

Improvements in the Measurement of Distillation Curves. 1. A Composition-Explicit Approach[†]

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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 the boiling temperature against the volume fraction distilled, is often cited as a primary design and testing criterion for liquid fuels, lubricants, and other important industrial fluids. While the distillation curve gives a direct measure of fluid volatility fraction by fraction, the information the curve contains can be taken much further; there are numerous engineering and application-specific parameters that can be correlated to the distillation curve. When applied to liquid motor fuels, for example, one can estimate engine starting ability, drivability, fuel system icing and vapor lock, the fuel injector schedule, and fuel autoignition, etc. It can be used in environmental applications as a guide for blending virgin stock with reclaimed oil, guiding the formulation of product that will be suitable in various applications. Moreover, the distillation curve can be related to mutagenicity and the composition of the pollutant suite. It is therefore desirable to enhance or extend the usual approach to distillation curve measurement to allow optimal information content. In this paper, we present several modifications to the measurement of distillation curves that provide (1) temperature and volume measurement(s) of low uncertainty and, most important, (2) a composition-explicit data channel in addition to the usual temperature–volume relationship. This latter modification is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. The analysis is done by gas chromatography coupled with specific or universal detectors. This second modification is the most significant change, since it is composition that is the most important underlying parameter that governs curve shape.

Introduction

One of the most important and informative 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. This volume fraction is usually expressed as a cumulative percent of the total volume. One most often thinks of distillation curves in the context of petrochemicals and petroleum refining,² but such curves are of great value in assessing the properties of any complex mixture.

For crude petroleum, the distillation curve can be divided into distinct regions that contain butanes and lighter, gasoline, naphtha, kerosene, gas-oil, and residue. The temperature at each of these cuts or regions provides an idea of the volatility of each cut. Thus, the relative difference between light crude and heavy crude can be “read” from the distillation curve.³ The detailed structures of the curves are sufficiently rich in information to allow differentiation (by an experienced user) of such diverse feedstocks as Alaskan north slope crude, Arabian light, Louisiana sweet, West Texas sour, and Bonny light (Nigerian). Products resulting from petroleum crude as multicomponent mixtures, such as gasoline, diesel fuel, jet fuel, kerosene, rocket propellant, and missile fuel, are also characterized by the distillation curve as a function of volatility.

The information that can be inferred from the distillation curve extends well beyond the rough description in terms of

fluid mixture volatility that was presented in the preceding paragraph. It has been possible in recent years to relate the distillation curve to operational parameters of complex liquid fuels.^{4–6} These parameters include engine starting ability, vehicle drivability, fuel system icing and vapor lock, the fuel injection schedule, and fuel autoignition, etc. For example, it is possible to directly correlate the fuel system icing rate (a consequence of intake manifold rarefaction) with the distillation temperature of various fractions of gasoline.^{7–9} The front end (low-temperature region) of the distillation curve of gasoline (up to approximately 70 °C) is used to assess and optimize ease of starting and the potential for hot weather vapor lock in engines. The mid-range of the gasoline curve (up to a temperature of approximately 100 °C) is used to assess and optimize cold weather performance, the operational readiness of a hot engine, and the acceleration behavior of a hot engine under load. The top range of the distillation curve is used to assess and optimize fuel economy in a hot engine. In addition to these applications to performance optimization and design, the distillation curve provides an avenue to long-term trend analysis of fuel performance, since changes in the distillation curve are related to changes in fuel performance.⁶

The distillation curve has been an important component in complex fluid modeling and in the development of surrogate mixtures. Indeed, most modeling approaches have sought to use distillation curves as either an input or an output, because of the wide acceptance of such curves.^{4,10} The desire in nearly all recent modeling studies has been to economically represent complex fluid properties. Because of computational overhead, mathematical complexity, and limitations in chemical analysis, the enumeration of every component has not been feasible, although it may be desirable. The more common approach has

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been the development of surrogates for complex fluid mixtures, composed of representative compounds. Clearly, one very important test of the reliability of a surrogate mixture is the reproduction of the distillation curve of the complex fluid by the surrogate.^{11–14}

In addition to these operational and design applications, distillation curves are important in evaluating the environmental impact of the use of complex liquid fuels and the reclamation of waste. Moreover, future application to inhalation toxicology testing is possible, as well as correlation of the distillation curve of diesel fuels with exhaust emissions.^{15–17} The emissions that have been studied include carbon monoxide, particulates, nitrogen oxides, and unburned hydrocarbons obtained from research engines. Among the most useful predictors found for these emissions are the 90% recovery point and the final boiling point of the distillation curve. Beyond the simple prediction of emissions, it has been possible to relate the mutagenic effects of diesel fuel emissions to the distillation curve as well.¹⁵ In this study, the Ames test was applied to the emissions from heavy-duty diesel engines and it was concluded that mutagenicity negatively correlates with cetane number and the upper distillation curve points. This implies that it is possible to use the distillation curve to aid in the design of fuels that have a decreased genotoxicity.

Environmental concerns over the use of turbine fuels have led to stringent emission standards for aircraft jet engines as well as motor vehicle engines. The emissions from turbine engines are dependent on the processing of the fuels, and droplet evaporation modeling has shown that emissions of these turbine fuels can be correlated with parameters from the fuel distillation curve.¹⁸

In addressing the problem of used oil reclamation, one approach that has been used successfully is the blending of processed used oil stocks in diesel fuel. Test vehicles have been run on such mixed fuels (with up to 3% used oil added) for up to 160 000 km. Bench tests of diesel fuels with up to 15% used oil have been done, although impaired performance has been observed at fractions greater than 10% (mass/mass). Current recommendations cover mixtures of up to 5% (mass/mass) reclaimed oil in diesel fuel. The characterization of the mixtures of diesel fuel with reclaimed oil is done by a variety of tests, among which the distillation curve is especially important.¹⁹ Similarly, the presence of appreciable quantities of corrosive components in crude oil is a significant concern. These components include the more familiar sulfur compounds, but also naphthalenic acids.²⁰ Appropriate blending with other stocks is essential to maintain an economical and environmentally acceptable product that can perform in the application that is intended, and the distillation curve is essential in such mixture design.

Related to the problem of reclaimed oil is that of oil lakes near oil wells, especially wells located in areas that have been involved in military conflict, such as in Kuwait. In that country, 700 oil wells were severely damaged.²¹ Large sludge oil lakes exist in and around approximately 300 of these oil wells. Studies are under way to determine if the addition of light crude oil to the sludge can produce a product acceptable for refining. The issue here is the chemical changes caused by weathering, and the potential of an increased concentration of corrosive components. The distillation curve is one of the main measures applied to the mixture of sludge oil with the light crude.

