

ASTM D86 DISTILLATION IN THE CONTEXT OF AVERAGE BOILING POINTS AS THERMODYNAMIC PROPERTY OF NARROW BOILING RANGE OIL FRACTIONS

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Abstract. *The average boiling points (ABPs) of narrow boiling range oil distillation cuts are important in predicting thermodynamic and physical properties of oils. Due to convenience, simple batch distillation methods, either at atmospheric or reduced pressure, are often used to separate shale oils into fractions, including narrow boiling range fractions, and it has been attempted to calculate average boiling points directly from the distillation data. Using wide industrial shale oil fractions from Estonian kukersite oil shale and based on ASTM “Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure” (ASTM D86), this paper is aimed to find out how much the average boiling points determined directly from distillation, as an arithmetic average of the initial and final temperatures of the thermometer during fractions collection, differ from actual average boiling points (AABPs). The actual average boiling points of narrow boiling range oil fractions, pre-prepared by the same ASTM D86 distillation, were measured afterwards using a recently developed thermogravimetric analysis (TGA) based experimental method, which requires only about 20 mg of sample. The study indicated that AABPs were always lower than the respective average values determined directly from ASTM D86 distillation data.*

Keywords: *kukersite oil shale, shale oil, boiling points, correlations, distillation.*

1. Introduction

Shale oils are “synthetic” crude oils produced industrially from solid oil shale via retorting, i.e. pyrolysis, at about 500 °C [1]. The organic matter in oil shale is mostly in the form of kerogen, an insoluble crosslinked macro-

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molecular material [2–5], which has to be broken down during the industrial production of oil. From time to time shale oil has been attracting attention [5, 6], from regional to worldwide energy communities, due to the large resources found around the globe [7]. The resources are estimated to be 4,700 billion barrels of oil [8]. Depending on the composition of the parent oil shale, oil can be rich in various heteroatoms [9] that can cause the thermodynamic properties to be different from those of conventional petroleum [10]. However, in the literature, there is quite little systematic thermodynamic property information, including thermodynamic property estimation correlations, available for shale oils. If to somewhat over-generalize, then it could be stated that the experimental data on the physical and thermodynamic properties of shale oils, such as boiling point, specific gravity and molecular weight, can be found mostly in works that are not studies about thermodynamic properties, but parts of studies about their chemical composition and wide technical fractions. Our literature search indicated that it was more or less valid for all shale oils. For example, in a recent summary for Estonian kukersite oil shale derived oils, it has been shown that the publicly available information is spotty and poorly suitable for evaluating the applicability of available thermodynamic property prediction methods, even for the simplest approaches based on “undefined” pseudocomponents [11]. In addition, concerning the thermodynamic properties and their prediction, there is one possible shortcoming to be pointed out. In many works, simple batch distillation has been used to fractionate shale oils to narrow boiling range fractions and it has been attempted to calculate average boiling points of fractions as arithmetic averages of the initial and final temperatures of the thermometer during fraction collection [12, 13]. If this approach results in a substantial error, then this shortcoming has to be taken into account because average boiling point is generally the first choice as an input parameter describing molecular size in property correlations [10, 14].

Our laboratory became interested in this problem during a project that aimed to develop thermodynamic property correlations, similar in form to conventional petroleum fuels correlations, for a specific shale oil, the shale oil derived from Estonian kukersite oil shale [11, 15]. In the aforementioned project, a simple batch distillation, such as “Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure” (ASTM D86) [16], was used to separate wide industrial fractions (gasoline fractions, fuel oil fractions) into narrow boiling range fractions (or cuts), for which accurate average boiling points were needed to develop thermodynamic property correlations.

