared gravimetrically as stock solutions. The uncertainty of the mass measurement of the mixture preparation was 0.005 g. Care was taken to minimize exposure of the fluids to the atmosphere, so that water uptake by the mixtures could be minimized.

Distillation curve measurements were performed on the same stock mixture, with the same apparatus, in three laboratories lo-
cated at 106 m (at Gaithersburg, MD), 1655 m (at Boulder, CO), and at 3094 m elevation (at Leadville, CO). The average atmospheric pressure at these three locations was (101.00, 82.73, and 70.06) kPa, respectively, with the uncertainty stated above. Time limitations at the Gaithersburg and Leadville locations allowed for only two replicate distillation curve measurements. We do not consider this to be a serious problem because, as discussed above, the uncertainties of the apparatus and approach have been thoroughly characterized. Many more measurements could be and were performed at the Boulder location, however, and the 50/50 (mol/mol) (n-decane + n-tetradecane) is commonly used as our diagnostically or calibration mixture.

3. Results and discussion

Representative distillation curve results, measured with the advanced approach and apparatus, are presented in table 1 for the 50/50 (mol/mol) of (n-decane + n-tetradecane), at atmospheric pressures of (101.00, 82.73, and 70.06) kPa. For each mixture, the raw temperature (corrected only for the thermocouple calibration) and the temperature adjusted with the SY equation (in which $K_2$ was assigned a value of 0.000109 for an average carbon chain of 12 units) are presented for each distillate volume fraction. The dramatic effect of even a modest change in the pressure during the measurement can be seen from these data. The temperature differences obtained from measurements at approximately sea level (where the atmospheric pressure was 101.00 kPa) and those measured at 3094 m (where the atmospheric pressure was 70.06 kPa) can be as much as 20 K. Application of the SY equation, which ideally would cause the three data sets to overlie, clearly brings the three sets closer together. This is most easily seen graphically. The data of table 1 are plotted in figures 1a and 1b, showing the raw and adjusted temperatures, respectively. One can see that all of the distillation curves show the typical sigmoid-shape characteristic of a mixture with a heavy and a lighter component (subjected to a simple rather than fractional distillation) and very few or no intermediate constituents. The curves begin with a pronounced upward slope, which then becomes steeper, and subsequent to this region the curves flatten out. This type of curve is also called a growth curve, because it describes the weight gain of mammals from birth to adulthood. Composition of the fluid in the boiling flask is changing most rapidly in the regions of the highest slope.

The goal of the SY equation is to achieve the situation in which the three curves presented in figure 1a overlie, essentially being superimposed upon the curve measured at 101.00 kPa. This is clearly not the result measured. The largest gaps between the three curves are seen in the parts of the curve where the compositions are changing rapidly: the beginning and the intermediate stages of the distillation. As we pointed out in the earlier work, the curves for this mixture will flatten out at the end of the distillation, and in this area the elluent from the condenser is essentially a pure n-tetradecane. This was demonstrated with the composition channel of the advanced apparatus. Thus, in the late flat portion of the three curves in figure 1b, the SY equation is attempting to represent the boiling temperature of a pure fluid.

To assess in more detail the reliability of the SY equation adjustment, we can examine the temperature range of all three data sets as a function of distillate volume fraction. By temperature range, we mean the difference between the SY-adjusted temperatures measured at (101.00 and 70.06) kPa, since the results at 82.73 kPa are always intermediate, for a given distillate volume fraction. This is shown graphically in figure 2, in which the raw and corrected ranges have been plotted. Ideally, the lower plot should be a straight line along the origin. This plot shows three distinct regions of the SY adjustment, and these correspond to the slope of the distillation curve discussed above. Region a (up to the maxima) corresponds to the initial region of moderate slope. The slope here, $\Delta T/\Delta V = 2.5 \text{ K/5\%}$, is approximately 2 K/5% with a spread or uncertainty of 0.4 K. We define this measure of $\Delta T (\Delta V = 5\%)$ as the number of degrees of temperature change corresponding to a 5% change in volume fraction, in a region of the curve with approximately constant slope. We then note the maxima in the center of the plot in both the raw temperature data and in the SY-adjusted temperature, and these occur, as stated above, in the area in which the compositions change most rapidly. Here, in region b, the slope, $\Delta T (\Delta V = 5\%)$, is approximately 2 K/5%, with a spread or uncertainty of 0.1 K. Finally, in region c, after the maxima, the curves level off to a slope $\Delta T (\Delta V = 5\%) \approx 0.4 \text{ K/5\%}$, with a spread or uncertainty of 0.3 K. Note that the last slope is actually quite small and not statistically significantly different from a flat line. We see a slight upturn at the very end of the distillation range; this is merely the onset of thermocouple lift-out in the advanced apparatus, and is not significant beyond being an experimental diagnostic. It is the point at which there is no longer enough liquid left in the flask to bathe the thermocouple, signaling the end of a measurement.

We can examine the effectiveness of the SY equation adjustment in each of these regions of distillation curve slope. In the region a of the distillation curve, where $\Delta T/\Delta V = 2.5 \text{ K/5\%}$, the temperature gap in our measured temperatures is reduced from approximately 16 K to between (4 and 5) K. In the region b (of the highest slope), $\Delta T (\Delta V = 5\%) \approx 2 \text{ K/5\%}$, the change is from 20 K to approximately 7 K, and in the “flat line” region, $\Delta T (\Delta V = 5\%) \approx 0.3 \text{ K/5\%}$, the change is from a gap of approximately 15 K to one of 2 K.