Clearly, from the foregoing discussion, there are many diverse applications for the information that is available from the distillation curve. As mentioned earlier, the most common

formulation of the distillation curve is a plot of boiling temperature (at ambient pressure) against volume fraction. In the American Society for Testing Materials (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, and 90%, and then the final boiling temperature (FBT).^{2,22} There are significant disadvantages associated with the ASTM D-86 test, and these have been well-documented. Large uncertainties can be expected when using the method. Often, specifications for complex fluids are presented in tabular form for the 10, 20, 50, and 90 vol. % fractions. It is common to give such specifications in terms of temperature ranges spanning up to 25 °C.²³ Note that this very large variability encompasses more the uncertainty inherent in the measurement than the variability of the fluid. The results from the ASTM D-86 test have little theoretical significance and cannot be modeled thermodynamically due to shortcomings with the approach.²⁴ This has led to calculational methods applied to the method to produce the true boiling point curve and the equilibrium flash vaporization curve.²² Moreover, other tests have been developed to characterize hydrocarbon mixtures in more quantitative ways, such as with gas chromatography in the ASTM D-2887 method.²⁵ The fact that the ASTM D-86 test remains important to industry, and is the only test that appears to be standardized,²⁴ makes it important to improve the method and get as much information as possible from it. Moreover, in the specification of complex fluids such as liquid fuels, distillation curve data are included as a matter of course; it is rare to find data from other, related tests.

The simplest apparatus for the measurement of distillation curves as set forth in ASTM D-86 embodies a Bunsen burner chamber for heating, a liquid bath with a condensate tube, and a graduated cylinder covered with blotting paper for a calibrated volume receiver.² This most basic approach suffers from numerous disadvantages. There are clear hazards associated with an open flame, even if it is shrouded in a heating chamber, when applied to hydrocarbon fluids. The use of a graduated cylinder as a receiver is problematic because distillate tends to splash into the cylinder, making a precise volume measurement difficult if not impossible. Deflectors are sometimes used to ameliorate (but not eliminate) this difficulty. This basic approach is embodied in several commercial instruments that function under essentially manual control.

The general importance of the distillation curve has led to the availability of commercial instruments that employ electric resistance heating and automated level-following (an optical method for meniscus detection) for the volume measurement and for control of the distillation rate.²⁶ While these commercial instruments provide improvement in terms of convenience, there remain serious shortcomings and opportunities for improvement. The commercial devices determine the IBT with a photocell that detects the first drop to fall into the receiver. This clearly produces a delayed response that usually overstates the IBT that is reported by these instruments. This delay results in a significant systematic uncertainty in the IBT; it is impossible to regard this value as a state point. Moreover, it is not uncommon for complex fluids to show an initial vaporization (noted by the onset of bubbles) followed by a lull and then the onset of sustained boiling. This subtle behavior is missed when using the commercial devices. In addition, one typically selects from a menu of programmed heating profiles for a given fluid (such as a gasoline), and this preselected heating profile will influence the measured value of the IBT. The program selected typically provides ballistic heating to a preset level and then

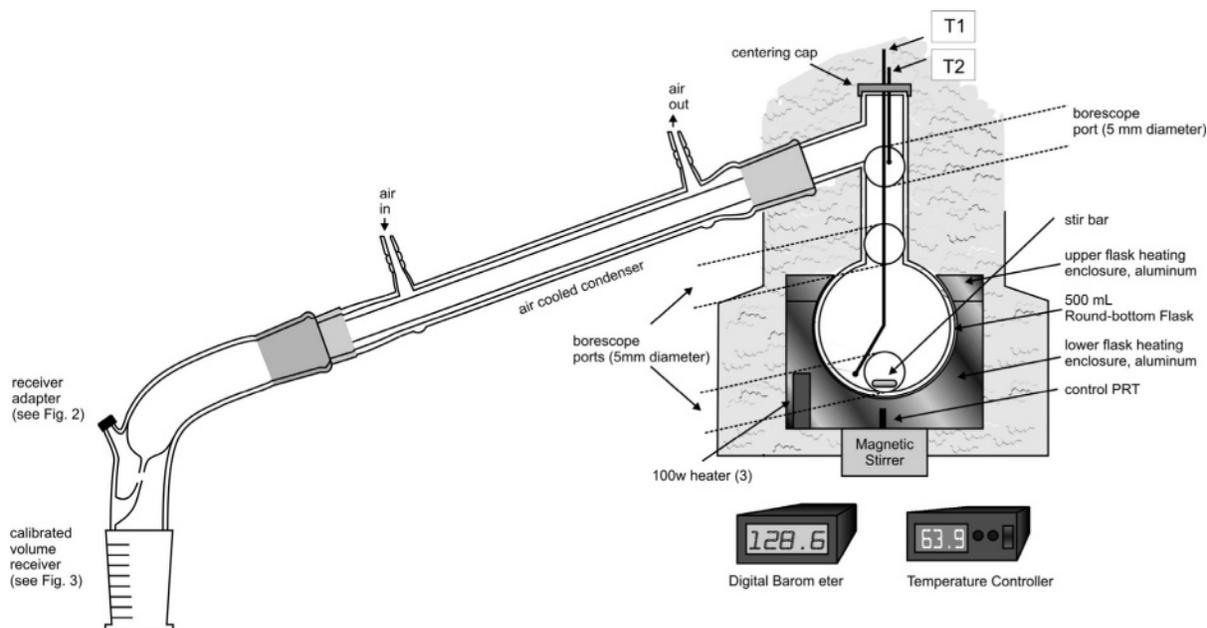


Figure 1. Schematic diagram of the overall apparatus used for the measurement of distillation curves. Note that the size of the bore scope observation ports are only 5 mm in diameter. The size is exaggerated on the figure to make the location clear.

controlled heating after the first 5 mL of liquid has been delivered to the receiver. This exacerbates the uncertainty in obtaining the IBT, and it makes the results from the measurement, to some extent, instrument-dependent. Also, since the distillation flask is not stirred in the commercial devices, the potential for local superheating and nonuniformity in the horizontal direction is significant. The need for stirring of the distillation flask contents has been a recent topic of discussion in standards committees.²⁷

While the shortcomings discussed above are serious, the information obtained from such instruments can be useful nonetheless for coarse quality control and oversight applications, especially given that most operators follow the same procedures. The current approaches cannot be used for most diagnostic or detailed applications, however. Moreover, far greater demands are placed on measurements by the desire to model fluid behavior with, for example, equations of state. For innovative technologies and design, there is a need for measurements that are understood at a fundamental level, with much lower uncertainties, and with none of the instrument dependencies found with commercial devices. Additionally, the information content of the distillation curve can be greatly expanded by adding a composition channel to the temperature channel. By this is meant an explicit composition measurement (both qualitative and quantitative) for each boiling fraction. This is important for even complex fluids because the actual information that is desired from a distillation is some understanding of how the composition varies with volume fraction and boiling temperature. This is the case whether the distillation is done to design or effect a separation (fractional distillation) or serves as a material characterization test (simple distillation).

