A Distillation Approach to Phase Equilibrium Measurements of Multicomponent Fluid Mixtures

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Supporting Information

ABSTRACT: By building on the Advanced Distillation Curve (ADC) approach to measuring the volatility of fuels and other fluids, the ADC with Reflux or ADCR technique was developed to address the difficulty of experimentally determining the vapor–liquid equilibrium of fluids containing many components. For fuels and other multicomponent mixtures, the ADCR collects data about the chemical compositions of both liquid and vapor phases across a range of temperatures, elucidating the two-phase region at constant pressure. Two simple mixtures were used to demonstrate the ADCR method: an n-decane/n-tetradecane binary and the Huber-Bruno surrogate, a ternary mixture designed to represent the volatility of an aviation turbine kerosene. These mixtures were chosen to test the method because they have been extensively studied and modeled in previous work. For both test fluids, the ADCR measurements of vapor–liquid equilibrium were in good agreement with model predictions. We conclude that the ADCR is a useful method for determining the T-P-x-y behavior of fluid mixtures with many components. The experimental approach presented may support the development of fuels, design of separations, and forensic sciences that use vapor analysis, especially arson fire debris analysis, by providing quantitative data with well-characterized uncertainty describing the relationships between the vapor and condensed phases of a fuel subjected to thermal weathering.

INTRODUCTION

Volatility is a two-phase property describing the tendency of a liquid or solid to partition to the gas phase. Like all physical properties, it is linked to chemical composition. The volatility of a pure substance is described by its vapor pressure at a given temperature, while for a mixture it is provided by a distillation or boiling curve. The related vapor–liquid equilibrium (VLE) of a mixture is a quantitative description of how each component is distributed in each phase at a given temperature and pressure. For simple binary mixtures, VLE is represented by bubble-point and dew-point curves. For binaries, low-uncertainty bubble-point measurements are possible for a wide range of temperatures and pressures.1 The most precise methods used to make these measurements use an equilibrium VLE cell into which a mixture with a well-known, constant composition is introduced. These instruments precisely monitor temperature and pressure, changing one of these and measuring the other to collect bubble-point data for that binary composition. The advantage of this method is very high-quality data: it avoids sampling of fluid and analysis of composition, which tend to introduce uncertainty. The time-consuming nature of VLE determination with an equilibrium cell, which can take weeks or months, is a major drawback of the approach.

Many binary data collected using equilibrium cells are available; the references provided here are only a small sample.1−6 These data are vital to the estimation of binary interaction parameters and associated development of mixture models, which represent fluid mixtures with many components using binary interactions between pairs, simplifying the more complex interactions occurring in the mixture. Most of the fluids that are useful to us in real world applications (e.g., gasoline and other fuels) contain hundreds of components with varying chemical and physical properties. It has not been practical or popular to study the VLE of these fluids, although a couple of approaches were described in the 1990s.7,8 Published VLE data or models for multicomponent fluid mixtures are extremely limited. Some recent studies interested in the design of carbon capture and storage or enhanced oil recovery processes examined mixtures of crude oil and carbon dioxide; however, the authors treated oil as a single component.9,10 Researchers working in thermodynamic property measurement and modeling have commented on the absence of available VLE data for multicomponent mixtures, particularly data relevant to energy and fuels.7,9,11 Such data are important for evaluating alternative fuels (including those intended as drop-in replacements), for the design of separation processes during production, and for fuel storage applications. Addressing this major research gap requires the development of an experimental method with well-characterized uncertainty designed for this purpose.

The ability to experimentally determine the VLE of fuels and develop high quality predictive models is important in forensic science as well as energy research. In 2009, the National Academy of Sciences urged the forensics community to strive for increased rigor in its techniques. Improving our knowledge of the VLE of multicomponent mixtures relevant to criminalistics is a crucial part of this effort, because vapor...
characterization methods are frequently used to analyze evidence. Specifically, vapor analysis is used in fire investigation to detect and characterize residual accelerants present on debris collected from a potential arson fire. The prediction of thermal weathering, which happens to a fuel during a fire, is an important consideration in this field and an active area of research. Current predictive methods, however, do not consider the role of VLE, which describes the relationship between the vapor that is analyzed and the fire debris sample. For all the above reasons, an experimental technique that can measure VLE and weathering of fluids with many components is needed. This article presents an apparatus and method for collecting these data.