4. Conclusions and recommendations

Following the measurements and analysis presented above, we can provide some general guidelines regarding the application of the SY equation to the measurement and presentation of distillation curves. We note at the outset that these recommendations must be viewed as provisional and general guidelines only. Our study was done on a well defined but very simple binary mixture of aliphatic hydrocarbons. We realize that, in practice, few samples are encountered that are analogous to an n-alkane binary. Most samples are highly complex fluids that contain aliphatic and
aromatic hydrocarbons, and compounds with hydroxyl, esters, ethers, and other heteroatoms. This is certainly the case with the wide variety of fluids that we have measured with the advanced approach. Moreover, we were only able to measure the curves at three atmospheric pressure regimes, in three locations. Our work with this binary mixture is therefore only a first step in determining how best to handle this aspect of distillation curve data.

First, we assert that the SY equation adjustment at 82.73 kPa (measured at 1655 m) performs better than that at 70.06 kPa (measured at 3094 m). We can assess this by taking the average of the differences of the SY equation-adjusted temperatures at (82.73 and 70.06) kPa as compared to those at 101.00 kPa, for the same distillate volume fractions. We note that the approximate average bias at 70.06 kPa is 5 K, and that at 82.73 kPa is 2 K. This is a systematic negative bias rather than a random uncertainty. It is clear from this that the adjustment performs more poorly as the pressure decreases, i.e. as the elevation of the laboratory increases. We recommend that the precision statements provided with distillation curve data that include the SY adjustment be de-rated when measured at elevations approximately above 1600 m. We choose not to make any more quantitative statements in this regard because our observations were made over only three pressures.

The shape of the distillation curves of more complex fluids is typically a very subtle sigmoid, rather than the very pronounced sigmoid we have shown for our test mixture. In Figure 3, we pro-
vide examples of a variety of complex fluid distillation curves that we have measured with the advanced approach (see the papers cited earlier in the introduction). In most cases with these complex, highly disperse, multicomponent fluids, the slope is fairly constant, although the undulation of the sigmoid is superimposed. Some of the fluids have distillation curves with very modest slope while others have rather steep slopes, corresponding to how quickly the composition is changing with temperature. Sometimes abrupt changes in slope occur within a single curve, as is observed with gasoline oxygenated with alcohols [20].

As a first approximation, we can draw some conclusions regarding the effectiveness and uncertainty of the SY equation adjustment based upon our simple measurements, and apply them to the more complex fluids on the basis of an approximation of the distillation curve slope. Following this line of reasoning and the discussion of curve slope in the preceding paragraph, we recommend that for moderate slopes, e.g. the first hatched area of figure 2, the maximum error or negative bias introduced by the SY equation be taken as between (4 and 5) K, for steep slopes (the second shaded area of figure 2), the error or negative bias is (7 to 8) K, and for gentle slopes (the third shaded area of figure 2), the error or negative bias is approximately 2 K. We recommend that when assessing the overall uncertainty of a distillation curve measurement, these values be considered, among other factors, in the propagation of overall uncertainty. We also recommend that the error or bias be adjusted upward as the atmospheric pressure decreases,
i.e. the laboratory elevation increases. We make no recommendations on the behavior and effectiveness of the SY adjustment below an atmospheric pressure of 70 kPa.

We now treat the implications of the above recommendations in the context of real samples. Considering the effect of the SY equation adjustment on the classical ASTM D-86 metrology and commercial instrumentation, one can conclude that given the numerous sources of systematic and random uncertainties inherent in the method, the SY equation adjustment in fact poses little additional difficulty. One simply must include the uncertainty in the overall propagation of uncertainty, and include the effects of elevation in such an analysis. Moreover, the method has been used with the SY equation adjustment for many decades, resulting in a very large body of measurements, with which consistency is desirable. When using the advanced distillation curve metrology, in which the temperature, volume, and pressure measurements are of much lower uncertainty, and in which the temperatures are true thermodynamic state points that can be related to composition, far more careful consideration must be given.

Measurements from the advanced distillation curve approach are used for fluid specifications and engineering designs, and also for the equation of state development.

The former will be by far the most common situation in which such data are used. Provided one understands that the SY adjustment has a systematic bias, and how measurement conditions can affect that bias, we recommend that the practice of adjusting distillation curve data with the SY equation continue. Indeed, it has been our practice to provide advanced distillation curve data with the SY adjustment, along with the measured pressure and the constant used in the SY equation. This allows the actual raw temperature data to be extracted (with appropriate precision) if needed. If this is done, there is no need to de-rate the precision statement for the bias of the SY adjustment, since the recoverable raw temperatures are only subject to random uncertainty. Moreover, we provide two sets of temperatures, \( T_k \) and \( T_h \), as discussed in the experimental section. This allows the user to compare data from the new approach with the very large body of data measured in the past, all of which have been adjusted with the SY equation.

If the data are to be used for modeling a fluid with an equation of state \([26,27]\), the SY equation adjustment poses a significant problem in all slope regimes. Under these circumstances, it is essential to avoid the use of the SY equation altogether and to use the raw temperature data presented as \( T_k \) along with the actual measured pressure. We have demonstrated that this will allow the development of equations that can represent fluid properties within experimental uncertainty for most properties. These include volatility, density, speed of sound, and transport properties \([26,27]\).

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