Experimental Section

The apparatus that has been developed for the measurement of distillation curves with a composition-explicit information channel is depicted schematically in Figure 1, with additional details provided in Figures 2 and 3. The distillation flask is a 500 mL round-bottom flask that is placed in a two-part aluminum heating jacket (alloy 6061), the lower part of which

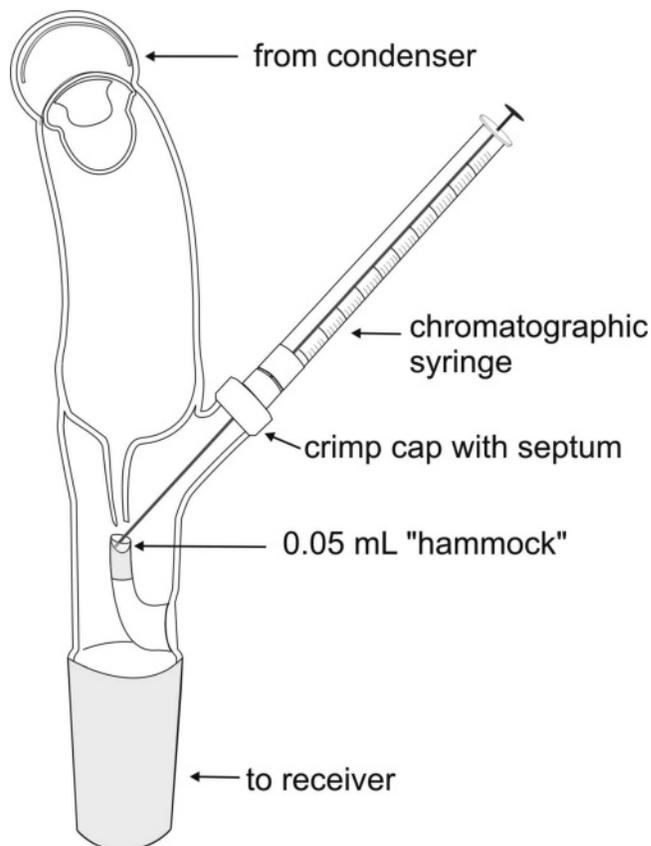


Figure 2. Schematic diagram of the receiver adapter developed for this work to provide on-the-fly sampling of distillate cuts for subsequent chromatographic analysis.

is contoured to fit the flask. The upper part is placed around the flask after the flask has been inserted into the contoured (lower) part of the jacket. This two-part enclosure effectively surrounds approximately four-fifths of the spherical section of the flask. Three cartridge heaters are placed in the lower, contoured part of the jacket, arranged in a "Y" pattern, to provide uniform heating axially about the radius of the enclosure. These heaters are controlled with a proportional integral derivative

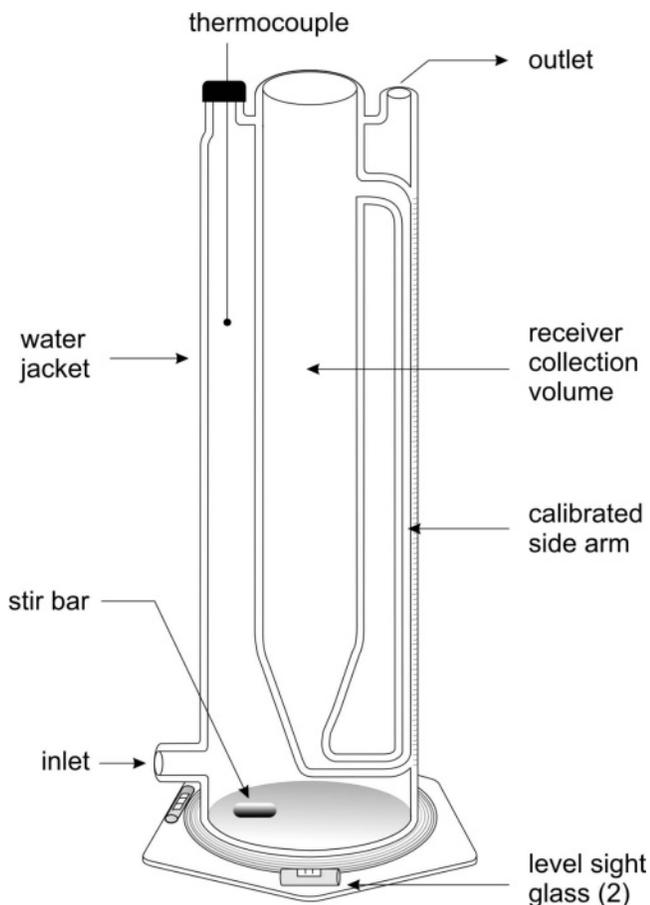


Figure 3. Schematic diagram of the level-stabilized receiver developed for this work.

(PID) controller in response to a platinum resistance sensor in the bottom of the lower jacket. Heating the flask in this way produces a temperature gradient in the vertical direction, while providing temperature uniformity in the horizontal direction. The jacket and heaters are capable of operation up to 350 °C, with a local uniformity of 0.2 °C. Note that this is the uncertainty in the control as well as the uniformity. All of the uncertainties reported in this work are estimates of a combined expanded uncertainty with a coverage factor of 2 (that is, 2σ). The jacket exterior is insulated with a Pyrex wool enclosure. This insulation extends the length of the distillation head. This ensures minimal heat leak in the vertical direction and, therefore, a small, constant temperature gradient to minimize refluxing. Three observation ports are provided in the insulation to allow penetration with a flexible, illuminated bore scope. The bore scope ports, illustrated in Figure 1, are placed to observe the fluid in the boiling flask, the top of the boiling flask (where the spherical section joins the head, and the distillation head (at the bottom of the take off). Note that the size of each of the bore scope ports is only 5 mm in diameter; the size is exaggerated in the figure simply to make the port locations clear. The use of small bore scope ports for observation prevents unnecessary heat loss and subsequent loss of temperature uniformity in the horizontal direction.

Above the distillation flask, a centering adapter provides access for two thermally tempered J-type thermocouples that enter the distillation head. Although a variety of temperature sensors can be used, including platinum resistance thermometers, the very small thermal mass of an exposed thermocouple junction offers a rapid response. One thermocouple (TC1) is centered at the low point of distillate takeoff (the typical

distillation head placement, as recommended graphically in ASTM-86), and the other (TC2) enters the distillation flask and is submerged in the fluid, to monitor the temperature of the bulk fluid. Both of these thermocouples were calibrated in an indium triple point cell traceable to a National Institute of Standards and Technology (NIST) standard. The repeatability of temperatures measured with these thermocouples indicated minimal drift with time. Monitoring the bulk fluid temperature in addition to the head temperature is valuable for modeling studies²⁸ and provides lower uncertainty in the overall test method. This thermocouple is well below the surface of the fluid, and the effects of local superheating are minimized by stirring the contents of the flask. This will be described in more detail below. The thermocouples positioned as stated provide a rapid response to temperature, with an uncertainty of 0.05 °C.

