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Method and Apparatus for Precision In-Line Sampling of Distillate*

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Abstract: In this short note we present a method and describe a simple apparatus for use with simple, fractional, and steam distillation operations in which the operator requires a precise measurement of instantaneous distillate composition as the distillation proceeds. There are many examples in which such a measurement will play a critical role. One such example is in the measurement of boiling or distillation curves, where one desires an explicit measure of distillation process temperatures as a function of distillate volume fraction. The ability to augment temperature-volume distillation curves with composition information is very helpful. The optimization of critical distillation conditions for the separation of sensitive solutes is another example in which instantaneous distillate composition is of value. The purification of reactants before a reaction is still another example. In all of these cases, it is the instantaneous composition that emerges from the condenser that is needed, rather than the integrated composition of the distillate that accumulates in the receiver. In this note, the apparatus and method are described, and an example is given with a mixture of n-decane/n-tetradecane.

Keywords: Distillation, instantaneous composition, sampling

INTRODUCTION

Distillation is a common separation method used daily in many areas of research and industry (1). In the chemical processing industry, it is the

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single most common separation method, responsible for the separation and purification of millions of tons of commodity chemicals (2, 3). Moreover, separations by distillation account for the largest single unit operation cost (4). Because of the importance of distillation, laboratory scale distillations often bridge the gap between bench scale processes and pilot scale processes, and finally, plant scale processes. Research performed for separation scale-up requires a high level of precision to determine optimal conditions not only for purity levels but also for the economical considerations that are inherent in the design of industrial separations. In these instances, distillation parameters must be optimized with measurements of an acceptably low uncertainty.

Another example in which low uncertainty is a requirement is in the measurement of distillation or boiling curves for important fluids (5). Distillation curves are graphical representations of the volume fraction of distillate plotted (or fitted) against the head and kettle temperatures. They are used as a diagnostic tool to approximate the vapor-liquid equilibrium of fluid mixtures such as petrochemicals. It is clearly desirable to augment volume-temperature data with composition data, since the main interest in the distillation process is the composition that can be obtained. In this case, what one desires is the instantaneous composition of the distillate that emerges to produce particular volume fraction, rather than the integrated composition that is accumulating in the receiver. Note that the word "instantaneous" in the present context denotes the composition at a given instant (or small unit) of time. It does not imply that the result is provided (or even needed) immediately.

Bench scale separations in the research laboratory can also benefit from high precision measurement of instantaneous distillate composition done in-line. This will allow verification of composition early in the process. The critical purification (dehydration) of benzene in Friedel-Crafts reactions is an example.

There are many examples of spectroscopic probes being used to monitor distillation performance. Most often, near-infrared spectroscopy is used, since this spectroscopy is amenable to fused silica capillary transmission of both the input and output signals, and therefore relatively facile remote detection in a process (6, 7). Raman spectroscopy has also been used for this purpose (8). Typically, such measurements are very uncertain from the quantitative standpoint, and are subject to the limitations imposed by the spectroscopic method (selectivity, discrimination between functional groups, overlap, etc.). It is possible to employ fraction collectors to collect the distillate in discrete cuts, but chemical analysis applied to even small collected volumes will provide an integrated composition. This is no substitute for a more reliable approximation of the "instantaneous" composition taken as a distillation cut emerges from the condenser. Moreover, such fraction collectors are expensive and prone to mechanical failure, and they are not useful with more volatile fluids.

EXPERIMENTAL

Our simple approach to instantaneous high precision monitoring of distillation processes is provided by a receiver transfer adapter that has been modified to deliver distillate directly into a calibrated small volume that is conveniently sampled with a chromatographic syringe. This transfer adapter is illustrated schematically in Fig. 1. 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 degree angle with respect to the horizontal. The wash-out effect was tested by placing a drop of hexane in the hammock with a long fine needle. Then, drop wise, acetone was allowed to fall from into the hammock, and a sample was withdrawn after each drop for chromatographic analysis. After the 4th drop

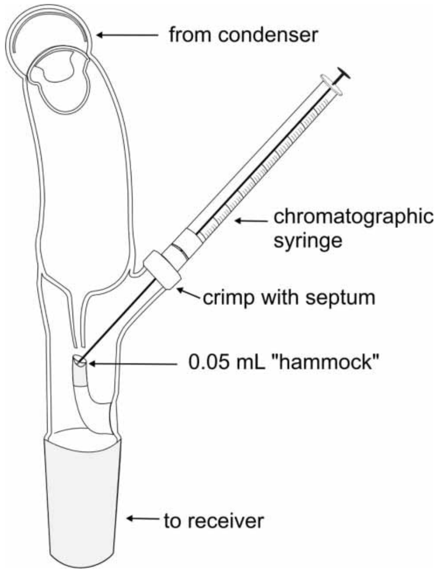

Figure 1. A schematic diagram of the receiver transfer adapter showing the 0.05 mL hammock being sampled with a chromatographic syringe. Not shown in this figure is the vacuum line adapter, which extends outward from the plane of the paper, just below the entry point of the drip line above the hammock.

(0.2 mL), hexane was present at too low a quantity to be integrated (that is, the signal to noise ratio was too low for reliable quantitation). Thus, sample carry-over as a source of uncertainty is very minor in the present context of monitoring distillation progress, and the measurement of distillation curves.