Generally, boiling range distributions from distillation can be used to assess the component distribution and volatility of the sample. In the petroleum industry, distillation data is used to assess the quality of crude oil and products [17]. There are various distillation based test methods, both standardized and non-standardized, developed for practical use [14, 18–20]. One of the simplest and oldest test methods for separation of continuous

mixtures at atmospheric pressure is ASTM D86 [16]. This method can be used to quantitatively determine the boiling characteristics of oil products with volatilities from gasoline to burner fuels. And yet, ASTM D86 is a simple batch distillation, with vapour being immediately channeled into a condenser), and therefore, it does not provide the actual boiling range of the oil. It has been pointed out that the ASTM D86 distillation curve may differ from the true boiling point (TBP) curve due to the partial condensation of the sample in the neck of the flask, the low level of separation (lack of true equilibrium between vapour and liquid) and the poor liquid holding capacity of the condenser [21]. The boiling point, in terms of distillation, may correspond to a perfect equilibrium under total reflux conditions. In practice, to obtain a TBP curve, distillation columns with 15 or more theoretical plates and high reflux ratios (often 5:1 or higher) are used. ASTM D2892 “Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)” is an example of such a method [22]. Therefore, ASTM D86 distillation curves start at a higher temperature and end at a lower temperature than TBP distillation curves, and present a narrower boiling range than the true boiling range [23]. Riazi [14] has developed correlations for conventional petroleum oils that relate to ASTM D86 and TBP temperatures. The correlations are based on calculating temperatures of one distillation from those of the other at the same vapourized volume percentages. However, these correlations are not meant to be applied for the direct calculation of accurate average boiling points of the narrow fractions collected during the distillation. Also, no experimental information could be found about how much ASTM D86 average boiling points differ from the actual average boiling points of collected fractions.

2. Experimental

2.1. Samples

The samples used in this study were the wide industrial shale oil fractions from Estonian kukersite oil shale [11, 15]. The samples were obtained from Narva Oil Plant of Eesti Energia (Estonia) that uses solid heat carrier technology [24–26]. As total shale oil has a wide range of properties and components [27–30], then in industry the oil was divided into wide “straight-run fractions” as preliminary products [13]. In this study, one gasoline “straight-run fraction”, four middle oil (fuel oil) “straight-run fractions” and one artificially modified (concentrated) fuel oil fraction were used. The fuel oils (FOs) had boiling ranges of about 300 °C and initial atmospheric boiling points (AtmBPs) of about 200 °C. The percent of fuel oil evaporated during atmospheric distillations at a distillation temperature of about 350 °C (cut temperature) was in the range of 30–35 wt%. The gasoline fraction had a boiling range of about 150 °C and an atmospheric initial boiling point of about 50 °C. In addition, a concentrated fuel oil sample (cFO) with a boiling range of also about 150 °C was made. This fuel oil was concentrated by

carrying out ASTM D86 distillations for one of the middle oil fractions up to about 350 °C. Four separate distillations for the same middle oil fraction were performed and the distillates collected were mixed together to get the concentrated fuel oil sample.

2.2. ASTM D86 distillation or Engler distillation

ASTM D86 distillation was used to separate wide industrial fractions (gasoline fractions, fuel oil fractions) into narrow boiling range fractions (or cuts). The ASTM D86 standard gives the user all the information he needs to carry out the distillation process (system parameters, sample parameters and experimental conditions) [16]. Here we used a standard setup and experimental procedure. In short, 100 ml of the sample was placed in a 125 mL glass flask. A gas burner was employed to heat the sample. The vapours were condensed in a condenser consisting of a 400 mm noncorrosive metal tube placed in a cooling bath. According to the standard the temperature of the cooling bath depends on the sample. For shale fuel oil (belonging to Group 4, according to the standard), the temperature of the cooling bath had to be 0–60 °C. For gasoline fractions (Group 2), the temperature had to be 0–5 °C. However, here we used tap water at 10 °C as cooling water when carrying out the fractionation of all samples, including gasoline, so with the gasoline the standard was not followed exactly. The condensed sample was collected at the rate of 4–5 mL/min and the rate was kept as constant as possible from the point at which 5% of the sample had been collected to the moment when only 5 mL of it remained in the flask. The temperature sensor (thermocouple) was mounted on the neck of the flask where the vapours flowed into the condenser. An important aspect of the ASTM D86 standard is that it is based on mercury-in-glass thermometers. When analyzing our results, the temperature correction was carried out according to the standard – the thermocouple readings were corrected to match the mercury-in-glass thermometer response time. The temperature reading should also be corrected to a pressure of 101.3 kPa. However, as barometric pressure was not measured during distillations, this correction was not included in the results. The temperature difference caused by the fluctuation in atmospheric pressure stayed below 2 °C. The boiling points of the fractions from ASTM D86 distillation were calculated as an arithmetic average of the initial and final temperatures of the thermometer during fractions collection. The accuracy of determining the ASTM D86 distillation boiling points was ± 1 °C.

