Short communication

Measuring the distillation curves of non-homogeneous fluids: Method and case study of two pyrolysis oils ☆

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ABSTRACT

Volatility is an important property in fuels research because it can significantly affect performance and because it is highly sensitive to changes in the composition of a mixture. In the laboratory, volatility is measured as a distillation curve. Difficulty arises when the fluid to be measured is non-homogeneous; that is, it has more than one liquid phase. Using the advanced distillation curve (ADC) method, we analyzed two such fluids, crude pyrolysis oils containing significant water that formed an aqueous phase separate from the organic phase. In this communication, we present a data analysis method that compensates for non-homogeneity in these samples and enables us to compare the organic phase to the experience base of previously measured petroleum and pyrolysis oils.

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1. Introduction

The distillation curve of a complex fluid is a measurement of the boiling temperature as a function of the volume fraction distilled. This measurement is critical to understanding the volatility of complex fluids and how fuels in particular behave in a refinery or an engine. This measurement of a fluid's volatility is also crucial to the understanding and modeling of fluid mixture thermophysical properties. The advanced distillation curve (ADC) method, developed at NIST, is an improved metrology for distillation curve measurement that provides a thermodynamically significant temperature measurement accompanied by a composition explicit data channel (composition measurement as a function of distillate volume fraction, DVF) [1–4]. It is an improvement to the traditionally used ASTM International D-86 method [5].

The ADC method was developed at NIST as a robust, data-rich distillation approach that has been described in depth in previous publications [6–11]. The ADC improves on the well-known D-86 distillation method in the following ways: (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume and pressure

measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, and (6) trace chemical analysis of each distillate fraction. Sampling very small volumes of the distillate yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for some understanding of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. This is critical when the fuel contains additives (such as cetane improvers, oxygenates or stabilizers) or unusual components (such as corrosives and manure sterols) [9,12–14]. The significant advantage offered by the ADC method is the ability to model the distillation curve with an equation of state [5,15]. The ADC method also features a much lower uncertainty budget than is obtainable by D-86 [1].

Importantly, this low uncertainty budget usually excludes consideration of sampling uncertainty, that is, how well an aliquot of fluid taken for ADC measurement represents the population material [16]. In previous fuel characterization studies using the ADC method, sampling uncertainty has been insignificant because the fluids measured were homogeneous, existing in a single, well mixed liquid phase. This is not always the case; indeed, unrefined pyrolysis fluids pose a particular challenge because the pyrolysis reaction can produce significant amounts of water. We encountered this challenge in the measurement of two crude pyrolysis oils, one made from ponderosa pine shavings and the other from dairy manure.

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Numerous feedstocks are currently in use in pyrolysis reactors and gasifiers, including municipal refuse, various types of plastic, agricultural waste, and other biomass [17]. Indeed, our lab previously performed ADC characterization on a crude oil produced from pyrolysis of swine manure and on two liquid fuels refined from crude polyethylene pyrolysis oil [9,18]. The appeal of alternative fuels sourced from waste is clear: the widespread use of waste feedstocks like the pine shavings and manure in this case would simultaneously reduce the need for fossil fuels and mitigate the load on landfills and pollution in the environment. For example, in 2006, livestock in Canada alone produced over 180 million metric tons (1.8e10 kg) of manure [19]. Although the fluids studied here were produced in a small, lab-scale reactor, a number of industrial scale plants exist in the United States for fuel production from the pyrolysis of waste [20].

2. Material and methods

2.1. Crude pyrolysis oils

The crude pyrolysis fluids were produced from ponderosa pine saw-mill residues (<5 mm) and dairy manure (dried and hammer milled; University of Idaho Dairy Farm) using a pilot scale auger pyrolysis unit (100 mm diameter, 450–500 °C, 20 kg h^{-1}) as described by Han et al. [21]. The condensed fluids were stored frozen and then adjusted to room temperature before measurement. Both fluids were visibly non-homogeneous, having separated into two phases, one primarily aqueous and one organic, and vigorous attempts to adequately mix them were unsuccessful. The pine oil was dark in appearance and smelled like pinene. The manure oil was dark in appearance and had an objectionable odor with notes of cigarette butts and fresh asphalt. In both fluids, we observed phase separation into a light brown aqueous layer and a nearly black, sticky, more viscous organic layer. Both fluids showed a tendency to form a frothy top layer after mixing.