Beneath the aluminum jacket, a magnetic stirrer drive is positioned to couple with a magnetic stir bar inside the distillation flask. Stirring the contents of the distillation flask is essential for maintaining horizontal temperature uniformity in the fluid. Indeed, although the cartridge heaters can provide a uniformity of 0.2 °C, stirring integrates variations throughout the volume, allowing the measured temperature from TC2 to be much more uniform and less uncertain. Since a vortex forms on the surface of the fluid because of the stirring, it is necessary to decrease the stirring rate as the measurement progresses, to prevent premature lift-out of the thermocouple, TC2, from the fluid. The lift-out of TC2 from the fluid is an inevitable result of the end of the measurement, however, and is a very useful indication of the end of a measurement. This is easily recognized as a sudden upturn in temperature.

Distillate is taken off the flask with a distillation head, into a forced-air-cooled condenser. Following the condenser, the distillate enters a newly designed transfer adapter that allows instantaneous sampling of distillate for chromatographic analysis.²⁹ (Since this is one of the major new features of this approach, it will be described in some detail. The position of the transfer adapter is shown in Figure 1 and is illustrated schematically in more detail in Figure 2. The flow path of the distillate is focused to drop into a 0.05 mL “hammock” that is positioned directly below the flow path. This hammock was made from a short section of borosilicate glass rod; the sample well was formed with a platinum stylus sized to produce the desired volume when pressed into the molten glass. Naturally, the actual size of a drop resting on the hammock at any given time will be determined by surface tension considerations, in addition to the volume of the hammock itself.

The distillate from the condenser drops into this volume before it falls into the receiver. The drop falling into the hammock causes most of the previous sample drop to be washed out. This washing-out is facilitated by the placement of the hammock at an approximate 15° angle with respect to the horizontal. Sample carry-over has been tested and was found to be a very minor source of uncertainty in the present context of monitoring distillation progress and the measurement of distillation curves. A crimp cap fixture is incorporated as a sidearm of the adapter. This allows a replaceable crimp cap with a silicone or Teflon septum (of the type used for chromatographic automatic sampler vials) to be positioned in line with the hammock. The distance from the crimp cap to the base of the hammock is suited to the needle length of typical gas chromatographic syringes.

To sample the distillate, one simply positions the chromatographic syringe, preferably equipped with a blunt tipped needle, in the well of the hammock. It is a simple matter to withdraw

samples as a function of distillate volume when a calibrated receiver is used for collection. The sample can then be directly injected into the gas chromatograph or added to a weighed vial containing an appropriate solvent. The first approach, direct injection of the harvested sample into the gas chromatograph, provides for fast analyses, while the second approach allows for multiple sample injections and a lower, explicitly determined uncertainty in composition. Either approach is suited to qualitative analysis, with gas chromatography–mass spectrometry (GC-MS), or gas chromatography–infrared spectrophotometry (GC-IR), or a more sophisticated combination (for example, GC-MS-IR). Moreover, specific detection systems may be coupled for the identification of trace species, such as may be provided with a sulfur chemiluminescence detector.

The motivation for locating the sampling point just before the receiver requires some discussion. It might seem advantageous (for example, in equation of state modeling work) to sample the distillate just as it condenses in the head. This approach is not workable for a number of reasons. The nature of the distillation process causes continually changing temperatures in the head. This will cause the composition to vary; it will be a function of a changing vapor–liquid equilibrium as the temperature of the condensing fluid changes as it moves from the head into the condenser. Sampling just before the receiver ensures that the relation of volume with composition is preserved and that the composition is measured at the same fluid temperature for each aliquot that is collected. While vapor–liquid equilibrium will undoubtedly control the composition at the receiver, the constant temperature will allow this to be modeled if need be. In addition to this consideration, one must consider the strong likelihood of vapor lock occurring in the syringe if the fluid is sampled in the head. Syringe vapor lock can be addressed with a vortex-cooled syringe,³⁰ but vapor lock in the needle will be impossible to address.

When the sample drops from the sampling transfer adapter, it flows into the calibrated receiver to allow a volume measurement. As mentioned earlier, the simple graduated cylinder that is often used for the volume measurement (and that is illustrated in ASTM-86) is not optimal because of the relatively large uncertainty, and the fact that distillate splashes into the cylinder, causing difficulty in determining the volume. The use of drop deflectors can help prevent splashing, but they can cause a higher uncertainty in the volume measurement because of hold-up on the walls of the receiver. Automated optical level followers make the volume measurement easier, but they can also be a source of uncertainty, and they make it impossible to sample the distillate. To improve the precision of the volume measurement, the calibrated receiver that is shown in Figure 3 was developed. Constructed of glass, this receiver consists of a central volume that gradually decreases in diameter at the base and connects to a small-diameter sidearm sight glass that is calibrated. The sidearm stabilizes the fluid level for a precise volume measurement as the distillation proceeds. The large inner volume and the sight glass are enclosed in a water jacket that contains a thermometer and a magnetic stir bar for circulation. The tube of the sight glass is actually glass-welded to the inside wall of the water jacket, to eliminate parallax in reading the volume. The water jacket allows the receiver to be maintained at a suitable temperature, and the stirrer ensures acceptable temperature uniformity. In normal operation, the tubulation in the lower part of the water jacket is closed, but when necessary it can allow thermostat fluid to circulate from an external bath. When an external circulation bath is used, the stirrer is not necessary. Two separate receivers have been made, with sidearm inside

diameters of 3 and 6 mm, respectively. The availability of these two sizes allows measurement of fluids with varying surface tensions.

The sidearm sight glass allows a volume measurement with an uncertainty of 0.05 mL. The sight glass is calibrated with the volumes of interest to the distillation curve (10–200 mL, in 10 mL increments) with a volumetric pipet. Calibration with the fluid(s) of interest will allow the user to check for unfavorable surface tension effects. The only common fluid that appears to require correction for differential capillary action is water; if the receiver is used for the measurement of aqueous mixtures, this must be explicitly addressed. Note that a sidearm of the same inside diameter as the receiver cylinder would of course eliminate the problem entirely, but would result in a very large receiver.

The volume measurement in the sidearm is unaffected by splashing in the collection volume, so the distillate is allowed to drop directly into the center of the collection volume space. This minimizes hold up on the walls of the vessel. Splashing causes some hold up, but this is much less than when a deflector is used. The base of the receiver is equipped with two bull's-eye type levels 90° apart to ensure that the liquid level in the large volume and the sidearm are collinear.

To perform a measurement, 200 mL of the fluid to be measured is placed in the round-bottom flask (typically with 100 mL pipets), and the thermocouples are placed in the appropriate positions. This fluid volume has been chosen for convenience; any volume suitable for the measurement can be used. To determine the heating rate, it is valuable to calculate the approximate phase behavior of the fluid with an equation of state. In this work, we have used an extended corresponding states model that has a predictive capability.³¹ A model such as this can provide a target temperature that can be expected to fall somewhat below the initial boiling temperature, but which can be approached rapidly. Prior experience with a particular fluid is also valuable in determining a target temperature, although a chemical analysis of the fluid can be used as well, in combination with the equation of state. As the predicted initial boiling point is approached, the heating rate can be decreased and the content of the flask observed (through the bore scope) for the onset of boiling. Once the initial bubbles are detected, the upper part of the round-bottom flask can be observed (with an illuminated bore scope) for the formation of condensation. Finally, the distillation head can be observed for condensation in a similar manner. Once distillation begins and vapors rise into the head, there is no further advantage in visual monitoring, and it is thus discontinued.