2.3. Average boiling point determination by TGA

To determine experimentally average boiling points of pre-prepared narrow boiling range fractions a recently developed experimental method was used. The method is based on thermogravimetric analysis (TGA) and requires only a small amount of sample, about 20 mg [31]. Using this technique it was convenient to determine weight average boiling points of oils with narrow boiling ranges in a fast manner [23]. The average deviation of the normal

boiling points was evaluated to be 1.2 °C (absolute average deviation 2.1 °C) [31]. The method is based on the measurement principle and procedure underlying the ASTM E1782 standard “Standard Test Method for Determining Vapor Pressure by Thermal Analysis” [32]. The standardized method itself is for measuring boiling points of pure substances at specific pressures [33], but at our laboratory the first principles of the method were extended to measuring the vapour pressure and initial boiling points of oil fractions with narrow boiling ranges [34, 35] and also to determining their weight average boiling points [31].

3. Results and discussion

In this paper, we present some of our observations based on the experimental data collected. An attempt is made to answer the following two questions: (1) How much do the average boiling points from ASTM D86 distillation differ from those measured afterwards using the TGA method? (2) Could a useful widely applicable empirical relationship between these two kinds of boiling points be derived? Hereinafter, the boiling points obtained as arithmetic averages of ASTM D86 distillation temperatures will be referred to as ASTM D86 boiling points, and the boiling points of the same fractions measured afterwards using the TGA method will be called atmospheric boiling points.

Figure 1 and Figure 3 compare the ASTM 86 boiling points and average boiling points of six distillations. The figures illustrate a situation where in the ASTM D86 distillation temperature correction for the mercury-in-glass thermometer reading is accounted for, and Figure 2 depicts uncorrected thermocouple based temperature measurements.

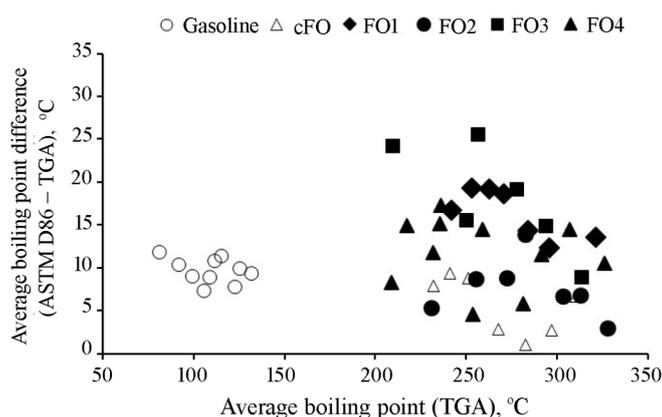


Fig. 1. Difference between the average boiling points obtained by TGA and ASTM D86 distillation, with the temperature correction for the mercury-in-glass thermometer accounted for. (The abbreviations used: cFO – concentrated fuel oil, FO1–FO4 – fuel oils of different distillations.)

