

DISTILLATION OF LIQUID FUELS BY THERMOGRAVIMETRY

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INTRODUCTION

The most widely used separation technique in the petroleum industry and other liquid fuel production processes as well as in much of the chemical industry is distillation. To design and operate an appropriate commercial and laboratory distillation unit requires a knowledge of the boiling point distribution of the materials to be separated. In recognition of these needs, the ASTM developed the distillation procedures of D86, D216, D447, D850, and D1078. They are widely used in laboratories for the purposes of sample characterization, product and quality control, and distillation column design. However, the significant drawbacks of these ASTM methods include 1). close monitoring of the distillation is required. This is particularly difficult for those samples which are very toxic and/or cause any other safety problems; 2). the sample under test must be transparent and free of separated water (1); and 3). results obtained by these methods are not particularly precise. This motivated the development of a novel automatic distillation system based on the use of a custom-built thermogravimetric apparatus.

Thermogravimetry (TG) can be used to determine variation in mass as a function of temperature and/or time. Thus, thermogravimetric techniques, in principle, could be used in study of any physical and chemical processes where changes in mass are function of temperature and/or time. Hence, either commercial or custom-built thermogravimetric apparatus provides flexible means and unique features for study of various physical processes and chemical reactions. In the state-of-the-art custom-built thermogravimetric system, a computer is generally used for data acquisition of time, temperature and mass.

Massoth and Cowley (2) utilized a stirred flow thermogravimetric reactor for catalyst studies of hydrogenation of 1-butene under steady-state conditions. Sears et al. (3) reported a pressurized thermogravimetric equipment for use in oxidizing atmospheres at high temperatures. Dean and Dadyburjor (4) used a continuous thermogravimetric technique, combined with a pulse microreactor and on-line gas chromatograph, to study deactivation of cracking catalysts by coking.

In this paper, design and operation of a custom-built thermogravimetric apparatus for the distillation of liquid fuels are reported. Using a sensitive balance with scale of 0.001 g and ASTM distillation glassware, several petroleum and petroleum-derived samples have been analyzed by the thermogravimetric distillation method. When the ASTM distillation glassware is replaced by a micro-scale unit, sample size could be reduced from 100 g to 5-10 g. A computer program has been developed to transfer the data into a distillation plot, e.g. Weight Percent Distilled vs. Boiling Point. It also generate a report on the characteristic distillation parameters, such as, IBP (Initial Boiling Point), FBP (Final Boiling Point), and boiling point at 50 wt% distilled. Comparison of the boiling point distributions determined by TG (thermogravimetry) with those by SimDis GC (Simulated-Distillation Gas Chromatography) on two liquid fuel samples (i.e. a decanted oil and a filtered crude oil) are also discussed in this paper.

EXPERIMENTAL

Apparatus. A schematic diagram of the thermogravimetric apparatus for distillation is shown in Figure 1. A K-type thermocouple was used to measure the boiling temperature. The thermocouple was supported by a tight bevel-seal (Kontes, Vineland, New Jersey) with the thermocouple vertical and centered in the tube of the distillation head and in such a position that the thermocouple end-point (i.e. thermocouple joint) is level with the lowest point of junction between head tube and head neck (see Figure 1). The signal from the thermocouple was first processed by a DIN Rail Thermocouple Transmitter (MCR-TC Series, Omega Engineering, Inc.). A Mettler PK300 Balance with precision of 0.001 g was used to monitor the mass change in the distillate receiver. A Mettler GC47 D/A Converter was used to transfer the digital signals from the balance to analog signals for data acquisition. Asystant+ data acquisition system with DT2805 A/D board (Asyst Software Technologies, Inc.) was installed in a IBM computer and used for data acquisition. Both temperature and mass signals were sampled at 1 Hz. A ASTM distillation head and 250-ml flask (Kontes) and an electric heater were used for distillation.

Distillation. For each distillation, about 100-g liquid fuel was transferred into the distillation flask. Both the empty flask (W_{flask}) and initial distilland liquid fuel (W_{initial}) were weighed using the balance. Adjust the electric heater referring to the instructions given in ASTM D1078 and record the temperature and distillate mass by the computer. After the

condenser tube has drained, the total mass of distillate weighed by the balance was recorded as recovery (W_{recovery}). Cooling the distillation flask to room temperature, the distillate left plus the flask ($W_{\text{left+flask}}$) was weighed by the balance. The amount of residue (W_{residue}) was obtained by the subtraction of W_{flask} from $W_{\text{left+flask}}$. The amount of distillation loss (W_{loss}), due to surface wetting, was estimated by subtracting W_{initial} and the sum of W_{recovery} and W_{residue} .