This method, which is called the Advanced Distillation Curve with Reflux or ADCR, is a modification of the Advanced Distillation Curve (ADC), an existing approach to measuring the volatility of fuels. The ADC was invented at the National Institute of Standards and Technology (NIST) to make low-uncertainty, thermodynamically accurate volatility measurements of a multicomponent fluid as a function of its composition across the distillation curve. ADC data can be applied to the development of equations of state describing the fundamental characteristics of fluids. ADC has also been used to model thermal weathering of fuels, an application that plays a role in the current work. Two hydrocarbon mixtures were chosen for the development and initial demonstration of the ADCR technique. The first, a binary mixture of n-decane and n-tetradecane, was the simple mixture used in the early testing of the classical ADC method. The second, three-component test mixture was selected to be more complex (in terms of number and heterogeneity of components) and for its relevance to energy and fuels. This mixture, the Huber-Bruno (HB) surrogate, was created in 2010 to represent the volatility of Jet-A with three components. The surrogate is composed of 31% n-dodecane, 38% n-tetradecane, and 31% 1,2,4-trimethylbenzene by mass.

### EXPERIMENTAL SECTION

**Materials and Analyses.** The n-decane (C10), n-dodecane (C12), n-tetradecane (C14), and 1,2,4-trimethylbenzene (TMB) used in the fluid mixtures, as well as n-octane used as a solvent, were obtained commercially and tested for purity by gas chromatography with flame ionization detection (GC-FID). All were >98% pure and were used as received. Samples collected during an ADCR experiment were taken using a 10 μL glass-barrel autosampler syringe and placed in autosampler vials containing solvent. All samples were analyzed using triplicate GC-FID injections. FID response factors were periodically checked.

**Apparatus.** The classical ADC apparatus consists of a boiling flask (or kettle), distillation head, air-cooled condenser, sampling adapter for distillate collection, and a level-stabilized receiver to measure distillate volume fraction (DVF). This is the pathway the fluid travels as it is distilled. While the distillation progresses, four variables are recorded: the temperature of the boiling fluid (kettle temperature or \( T_k \)), the temperature of the vapor in the distillation head (head temperature or \( T_h \)), the DVF as it is collected in the receiver, and vapor composition obtained by sampling the distillate. More detailed descriptions of the apparatus and procedure for the classical ADC method are available in previous publications.

The ADC already collects three of the four variables required to describe VLE: temperature (\( T \)), pressure (\( P \), which is constant), and vapor composition (\( y \)). The reflux modification introduced in this
work allows for the measurement of liquid composition (x) and therefore the estimation of VLE. The challenge, however, in obtaining liquid composition during distillation is that a boiling liquid is a two-phase fluid and cannot be reliably sampled. Any sample collected while the fluid in the kettle is boiling will not be representative of the bulk liquid phase due to the entrainment of bubbles in the syringe or any other sampling device. The solution introduced by the ADCR apparatus is to isolate the fluid in the kettle from the distillate once it reaches the target temperature (Tf) for a VLE measurement. The target Tf is selected by the experimenter, and the fluid is heated, distilled, and collected in the receiver as in ordinary distillation until this temperature is reached. By separating the phases when the liquid has achieved the target Tf, the fluid in the kettle may be allowed to cool and resume a single phase before it is sampled, without changing its composition. This physical separation is imposed using a three-way valve with a switchable internal channel, which we call the reflux junction. The reflux junction is shown in situ in the apparatus in Figure 1 and illustrated schematically in more detail in Figure 2. This switchable valve, made from a borosilicate glass standard taper joint, replaces the normal distillation head used in the classical ADC. When the ADCR is assembled, the valve’s bottom branch is connected to the middle neck of a three-necked round-bottom boiling flask. The other two necks of this flask are used for the placement of a thermocouple that monitors Tc and for liquid sampling through a septum cap. The left branch of the reflux junction is connected to the condenser, adapter, and receiver. The right branch is connected to a vertically positioned reflux condenser. The top of the reflux condenser is capped with aluminum foil to minimize the escape of vapor when operating in reflux mode. Neither recovery volumes nor visual inspection ever indicated vapor loss.