As distillate vapors first form in the condenser, a sampling syringe (typically a 10 μ L gastight chromatographic syringe) is positioned in the 0.05 mL hammock of the transfer adapter. As the first drop emerges from the condenser, it is possible to withdraw an aliquot for analysis. Similarly, as the fractions for 10, 30, 50 mL, and so on, emerge from the condenser, one can obtain analytical aliquots in addition to the temperature–volume data. The small size of the analytical sample has no effect on the volume measurement. Finally, the composition of the last drop to emerge from the condenser, along with its volume fraction, can be obtained. Typically, this is not 100%, but rather 96–98% due to hold up in the apparatus. While a fresh syringe can be used for each aliquot, maintaining the syringe in a heated, evacuated chromatographic syringe cleaner between samplings has proven to be an acceptable approach.

It is best to maintain a constant mass-transfer rate during the distillation. This can be measured at the condenser exit. In

commercial devices, this is done with a PID controller with a response fed back into the heater controller. This is often a source of uncertainty. In the developmental apparatus described in this paper, the constant mass-transfer rate is obtained by manually programming the PID controller. Because of the design of this apparatus, however, it is far less critical to maintain a constant mass-transfer rate.

The temperatures recorded for the distillation curve are measured at local atmospheric pressure. This must be corrected to the value that would be obtained at 1 atm. For this reason, a digital barometer is used to measure the atmospheric pressure before and after the measurement. The uncertainty of the digital barometer used in this work was 0.15 Pa. The average of these two pressures is used to correct the temperature readings to standard atmospheric with a modification of the Sidney Young equation. The procedure of ASTM-86 specifies that the correction be done with the following equation:

$$C_c = C(760 - P_a)(273 + T_c) \quad (1)$$

where C_c is the correction added to the observed temperature, C is a constant, 0.000 12, P_a is the atmospheric pressure in mmHg, and T_c is the measured temperature in °C. In fact, the original Sidney Young equation specifies that C_c is dependent upon the average hydrocarbon chain length of the fluid, ranging from 0.000 135 for a single carbon to 0.000 119 for eight carbons. A linear correlation of these factors can be used to predict a value for simple fluids. It should be noted that the Sidney Young equation may have significant limitations when applied to correct boiling point temperatures more than 5 kPa from standard atmospheric pressure.³²

Results and Discussion

As a test system for the new method and apparatus, we have used replicate mixtures of *n*-decane + *n*-tetradecane (CAS Registry Nos. 124-18-5 and 629-59-4, respectively), with the mixtures having mole fractions of 50/50 and 75/25. These research grade fluids were obtained from a commercial source, and their purity was checked by gas chromatography with mass spectrometric detection (30 m capillary column of 5% phenyl dimethyl polysiloxane having a thickness of 1 μm, temperature program from 90 to 225 °C, 7 °C/min). The purity was found to be better than 99.99, mass/mass, and the fluids were used as received. The mixtures (at a nominal 50/50 and 75/25 (mol percent); actual compositions as prepared gravimetrically are provided in Tables 1 and 2) were prepared gravimetrically as stock solutions. The uncertainty of the mass measurement 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. Three distillation curves were measured with the 50/50 mixture and two were measured with the 75/25 mixture. In this paper, temperatures measured by TC2 in the liquid will be referred to as T_k . This nomenclature arises from tradition; the distillation flask is often called the kettle. Temperatures measured with TC1 will be called T_h , referring to the position centered at bottom of the takeoff in the distillation head.

For the 50/50 mixture, bore scope observation allowed measurement of the temperature for the appearance of the first vapor bubble at 191.8 °C, measured by TC2 in the liquid. Typically, the first bubbles will appear intermittently and will quell if the stirrer is momentarily stopped. Sustained vapor bubbling in the distillation flask was observed at 193.6 °C. In the present context, sustained bubbling is also somewhat intermittent, but it is observable even with the stirrer momen-

Table 1. Representative Data for the Distillation Curve Data of a 50/50 Mole Fraction Mixture of *n*-Decane + *n*-Tetradecane (Actual Composition, 0.499/0.501)^a

vol fraction, %	T_k^{obs} , °C	T_k , °C	x , C10	x , C14
0.025			0.966	0.034
5	192.8	200.0		
10	195.0	202.2		
15	197.7	205.0	0.918	0.082
20	200.7	208.0		
25	204.3	211.7	0.896	0.104
30	208.3	215.7		
35	213.8	221.3	0.875	0.125
40	221.2	228.8		
45	230.0	237.8		
50	236.7	244.6	0.416	0.584
55	240.7	248.6		
60	242.8	250.8		
65	244.0	252.0	0.049	0.951
70	244.5	252.5		
75	244.6	252.6	0.000	1.000
80	244.4	252.4		
85	244.4	252.4	0.000	1.000
90	245.3*	253.3*		
95	250.5*	258.6*		
98			0.000	1.000

^a The uncertainties are provided in the Experimental Section. The asterisk indicates that the temperature was measured after lift-out of TC2 and therefore is not part of the distillation curve proper, merely an indicator of the end of the measurement. Temperatures noted as T_k are corrected to 1 atm with the modified Sidney Young equation. The actual observed temperatures are presented as T_k^{obs} and were measured at 82.46 kPa.

Table 2. Representative Data for the Distillation Curve of a 75/25 Mole Fraction Mixture of *n*-Decane + *n*-Tetradecane (Actual Composition, 0.747/0.253)^a

vol fraction, %	T_k^{obs} , °C	T_k , °C	x , C10	x , C14
0.025			0.986	0.014
5	178.9	185.4		
10	179.7	186.2		
15	180.4	186.9		
20	181.5	188.0	0.969	0.031
25	182.6	189.1		
30	184.0	190.5	0.958	0.042
35	185.3	191.9		
40	187.6	194.2	0.949	0.050
45	189.7	196.3		
50	192.8	199.5	0.929	0.071
55	196.4	203.1		
60	202.6	209.4	0.875	0.125
65	210.8	217.7	0.848	0.152
70	221.6	228.7	0.773	0.227
75	234.8	242.1		
80	241.9	249.3	0.173	0.827
85	243.9	251.3		
90	249.2*	256.7*		
95	257.5*	265.1*	0.000	1.000
98			0.000	1.000

^a The uncertainties are provided in the Experimental Section. The asterisk indicates that the temperature was measured after lift-out of TC2 and therefore is not part of the distillation curve proper, merely an indicator of the end of the measurement. Temperatures noted as T_k are corrected to 1 atm with the modified Sidney Young equation. The actual observed temperatures are presented as T_k^{obs} and were measured at 83.82 kPa.