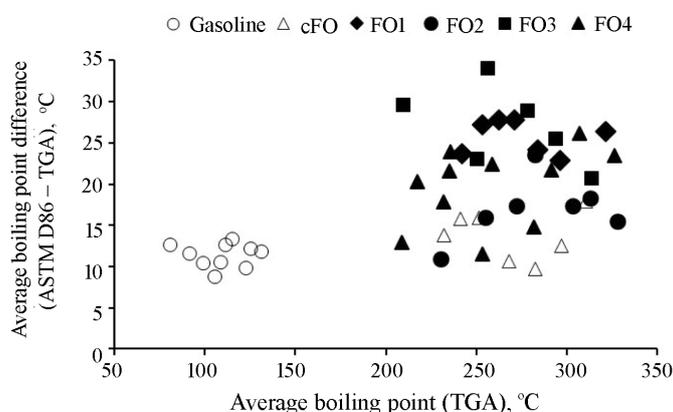


Fig. 2. Difference between the average boiling points obtained by TGA and ASTM D86 distillation using measured thermocouple temperatures. (The abbreviations used: cFO – concentrated fuel oil, FO1–FO4 – fuel oils of different distillations.)

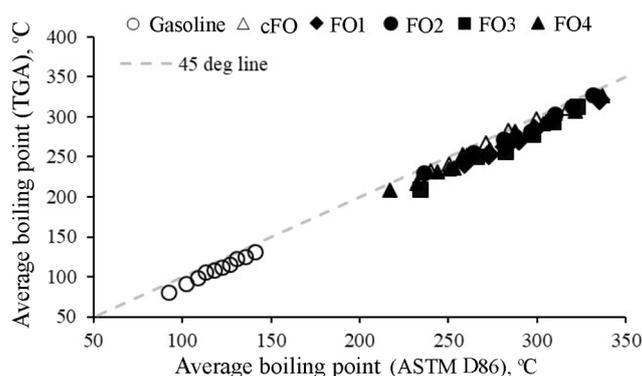


Fig. 3. Comparison of the average boiling points obtained by TGA and ASTM D86 distillation, with the temperature correction for the mercury-in-glass thermometer accounted for. (The abbreviations used: cFO – concentrated fuel oil, FO1–FO4 – fuel oils of different distillations.)

From Figure 1 and Figure 3 several observations can be made. First, as expected, the comparison revealed a deviation between those two values, with ABPs always lower than the ASTM D86 boiling points. Second, it can also be seen that the difference was smaller for narrow boiling range technical fractions (in the figures, open circles – gasoline with a boiling range of 150 °C; open triangles – concentrated fuel oil or cFO with a boiling range of 150 °C) and larger for wide boiling range fractions (in the figures, solid points or various fuel oils with boiling ranges of 300 °C). The fuel oil was concentrated by carrying out four separate ASTM D86 distillations for the same middle oil fraction up to the same temperature. Then the distillates collected were mixed together to get “concentrated fuel oil” for another

ASTM D86 distillation (open triangles in the figures). The final observation from the data was that there was a considerable scatter of boiling points among the fractions both from the same distillation and from different distillations.

Based on the data in Figure 1 and Figure 3, it can be inferred that an important cause of the difference between ASTM D86 boiling points and ABPs could be an interplay between the residence time in the condenser and the heating rate of the sample. While the vapours condensed and moved through the condenser and were collected, the measured vapour temperature in the flask continued to increase, resulting in a delay between the measured vapour temperature and the actual condensation temperature of the drop collected at the end of the condenser. How fast the liquid flowed in the condenser depended on viscosity and how fast the vapour temperature in the flask increased depended on the width of the sample's boiling range.