A custom-made polytetrafluoroethylene (PTFE) valve plug, also illustrated schematically in Figures 1 and 2, fits into the valve body to complete the reflux junction. This plug incorporates a cylindrical channel that aligns with two adjoining branches of the junction. The square notch on the plug’s face is used together with a (3/8 in. nominal) socket driver to rotate the plug between operating modes. A thermocouple well, drilled into the plug on axis, is used to measure the head temperature, Tc (inset, Figure 1). Although during an ADCR experiment, Tc (the fluid temperature of the VLE data point) is used to decide when to stop the distillation, Tf is an important quantity to track for several reasons. Most importantly, Tf represents the temperature of an equilibrium stage within the apparatus. The ADCR is not a perfectly simple distillation: the temperature gradient between the kettle and head causes fractionation. Accounting for this physical phenomenon in the corresponding distillation model requires the inclusion of an equilibrium stage at temperature Tf where rising vapor re-equilibrates and partially condenses in the apparatus.

Figure 2. Schematics of the reflux junction in both operating modes. The junction is operated in distillation mode (left) until the boiling fluid reaches the target temperature (Tf). The plug is then turned to reflux mode (right), preserving the composition of the liquid for sampling.

Acknowledging the role of Tf in ADCR is a crucial step in modeling and data interpretation.

Procedure. Each ADCR experiment begins by pipetting the initial volume of liquid—200 mL for the binary mixture and 100 mL for the ternary surrogate—into the three-necked round-bottom flask. The thermocouple submerged in the liquid must not be touching the flask or be disturbed by the magnetic stir bar; the thermocouple in the vapor, inside the PTFE plug, must be centered and must not touch the walls of the channel. The fluids used in this work are not volatile enough to require cooling of the distillation or reflux condensers, but for lighter mixtures, both condensers should be chilled. The rate of distillation is controlled by a temperature program applied to the heating mantle that surrounds the kettle. When an experiment begins, and ordinary distillation is desired, the channel inside the reflux junction is positioned to allow the distillate to flow along the path between the kettle and the volume receiver. The distillation is stopped at the target Tf by turning the valve plug from distillation mode to reflux mode (Figure 2) and ending the heating program. An aliquot of distillate from the sampling adapter is collected for vapor-phase composition, and a sample of the liquid is collected from the kettle after it stops boiling.

The uncertainty in kettle temperature in the ADC apparatus is 2 °C; for the head temperature, it is 4 °C. The uncertainty in volume measurements is 1 mL. All uncertainty values presented in this work reflect expanded uncertainty calculated with a coverage factor k = 2 providing a 95% confidence interval. Before using the ADCR for VLE, the published distillation curves of both test mixtures were successfully replicated using the new method. A detailed discussion of those experiments and results can be found in Supporting Information.

Theory. In previous work with the ADC, the distillation curve was modeled as a simple batch process where boiling vapor leaves the kettle at a constant flow rate and passes directly into a condenser without any reflux.23,26-28 The liquid is assumed to be at its bubble point and in equilibrium with the vapor phase. A mixture model based on Helmholtz form equations of state, as implemented in the NIST REFPROP computer program, was used to model the VLE of the fluids studied here.29-31 Any model, including simpler equations of state such as the Peng–Robinson EOS, could also be used to model the VLE.32 The Helmholtz models are generally more accurate but require high-quality experimental data to develop. These models were accessible, so Helmholtz models were chosen over the much simpler Peng–Robinson formulations. If one does not have Helmholtz models, the Peng–Robinson model may be substituted; this may be useful for situations where one is interested in a fluid with limited property data, as it requires only the critical point andacentric factor to model a fluid.