The other important feature of the transfer adapter is the crimp cap fixture that is incorporated as a side arm. 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 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 of an appropriate solvent. The first approach, direct injection into the gas chromatograph, provides for fast analyses, while the second approach allows for multiple sample injections and a lower uncertainty in composition.

As an example of the operation of this device, mixtures of n-decane/n-tetradecane were distilled, in order to measure the distillation curves of these mixtures. The mixtures that were used had a 50/50 and 75/25 mole percent composition of n-decane/n-tetradecane (although in this note we discuss only the 50/50 mixture, as an example). These mixtures were prepared gravimetrically, and the distillation temperatures (kettle and head) were monitored with two calibrated J-type thermocouples having measurement uncertainties of $\pm 0.05°C$. The distillate was collected in a calibrated receiver having a volume uncertainty of ± 0.5 mL. At the first drop of distillate, and then at selected volume fractions during the distillation process, 7 μL aliquots of distillate were collected with a gas-tight chromatographic syringe, and injected into pre-weighed vials containing n-octane as a solvent. After mixing, the samples were placed in automatic sampler vials and analyzed by gas chromatography with flame ionization detection. A temperature program was used to rapidly elute the mixture components while retaining optimal chromatographic conditions. The separation was easily done with a 30 m capillary column coated with a 0.1 μm film of polydimethylsiloxane. Six replicate analyses of each sample were performed in order to minimize and assess the composition uncertainty.

RESULTS AND DISCUSSION

While a typical distillation curve is presented as volume fraction against head temperature, the new approach allows a precise distillation curve to be obtained as composition against volume fraction, shown in Fig. 2. This curve was obtained for a 50/50 mole percent mixture. The composition

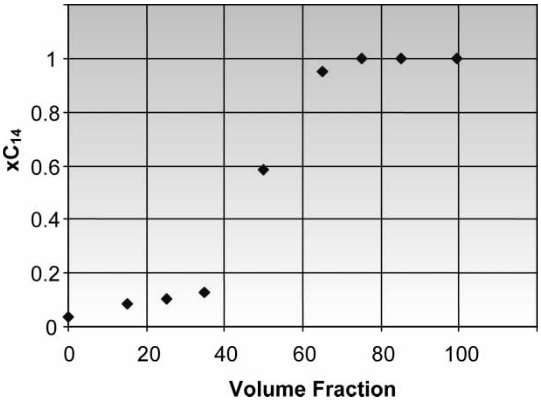

Figure 2. A plot showing the composition of distillate from a 50/50 mole percent mixture of n-decane/n-tetradecane, as a function of distillate volume fraction. The y-axis is explicit in n-tetradecane mole fraction. The error bars on these points are comparable to the size of the plotting symbols.

uncertainty is typically 0.25 percent in mole fraction (expanded uncertainty with coverage factor $k = 2$). The low uncertainty results from the ability to perform multiple analyses, off-line, of the small (approximately instantaneous) aliquots taken at the hammock. Although the temperature-against-volume fraction presentation of distillation curves is very familiar, and is the basis for many test methods and diagnostic procedures, the composition-explicit presentation is in many ways far more useful. This approach provides the information that is actually desired, namely composition. While not necessarily a replacement for the temperature data, the composition data are clearly a valuable addition.

This approach can be easily used for distillations done at reduced pressure. In these instances, the use of sandwich type septa in the crimp caps is recommended. These are septa with a layer of silicone topped by a layer of Teflon. The crimp cap will begin to leak slightly after the first sample is withdrawn, however if the syringe needle is kept in the same hole in the septum between samplings, the leak rate is minimized and the low pressure is maintained until the syringe is withdrawn.

Although in the example presented above for n-decane/n-tetradecane, the chromatographic analyses took several hours to complete (six replicates of nine solutions, plus a solvent blank), other analytical methods could be employed to provide the required information in real time. The example mentioned earlier of the Friedel-Crafts alkylation of benzene, for example, requires the benzene to be dry (that is, the water content should be lower than 1 ppm, mass/mass). This is usually done by azeotropic distillation; when the distillate no longer contains water, the benzene remaining in the kettle is dry. Analysis of the distillate (for example, by Karl Fisher coulombic titrimetry) that accumulates in the receiver will always reveal the presence of water. In fact, the only way to use an analysis of the accumulated distillate to monitor this distillation is to observe the point at which the water concentration begins to decrease (as dry benzene enters the receiver). This is uncertain and inconvenient. While the application of a fraction collector is possible, this is clearly also inconvenient. On the other hand, the use of the hammock adapter presented here makes the determination very simple. One simply withdraws an instantaneous aliquot with a tared syringe, and after a final mass measurement, the sample can be injected into the Karl Fisher reactor for titration.

CONCLUSIONS

The application of the receiver adapter that has been presented in this note extends the scope of useful information that can be derived from measured distillation curves. Moreover, the adapter can be used to monitor the progress of any distillation procedure, for a wide variety of applications. The adapter as presented is amenable to several modifications. Already mentioned are distillations performed at reduced pressures. Beyond this, the adapter can be reduced in size to function with micro scale laboratory apparatus. This is advantageous when dealing with high value or toxic distillates. Alternative means of sampling can also be used with the adapter. For example, instead of a chromatographic syringe, one can use a solid phase microextraction (SPME) needle for sampling.

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