tarily stopped. Vapor was observed rising into the head when T_k reached 196.5 °C, which is considered to be the initial boiling temperature for the mixture. It is at this point that the bubbling is sustained and no longer intermittent and is observed to occur with or without stirring. These temperatures were measured at the average atmospheric pressure measured at 82.46 kPa and are corrected with the modified Sidney Young equation, as discussed earlier, in which $C = 0.000 109$ for an average carbon chain of 12 units. Likewise for the 75/25 mixture, performed at an average atmospheric pressure of 83.82 kPa, the initial

Table 3. Comparison of the Observed Initial Boiling Temperatures (T_k^{obs}) with Those Calculated with an Extended Corresponding States Approach ($T_{\text{IBT}}^{\text{ECS}}$) and a Helmholtz Energy Approach ($T_{\text{IBT}}^{\text{H}}$)^a

temp, °C	50/50 mixture	75/25 mixture
T_k^{obs}	190.3 (82.46 kPa)	178.1 (83.82 kPa)
$T_{\text{IBT}}^{\text{ECS}}$	191.3	177.3
$T_{\text{IBT}}^{\text{H}}$	190.7	177.1
T_k	196.5 (101.3 kPa)	184.6 (101.3 kPa)
$T_{\text{IBT}}^{\text{ECS}}$	200.2	185.0
$T_{\text{IBT}}^{\text{H}}$	199.6	184.8

^a The first three entries are at the observed pressures, while the last three compare calculated values with measurements corrected to standard atmospheric pressure with the modified Sidney Young equation (designated T_k).

bubbling was observed at 182.0 °C, bubbling was sustained at 183.3 °C, and vapor was rising into the head at 184.6 °C (the initial boiling temperature). It must be noted that although vapor was observed to rise into the head at the temperature taken to be the initial boiling temperature, the reading of TC1 was only 65–70 °C. This is because, early in the distillation, insufficient mass transfer through the head prevents a reliable response. The only valid measurement of the initial boiling temperature is that made directly in the fluid.

It is instructive at this point to contrast these observed temperatures with what would have been obtained if the initial boiling temperature had been determined at the point at which the first drop passed into the receiver. Recall that this is the point at which the initial boiling temperature is determined when using a commercial distillation curve instrument. For the 50/50 mixture, the difference in temperature was found to be approximately 7 °C, and for the 75/25 mixture, this difference was approximately 11 °C. In fact, for all of the distillation curves that have been measured as part of this work, the differences ranged from 7 to 13 °C, and averaged 9.4 °C. It is clear that a significant systematic error is introduced by reporting the initial boiling temperature as the first drop of distillate enters the receiver. Differences such as these have been reported previously.²⁴

The measurement of temperature directly in the fluid allows comparison of measured thermodynamic state points with selected models and is a major advantage of the approach presented here. It is possible, for example, to compare the observed initial boiling temperatures with those predicted from thermodynamic models. In Table 3, the observed initial boiling temperatures of the 50/50 and 75/25 mixtures are presented along with predictions from an extended corresponding states treatment ($T_{\text{IBT}}^{\text{ECS}}$)³³ and a Helmholtz energy treatment ($T_{\text{IBT}}^{\text{H}}$).³⁴ While additional phase equilibria data on the *n*-decane + *n*-tetradecane mixture could significantly improve the agreement with the models, this initial comparison with the measured IBT is very good.

Representative distillation curves for the mixtures (at 50/50 and 75/25 (mole percent)) are presented in Figure 4a,b, respectively. The figures present the measurements from TC2 positioned in the distillation flask (in Figure 1), referred to as T_k . The measurements of T_k against volume fraction for the representative data sets are presented in Tables 1 and 3. The observed temperatures (at ambient pressure) and the temperatures that have been corrected to standard atmospheric pressure with the modified Sidney Young equation are presented.

There are several reasons for presenting T_k rather than the temperature measured at the bottom of the distillation head takeoff, T_h . Provided one has eliminated the potential of local superheating by appropriate design of the apparatus, the temperature represented at T_k is a true state point at which the

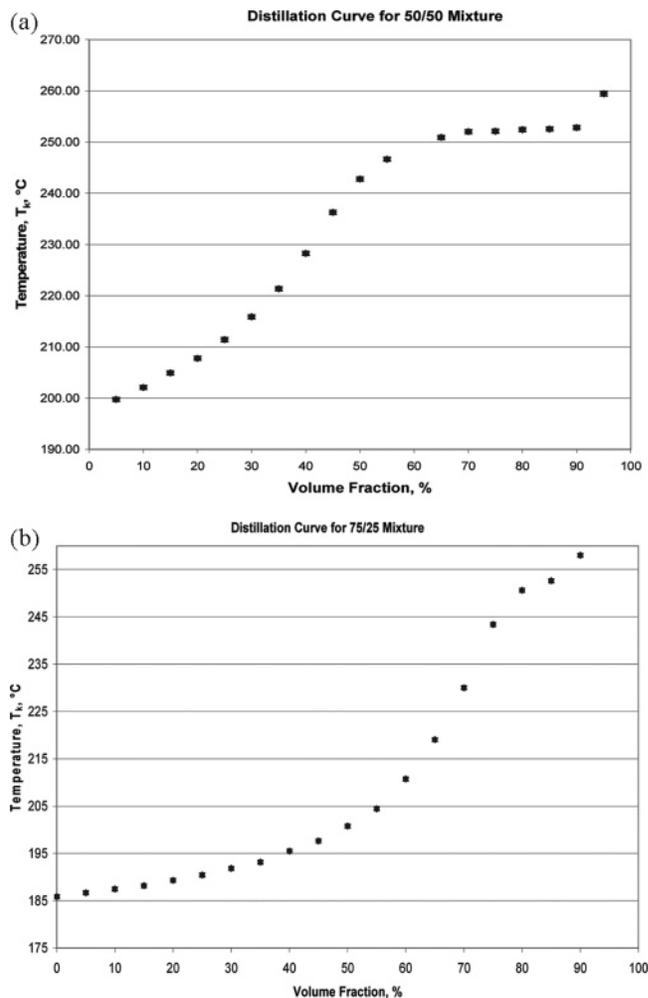


Figure 4. Representative distillation curve for (a, top) a 50/50 and (b, bottom) a 75/25 (mole percent) mixture of *n*-decane + *n*-tetradecane, measured with TC2 inside the fluid. Note that the second inflection at a volume fraction of approximately 97% is the lift-out of TC2, as explained in the text. It is not part of the distillation curve proper, but it is an indicator of the end of a measurement. The error bars represent an uncertainty of two standard deviations.

vapor and liquid phases are in equilibrium, even if this equilibrium is changing (relatively slowly) in time. In the present apparatus, this has been achieved with the uniform aluminum heating enclosure and by stirring the fluid in the distillation flask. In this respect, the temperature measured in the fluid is apparatus-independent. In contrast, the temperature measured in the head is subject to great variability caused by changes in mass transfer through the head. This is alluded to in ASTM-86, where this unfavorable behavior has been described as hesitation.² Note that the presence of moisture in the sample can produce a similar observation. The physical distance between the distillation flask and the distillation head will greatly affect the measured temperature T_h . These factors combine to render T_h at least somewhat, if not significantly, instrument-dependent. This point will be further expounded upon later.