The standard REFPROP computer program contains n-decane and n-dodecane but does not contain n-tetradecane or 1,2,4-trimethylbenzene.33 For n-tetradecane, a REFPROP fluid file previously developed for work on jet fuel surrogate models was used.32 Similarly, a REFPROP fluid file for 1,2,4-trimethylbenzene was developed for a project on diesel fuels.33 Both fluid files can be obtained from NIST. VLE calculations can be very sensitive to the values of binary interaction parameters that are used. Due to lack of experimental data, the REFPROP program does not have values obtained from fitting experimental data for the binary pairs (C10/C14, C12/C14, C12/TMB, and C14/TMB) that are needed in this work; when experimental data are unavailable, the REFPROP program estimates the binary interaction parameters from an algorithm.34 Since this algorithm was developed with one and two carbon hydrofluorocarbon refrigerants, it was not clear that it would perform well for the systems in this work that involve larger hydrocarbon molecules, so experimental initial boiling temperature (IBT) data collected in this work were used to validate the binary interaction parameters. It was found that the estimation algorithm was adequate for n-alkane pairs, but it was necessary to fit experimental data for the pairs with 1,2,4-trimethylbenzene. The values of the binary interaction parameters γ12 and γ13 used in the Kunz-Wagner mixture model were determined to

DOI: 10.1021/acs.energyfuels.9b01366
Energy Fuels 2019, 33, 7908–7915
be \( \gamma_1 = 0.9968 \) and \( \gamma_C = 1.0521 \) for C14/TMB and \( \gamma_T = 0.9970 \) and \( \gamma_C = 1.0345 \) for C12/TMB.\(^{30}\)

In the simplest distillation procedure, one first assumes there is a fixed amount of feed at a known pressure and a known liquid composition \( x_i \). The bubble-point temperature \( T_{bub} \) and equilibrium vapor-phase compositions \( y_i \) are then calculated with a mixture model. A constant number of moles \( (n_f) \) at the equilibrium vapor composition \( (y_i) \) are next removed from the system. A mass balance equation is used to determine the new liquid composition left in the kettle and the remaining volume of liquid. Figure 3a illustrates this process. This process is then repeated until the liquid in the kettle is gone, and a distillation curve is created by plotting the kettle temperature (the series of bubble-point temperatures \( T_{bub} \)) against the volume fraction collected in the receiver. In the original ADC work, a large volumetric shift of up to 24 mL was applied after the modeled curve was calculated in order to match the experimental curve.\(^3\) At the time, this was explained as a correction for dynamic holdup due to the volume of the glassware and transit time to the condenser before it reaches the sampling point. Although dynamic holdup does contribute to the need for the empirical shift applied in the older ADC models, the magnitude of those shifts could not be fully explained. The results of this work indicate that the addition of a single stage operating at the head temperature \( T_h \) to the distillation curve calculation accounts for part of the empirical shifting factor, allowing the use of a smaller and more realistic volumetric shift attributable to the amount of fluid in transit during distillation. These findings indicate that reflux is occurring during ADC and ADCR measurements and that the phenomenon can be modeled.

### RESULTS

All temperatures were measured at ambient pressure in Boulder, Colorado (about 83 kPa). The experimental pressures that correspond to the data sets are always provided.

**Measurement and Comparison to Models: C10/C14 Binary.** Figure 4 graphically presents the ADCR results and predictive model for the binary system n-decane/n-tetradecane. VLE was measured at 13 target temperatures \( (T_L) \) chosen a priori to provide good resolution across the two-phase region of the \( T-x-y \) diagram. Each data point represents the average of four individual experiments.

There was very good agreement between the ADCR results and the model. The dew curve (upper left curve, representing vapor composition) predicted by the model is faithfully produced by the ADCR experiments. At all temperatures, measured composition agrees with the model within experimental error. The most scatter in the data was apparent in the vapor composition at temperatures between 223 and 245 °C. In this region of the \( T-y \) diagram, the vapor mass fraction of C14 is changing very rapidly with small changes in temperature; that is, the slope of the dew curve is very shallow. Although it is less pronounced, the same trend occurs along the bubble (lower) curve: the liquid composition measurements are more scattered at low temperatures, where this curve is shallowest and C14 concentration is changing rapidly with temperature. In general, the repeatability of liquid composition was better than for the vapor phase. We attribute this to the larger amount of liquid remaining in the kettle, which made its composition less sensitive to variability among independent experiments. It was much more repeatable than vapor composition, the sample for which is collected from the smaller quantity of fluid in the sampling adapter (volume 0.05 mL).\(^{14}\) The vapor is also affected by more potential sources of variation among replicates than the liquid because it must undergo the re-equilibration step and flow through the condenser before it reaches the sampling point. Although the uncertainty in vapor composition is greater than the uncertainty in liquid composition, the model and measurements of the liquid do not agree as well as they do for vapor composition. A detailed discussion of this phenomenon is available in Supporting Information.
Figure 4. This T-x-y diagram for n-decane/n-tetradecane, plotted in terms of n-tetradecane mass fraction, describes the mixture’s VLE as a function of kettle temperature. The upper curve (dew curve) represents the vapor composition yC14, and the lower curve (bubble curve) represents the liquid composition xC14. $P_{\text{model}} = 83.18$ kPa.