We attempted to mix the fluids by first placing them into one-gallon (nominal) uncoated steel paint cans. We added a handful of clean stainless steel nuts to each can to aid in agitation and mixed each can with a commercial paint shaker. This mixing operation was not effective at homogenizing the fluids.

While we were loath to change the composition of the bulk fluids, we attempted chemical homogenization by adding a surfactant to a small aliquot. We conducted a test combining a small sample of organic phase from the manure oil with 1% (mass/mass) cetyltrimethylammonium bromide (a cationic surfactant) dissolved in a roughly equal volume of water. We found that the surfactant did have a minor effect on promoting mixing; however, even with the application of heat to the oil-water-surfactant mixture, most of the organic material remained in a sticky layer separate from the water phase. Insufficient sample was available for testing additional surfactants or other means of homogenization. This led us to develop a curve offset method that can be applied to ADC measurements.

2.2. Advanced distillation curve

The ADC protocol has been described in detail in previous publications [1–4]. The result of an ADC measurement is a temperature-volume-composition data matrix that includes two temperatures, the kettle temperature (T_k) and head temperature (T_h), and a composition analysis for each DVF. T_k is the thermodynamically consistent value characteristic of the remaining mixture in the kettle as distillation progresses. As in prior work on crude petroleum and pyrolysis oils, the temperatures we report have been adjusted to standard atmospheric pressure (101.325 kPa)

using the modified Sydney Young equation in which the constant term was assigned a value of 0.000109 (corresponding to a hydrocarbon chain of 12) [4,22–25]. We acknowledge that the composition of these fluids deviated significantly from dodecane, especially in the aqueous region of the distillation curve; however, applying the Sydney Young constant for water (0.000099) results in negligibly different (<1 °C) corrected temperatures. Applying the Sydney Young constant for phenol (0.000107), sometimes used as a pyrolysis fluid model compound, results in <0.2 °C differences in corrected temperatures. Taking all of this into consideration, we chose to continue using the constant value 0.000109, as it enables us to most directly compare the results to the distillation curves of relevant previously measured crude oils for which the same constant was used [24]. For each of three replicate distillation curve measurements, a starting volume of 200 mL was measured by automatic pipette.

The uncertainty in our pressure measurements was 0.03 kPa, including uncertainty in the calibration with a corrected, fixed cistern mercury barometer. The uncertainty associated with temperature measurements was 1 °C, including uncertainty in calibrations with fixed point cells [26]. The uncertainty in the volume measurements used to determine distillate volume fraction was 0.05 mL.

3. Results and discussion

3.1. Karl Fischer coulombic titrimetry

Because we observed an obvious separation between aqueous and organic phases, it was important to determine the water content of both crude pyrolysis oils. Each phase of the composite oils was measured separately, in triplicate, using the Karl Fischer coulometric titration method [27]. Samples were introduced by chromatographic syringe (5 μL for the aqueous phases and 2 μL for the organic phase). The organic fraction of manure oil was too viscous (even at elevated temperature) to introduce reproducibly to the titration cell, so we do not report a moisture value. As we suspected, the aqueous fraction of both oils contained more than 80% water by volume. Table 1 details the results. These measurements are consistent with our later findings using ADC.

3.2. Raw distillation curve results

The raw distillation curve data are presented in Fig. 1 and Table S1 in Supplementary Information. The fluids boiled near 100 °C (vaporization of the aqueous phase) for a significant portion of the total distillation volume before markedly increasing at the onset of vaporization of the organic constituents, the point we call the water-organic inflection. As the plots show, the amount of water varied significantly among replicates of the same fluid, which indicated that the fluids were not successfully homogenized. Had they been, the DVF of the water-organic inflection would have been repeatable. The high-boiling region after the water-organic inflection is due to the vaporization of the organic fraction.

It is important to note that the distillation temperatures of the low-boiling region were not perfectly constant and were also slightly elevated above the boiling temperature of pure water. This

Table 1
Water content (% volume) for each fraction of both crude pyrolysis oil. The manure oil's organic fraction was too viscous to make a measurement. The upper and lower values provided are based on expanded (k = 2) uncertainty.

	Pine oil	Manure oil
Aqueous fraction	82.1% ± 1.6%	83.1% ± 1.6%
Organic fraction	12.6% ± 1.4%	