The typical reproducibility of replicate distillation curves is illustrated in Figure 5, in which three measurements of the 50/50 mixture are presented. Here, T_k is plotted against volume fraction. The systematic deviations in the temperature readings against volume fraction, while very small, are nonetheless larger than the uncertainty of the temperature measurement from TC2. These deviations are the result of performing the measurements at different atmospheric pressures (on different days), limitations in the correction to standard atmospheric pressure with the

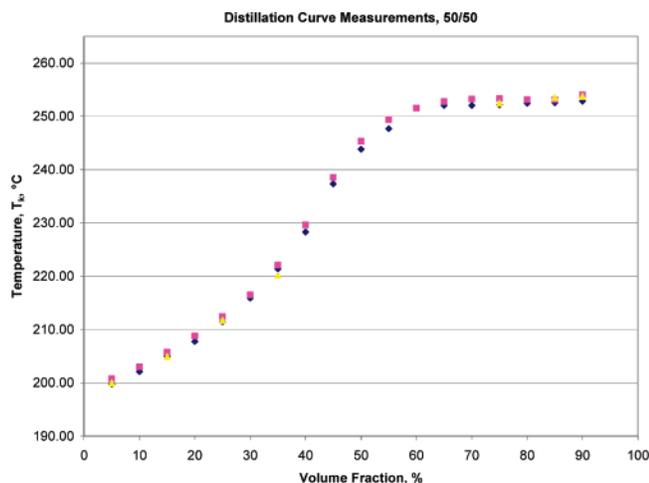


Figure 5. Typical reproducibility of the distillation curve, in which three separate measurements for the 50/50 (mole percent) mixture of *n*-decane + *n*-tetradecane are presented.

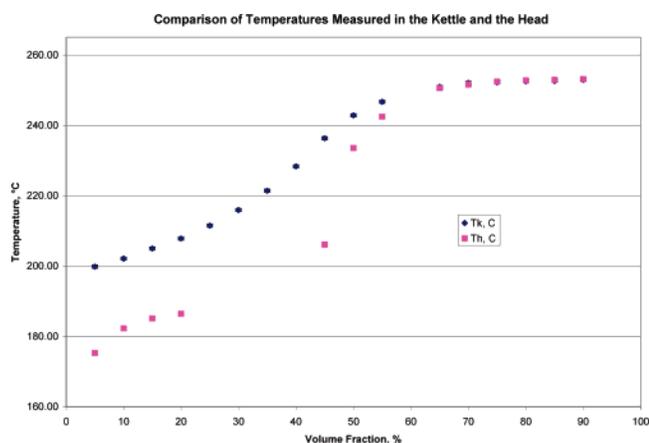


Figure 6. Comparison of measurements taken with TC1 (in the head) and TC2 (in the kettle), for the 50/50 (mole percent) mixture of *n*-decane + *n*-tetradecane. It is clear that, at the beginning of a distillation, the head temperature significantly lags the temperature of the fluid in the kettle. In the latter stages of the measurement, the plotting symbols overlap.

Sidney Young equation, minor composition variations among the starting (stock) mixtures, and uncertainty in maintaining a constant mass transfer of vapor through the distillation head.

The typical relationship between T_k and T_h for the 50/50 mixture of *n*-decane and *n*-tetradecane is provided in Figure 6. Note that, for this measurement, an effort has been made to maintain a constant rate of mass transfer through the distillation head by increasing heat input to the distillation flask as the measurement progresses. Nevertheless, it is clear from this figure how, at the start of the measurement, T_k leads T_h ; then, as the distillation proceeds, the temperatures become closer while not becoming equal. This relationship between T_k and T_h has been found for all the measurements done for this work.

The distillation curves in Figure 4a,b have the sigmoid shape that is expected for a well-defined mixture with components that differ appreciably in size and relative molecular mass. In the 50/50 mixture, one can observe symmetry about the inflection point, while for the 75/25 mixture the inflection is skewed from the heavier component.

The application of the adapter shown in Figure 2 allows for periodic sampling, on-the-fly, of the distillate cuts emerging from the condenser. Moreover, these cuts can be directly and unambiguously related to the volume fraction, since there is negligible delay between a drop becoming available for sampling

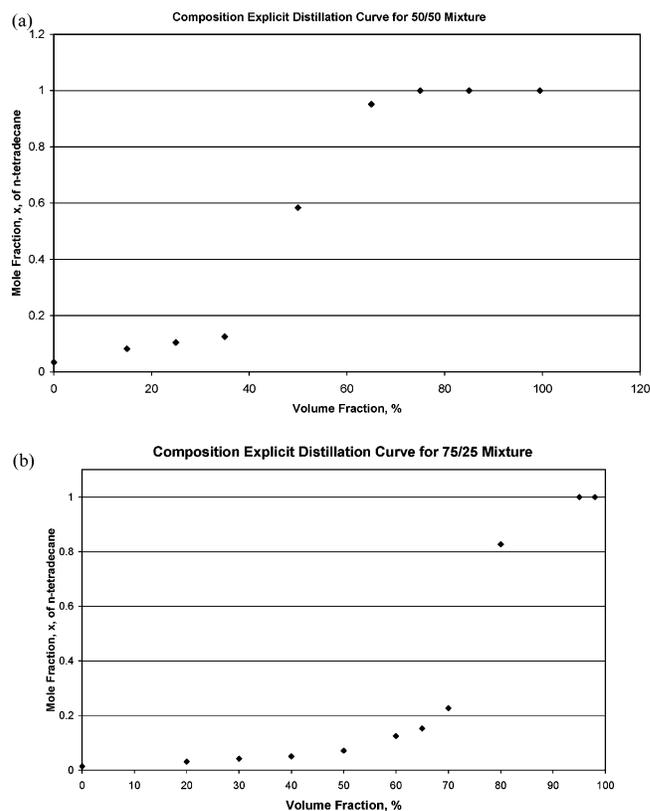


Figure 7. Composition-explicit distillation curve expressed as the mole fraction of *n*-tetradecane as a function of volume fraction for (a, top) a 50/50 and (b, bottom) a 75/25 (mole percent) mixture of *n*-decane + *n*-tetradecane. The error bars are smaller than the plotting symbols on the figure.

in the hammock of Figure 2 and its integrated volume measurement. In this work, aliquots of 7 μL of emergent fluid were withdrawn and added to a vial containing a known mass of solvent (*n*-hexane). Samples were taken to correspond to T_k –volume fraction data pairs, thus providing a composition channel of data for the distillation curve. Distillate cut samples, in *n*-hexane, were then analyzed with a gas chromatographic method (30 m capillary column, 0.250 mm outside diameter, coated with 1 μm of dimethyl polysiloxane, temperature programmed from 90 to 250 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$, autosampler injection into a split injector set at 100:1, flame ionization detection). Calibration was provided by external standards (a mixture of *n*-alkanes from C_9 to C_{15}) measured before and after each solution cut.