The expanded uncertainty in $T_1$ ($2{^\circ}$C) and $T_2$ ($4{^\circ}$C) is due to (1) the accuracy of the thermocouples, (2) calibration of the thermocouples, and (3) small variations in ambient pressure ($\pm 1.4$ kPa) among replicates. To determine the effect of these pressure differences on temperature, the modified Sydney Young equation was used to shift the measured temperatures to the pressure used in the model, resulting in a maximum adjustment of 0.5 $^\circ$C. Finally, since the data are averages representing multiple independent experiments, (4) small deviations in the actual $T_{\text{set}}$ about the target $T_k$ (0.15 $^\circ$C on average) were also considered. Uncertainty in composition was determined on the basis of (1) the effect that the uncertainty in temperature would have on composition (calculated using the model), (2) the effect of slight changes in the FID response to each compound, and (3) the repeatability of three replicate injections of each sample. Calculated uncertainties are presented alongside the measurements in Supporting Information Table S1.

Measurement and Comparison to Models: Ternary Huber-Bruno Surrogate. Triplicate ADCR experiments using the Huber-Bruno surrogate were conducted at each of five target temperatures evenly spaced across the distillation curve. Figure 5 compares the resulting values to the model. The data are presented in Table S2 alongside model predictions.

Agreement between the HB surrogate model and the ADCR measurements is good. The areas of greatest deviation are in the vapor mass fraction of TMB and in the liquid mass fraction of the alkanes at high temperatures. Differences between the ADCR equilibrium stage and model equilibrium stage estimation are the most likely cause of disagreement. Figure 5 represents mass fractions of each component as stacked areas. To read the plot, for any given temperature along the x-axis, a vertical line can be drawn through both the lower (liquid composition) and upper (vapor composition) area plots. The length of the line segments inside each shaded area provide the mass fractions of each component present in each phase of the mixture at that temperature and pressure. By locating a known composition of one phase on either the upper or lower stacked area plot, one can trace the vertical line at the corresponding temperature, and the other stacked area plot predicts the composition of the other phase. With Figure 5, we created an approach to visually display this type of VLE data. We are not aware of any previous graphical representation of this type of data in the literature.

The sources of uncertainty in these experiments were the same as for the C10/C14 mixture in the previous section. Uncertainties in vapor composition were lower for this mixture than for the binary in the last section. As discussed, the high variability in some composition measurements was due to rapidly changing composition with small temperature changes in some parts of the binary T-x-y curve. Composition of this mixture changed more gradually with temperature, reducing the uncertainty in the average. Uncertainty values are presented alongside the data in Table S2.

Accounting for Holdup. As discussed earlier, adding an equilibrium stage in the distillation model reduced the need for the empirical shift that has been used to make previous measurements and models agree, but it is still reasonable that a small volume adjustment would be necessary based on dynamic holdup, a physical and temporal delay in the ADCR apparatus. This delay exists between the instant a parcel of vapor leaves the kettle and the time it arrives at the adapter where the vapor is sampled for composition (Figure 1). This separation in time and distance implies that the vapor being sampled at the adapter originated from the kettle at a slightly earlier time and therefore a lower temperature. We correct for this delay by adjusting the model-predicted temperatures corresponding to vapor-phase composition. The magnitude of the dynamic holdup correction depends on the internal volume of the ADCR glassware and the surface tension, density, and initial boiling temperature of the fluid. Ferris and Rothamer presented an approach to determining dynamic holdup for the same 50/50 (mol) C10/C14 mixture used in this work.