Here it is worth mentioning that Huang et al. [19] stated in their work that the residence time of the distillate in the condenser did not substantially affect the determination of the boiling point. To prove it, the researchers carried out experiments with different pure substances and found that the first drop from the end of the condenser fell when the sample reached its boiling point. However, unlike pure substances, mixtures do not have a constant boiling temperature. When carrying out the experiment using a pure substance, the measured vapour temperature cannot rise as long as there is enough sample remaining. For mixtures, however, there is a continuous change in the composition of the mixture while the vapours progress through the condenser, and during this time period the measured vapour and liquid temperatures will continue to change. To visually analyze and evaluate the delay, a system similar to the ASTM D86 setup was constructed and an experiment was carried out with two pure compounds with different viscosities – tetradecane and glycerol. A transparent glass pipe, with parameters similar to the ASTM D86 condenser (length 400 mm, inside diameter 14 mm, wall thickness 1.5 mm) was placed in a water bath at the same angle as used in ASTM D86 distillations. The water used for cooling came from the tap and its temperature was 10 °C. The viscosities of tetradecane and glycerol at 10 °C were, respectively, 2.92 mPas [36] and 3900 mPas [37]. During the experiment, drops of the oil that was dark in color with a water-like consistency were injected into the glass cooler through a small pipe and their flow was visually monitored as it moved through the glass pipe with the condensing sample. The average flow rate per unit length was recorded. Based on the experiments carried out with the pure substances, it was observed that it took the drops on average 41 seconds with tetradecane and 72 seconds with glycerol to move through the condenser with the same parameters as the condensing tube used in ASTM D86 distillation.

In order to keep the distillation rate within the requirements of the standard (i.e. sample collection rate of 4–5 mL/min), the rate of heating, in our experience, was varied between 10 and 20 °C/min. Therefore, the delay

(or difference between the ASTM D86 boiling point and the actual boiling point of the collected fraction) would be about 8 to 25 °C (residence time multiplied by the heating rate) depending on the experimental parameters (heating rate and sample flow rate). Experimental data in Figure 1 indicates the difference between ABPs from TGA and ASTM D86 boiling points to be between 0 and 25 °C (the majority of points deviating between 5 and 20 °C) when the mercury-in-glass thermometer correction was applied. The deviation was about 5 to 35 °C (with the majority of points between 10 and 30 °C) when using just the temperatures measured with the thermocouple (Fig. 2). For technical fractions with narrower boiling ranges (open points) the absolute average deviation was found to be about 8 °C when using the corrected thermocouple temperatures, and about 12 °C when using the uncorrected thermocouple temperatures. For technical fractions with wider boiling ranges (solid points) the deviations were, respectively, 12.2 °C and 21.2 °C. The deviation seen with oils matched the rough estimate based on experiments with pure compounds. The deviation close to 0 °C for shale oil middle oil fractions at higher temperatures (around 300 °C and higher) may be an experimental error due to the sample decomposition, either while measuring TBP's with TGA or during the distillation itself.

Figure 1 and Figure 2 reveal a considerable scatter of boiling points, and so, the distillation process was more complex. For example, there was no visible trend showing that the difference between ASTM D86 boiling point and ABP values was bigger for fractions with higher average boiling points, even though higher boiling fractions had higher viscosities, which in turn affected their rate of flow in the condenser. Another factor causing the fluctuating (and often random) behaviour of the results could be the changing heating rate. When the distillation rate drops too much, the amount of energy given to the system has to be increased. Quick adjustments to the flame affect the distillation rate with a delay, due to the time required to heat the sample, but the rising hot air current could affect the vapour thermocouple faster. Also, the deviation was often bigger for the first and last cuts of the distillation and smaller for the middle cuts (Fig. 1 and Fig. 2) because the heating rate (temperature change) per unit volume collected has to be higher at the beginning and end to keep the distillation rate as constant as possible.

4. Conclusions

To summarize, this work analyzed the difference between the ASTM D86 boiling points and actual average boiling points for continuous oil mixtures. There was observed a similar trend: the average boiling point found for a cut by the thermogravimetric method was always lower than the one calculated from ASTM D86 distillation data (as an arithmetic average of the initial and final temperatures of the cut). This was shown to be mostly due to an

interplay between the flow time (residence time) in the condenser and the heating rate of the sample. However, the fluctuating behaviour of the deviation makes it difficult to develop a general widely useable equation that would allow true boiling point values to be calculated accurately for fractions obtained from ASTM D86 distillation. Therefore, caution should be exercised when using average boiling point values derived from simple batch distillation (as an arithmetic average of the reported initial and final temperatures of the cut) to estimate the thermodynamic properties of the cut or methods of their prediction.

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