The measured compositions as a function of volume fraction for representative 50/50 and 75/25 mixtures are shown graphically (with composition expressed as mole fractions) in Figure 7a,b, respectively. The compositions associated with the T_k –volume fraction pairs are also listed in Table 3. Note that not all of the composition measurements can be related to a volume fraction. It is of interest, for example, to obtain a sample of the very first drop of fluid to emerge from the condenser. This analytical sample has no volume measurement (other than perhaps the approximate volume of the hammock) associated with it. Likewise, the very last drop of distillate is delivered to the hammock after the thermocouple TC2 lifts out of the fluid, producing an invalid temperature (see the discussion of lift out in the Experimental Section). Thus, the analysis of this cut has no associated T_k value. While the analyses of these cuts are interesting and important, they are not actually part of the composition channel of data associated with the distillation curve, but rather provide additional information.

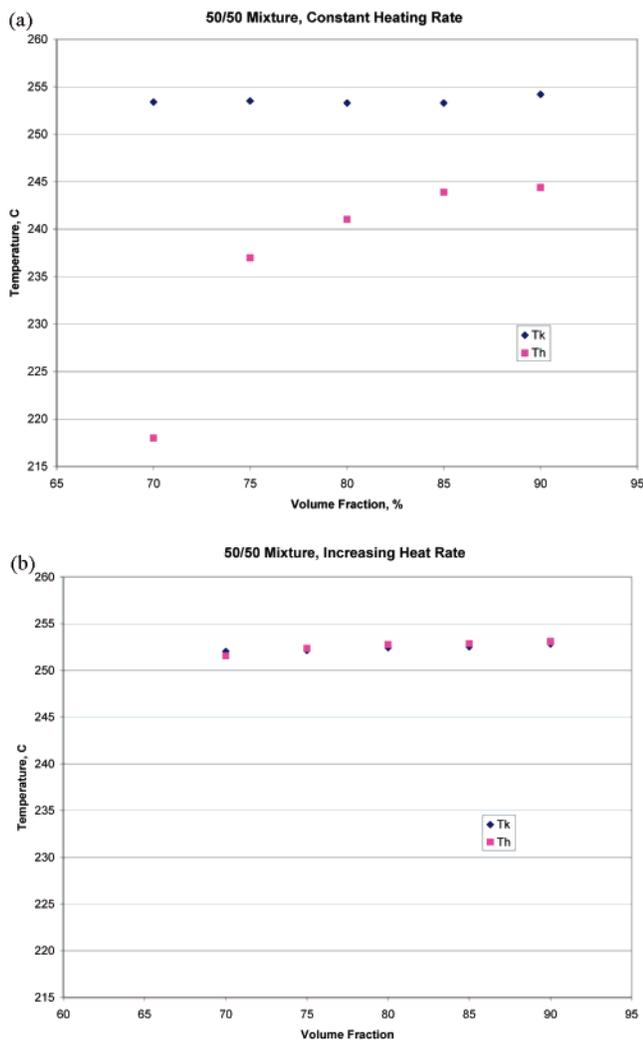


Figure 8. (a, top) Part of a distillation curve measured for a 50/50 mixture of *n*-decane + *n*-tetradecane, in which the heating rate has been maintained constant. Note that the T_k readings are essentially constant, at 253.3 °C. (b, bottom) Part of a distillation curve measured for a 50/50 mixture of *n*-decane + *n*-tetradecane, in which the heating rate has been increased as the measurement progressed. This produces a constant distillation rate. Note that the T_h readings converge with the T_k readings and are essentially constant, at approximately 253.3 °C.

It is clear that the general shape of the distillation curve (Figure 4a,b) is reflected in the changing composition of the cuts shown in Figure 7a,b. In the case of the 50/50 mixture, symmetry about the inflection is apparent, while in the case of 75/25, the curve inflection is skewed toward the heavier component. Thus, when considering the plot showing the mole fraction of *n*-decane, the inflection is reached only after a much longer period of distillation. The composition channel is invaluable in that composition is the actual parameter that is desired from a distillation. Moreover, modeling of equilibrium in mixtures generally requires explicit knowledge of cut composition.

Beyond the obvious intrinsic value of the composition channel, this information provides additional justification for presenting the distillation curve in terms of T_k rather than in terms of T_h . It was stated earlier that T_h is to some extent instrument-dependent and that one must increase the heating rate during the course of a measurement to maintain a constant mass-transfer rate. This is demonstrated in Figure 8a,b, in which the volume fractions between 70 and 100% are presented for distillation curves for a 50/50 mixture of *n*-decane + *n*-tetradecane. The data shown in Figure 8a were obtained at a

constant heat input, while those shown in Figure 8b were obtained with an increasing rate of heat input. In both cases, the measured T_k indicate essentially a constant value of 253.3 °C. In Figure 8a, the values of T_h approach those of T_k but never reach that value. In Figure 8b, with increasing heating rate, the temperatures are able to asymptotically converge. The inference from the T_k values is that a pure fluid is boiling; only one component remains.

To determine which temperature is valid, one can look to the composition measurement channel. The measured mole fraction of *n*-tetradecane for each of these points in Figure 8a,b is 1; no *n*-decane was found on the chromatograms of these cuts. Clearly, a constant boiling fluid is expected for a fluid that is (by that point in the distillation) essentially a single component. This is what is in fact observed with the measured, constant temperature represented by the T_k values in Figure 8a,b, at 253.3 °C. This argument is substantiated by comparison of the normal boiling temperature of *n*-tetradecane, 253.7 °C, with the values of T_k .³⁵ It is clear that the T_h values in Figure 8a are not meaningful, while the T_k values on both figures are meaningful (regardless of how the measurement is performed) and consistent with the measured cut composition. In contrast, the measurement of T_h is dependent on how well the distillation rate is controlled.

Conclusions

This paper demonstrates that it is possible to add a chemical composition channel to the temperature–volume fraction information available from a distillation curve. The value of this information is clear from the multitude of distillation curve applications that have been described in the Introduction. The overall appearance of the composition channel data has been shown to mimic the temperature channel. Quantitatively, the composition channel is consistent with the temperature channel. When the temperature channel of the distillation curve indicates a leveling off to a constant temperature, the corresponding composition channel confirms that the mixture has in fact progressed (by distillation) to a pure fluid. In addition to the composition information, it is possible to decrease experimental uncertainty by eliminating unfavorable temperature gradients, thereby enabling measurement of the temperature directly in the fluid. This measurement is physically meaningful and is apparatus-independent. Measurement of the temperature in the traditional position, at the bottom of the takeoff in the head, produces measurements that are not always meaningful and which are always to some extent apparatus-dependent. Moreover, the approach used here provides initial boiling temperatures that are physically meaningful. All of these improvements make the distillation curve more amenable to thermodynamic modeling, which has historically been a major complaint about current approaches. In addition to these modifications, the introduction of the level-stabilized receiver significantly decreases the uncertainty of the volume measurement.

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