The dynamic holdup offset is applied to a distillation curve in progress. Static holdup is the smaller effect relevant to a T-y...
curve. The amount of fluid held up between the kettle and receiver while a distillation is in progress and material is actively moving through the apparatus (dynamic holdup) is greater than that which remains after a distillation ceases, because the fluid has time to finish traveling to the receiver (static holdup). Static (4 mL) and dynamic (10 mL) holdup were accounted for in the models represented in Figures 4, 5, S1, and S2.

**DISCUSSION**

The Advanced Distillation Curve with Reflux (ADCR) technique can be used to experimentally determine vapor-liquid equilibrium and study T-x-y relationships that contribute to the development of models for thermally weathered fuels and their vapor composition. This approach is an improvement of the ADC method for measuring the distillation curve of a fluid as a function of its composition. The ADCR uses a three-way reflux junction to physically separate the vapor and liquid phases, preserving the fluid’s VLE at a desired temperature. The ADCR method can measure the vapor-liquid equilibria of multicomponent fluid mixtures that are more complex than the binaries conventionally studied using VLE equilibrium cells. Our method dramatically reduces the amount of time required for data collection: we made as many as six measurements per day. We must note, however, that conventional equilibrium cell methods are lower in uncertainty, especially in the flat regions of a binary T-x-y curve where composition is changing rapidly. Measurement time and uncertainty must therefore be considered when deciding to use the ADCR method for a given mixture and application. The ADCR method also provides vapor composition information, which the bubble-point experiments, mentioned previously, do not. This work also introduces a new visual representation of VLE data at multiple state points for a multicomponent mixture.

We demonstrated the method using two hydrocarbon mixtures: an \( n \)-decane/\( n \)-tetradecane binary and the three-component Huber-Bruno (HB) surrogate. Agreement between models and experiments was good for both mixtures. More scatter in the vapor composition data was expected and observed in both cases. It was discovered during this work that distillation models can be improved by adding an equilibrium stage, where a parcel of vapor leaving the kettle re-equilibrates at the head temperature. This reflects the fractionation occurring within the apparatus during the distillation and helps explain the need for an empirical correction in previous work. Measurements of the HB surrogate also helped optimize

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**Figure 5.** This T-x-y plot compares the Huber-Bruno model to measurements using ADCR. \( T_k \) on the horizontal axis is plotted against both liquid and vapor compositions of the three components on a mass basis. TMB = 1,2,4-trimethylbenzene, C12 = \( n \)-dodecane, and C14 = \( n \)-tetradecane. All measurements were made at ambient Boulder, Colorado, pressure, and the model is calculated at \( P = 83.18 \) kPa.
the binary interaction parameters used in the model for that mixture. These proof-of-concept experiments indicate that the ADCR is capable of studying mixtures of increasing complexity, although, of course, data analysis will present a challenge with the addition of components. The ADCR will continue to be used to measure VLE for multicomponent fluids with the long-term goal of investigating real fuels, mixtures which contain hundreds of components or more, introducing a data analysis challenge. In future work, an initial approach may be to choose a suite of marker compounds within and representative of these mixtures. In addition, fluids with higher volatility, like gasoline, and mixtures which form azeotropes are both potential targets of future work. The availability of good equations of state and mixture models is a limitation to the types and complexity of fluids that can currently be studied using this approach, although the ADCR technique can be used for any fluid. A more granular set of measurements, i.e., high resolution in the temperature dimension, could circumvent the need for model comparisons. This method may be used to study new fuels and optimize separations. The ADCR may also be directly connected with vapor analysis of arson evidence, and future studies combining the two methods could explore its potential in this area.

## ASSOCIATED CONTENT

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.9b01366.

Comparisons to published distillation curve data; ADCR results in tabular format; extended discussion of sources of error in liquid composition measurements for the decane/tetradecane binary mixture (PDF)

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### Notes

The authors declare no competing financial interest.

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## ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the NIST Special Programs Office.

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