Cleaning System. The apparatus system is cleaned in place by a series of suitable low-boiling solvent distillation. The number of cleaning distillations and type of solvent used are selected based on the distilland being studied. The effectiveness of cleaning can be monitored by analysis of the distillate streams (e.g. by GC analysis). After cleaning, the distillation glassware are placed into an oven and the temperature set above the boiling point of the solvent used.

Data Processing. The collected mass data were processed using an 11-point smoothing filter of the Linear Regression & Error Analysis procedure (5).

Materials Studied. A decanted oil and a filtered crude oil, together with seven other liquid fuels (designated as Samples A, B, C, etc.), have been studied using the thermogravimetric distillation apparatus. Pure organic compounds from low boiling point to high boiling point, such as methylene chloride (99.9+%), tetralin (1,2,3,4-tetrahydronaphthalene, 99%), and 1-methylnaphthalene (98%) from Aldrich Chemical Co., have been used for testing and calibrating the apparatus.

RESULTS AND DISCUSSION

Calibration of the Apparatus System Using Pure Organic Compounds. Several pure organic compounds have been used to test and calibrate the thermogravimetric apparatus. In theory, transfer time of distillate through the condenser, as a delay effect, should be corrected for accurately determining the boiling point distribution (i.e. Weight Percent Distilled vs Boiling Point) and characteristic distillation parameters, such as Initial Boiling Point (IBP), Final Boiling Point (FBP) (or Decomposition Point, DP). Results of the tetralin distillation using the TG method are shown in Figure 2. Surprisingly, there was no distillate-transfer time observed (see Figure 2). The dashed-line in Figure 2 defines the time required by the distillate being transferred through the condenser. The results shown in Figure 2 indicate no delay effect, i.e. as soon as the temperature reaches the tetralin boiling point, the first drop of tetralin falls into the distillate receiver. The same results were obtained in distillations of methylene chloride and 1-methylnaphthalene. The reason of these phenomena may be due to that the condenser surface was wetted by the vapor of the sample before its boiling point was reached. The Weight Percent Distilled vs. Boiling Point for the tetralin is shown in Figure 3. That the boiling point was increased after 95 wt% distilled is apparently due to impurities in the tetralin. The results of duplicate tetralin distillations are summarized in Table I. Weight percent distillation recoveries, residues, and losses, plus the boiling points observed, together with the literature value (6), are also given in Table I.

Distillation of Liquid Fuels. Plots of the Weight Percent Distilled vs. Boiling Point for the seven liquid fuels using the TG method are shown in Figures 4-10. Based on ASTM definition (7), the IBP (Initial Boiling Point) is the temperature detected as the first drop of condensate falls into the distillate receiver. Thus, in this TG method, the Initial Boiling Point was the temperature recorded at which the distillate mass is above zero. The mass of the first drop of the distillate recorded for these liquid fuels was in the range of 0.005 to 0.02 g. The Final Boiling Point (FBP) (i.e., the end point or decomposition point) was the maximum temperature recorded during the test. If no residue was left in the distillation flask, the dry point, instead of FBP, was reported. Characteristic distillation parameters (e.g. IBP, FBP, BP @50 wt%), together with the weight percent distillation recoveries, residues, and losses, of the seven liquid fuels are summarized in Table II.

The first derivative of TG distillation (i.e. $d(\text{wt}\%)/dt$) vs boiling point for Sample A is shown in Figure 11. This plot indicates the density function of distillate against boiling point. It can be used as additional information for characterizing the boiling property of liquid fuels.

Comparison of TG Distillation with SimDis GC. Plots of the Weight Percent Distilled vs. Boiling Point using the TG method (solid line) and SimDis GC technique (dashed line) for a filtered crude petroleum and a decanted oil are shown in Figures 12 and 13. The results show significant differences. It is more evidenced when the characteristic distillation parameters (e.g. IBC, FBP, BP @50 wt%) of the two samples determined by the both methods are summarized in Table III. These deviations of the SimDis GC method from the distillation may be resulted by the interactions between the tested sample and the selected column packing and by the differences in properties and distillation characteristics between the calibration standards and tested samples. The weight percent distillation recoveries, residues, and losses are also included in Table III. Compared to the SimDis GC

method, the TG technique, when operated under atmospheric pressure, is limited to measuring the boiling point up to about 380 °C.

CONCLUSION

The custom built thermogravimetric apparatus for distillation provides an accurate, convenient, and simple determination of boiling point distribution of liquid fuels. It has potential as a modified method to replace the widely used ASTM distillation methods. Boiling point distributions of two oil samples determined by the thermogravimetric method and SimDis GC technique show significant differences. These deviations of the SimDis GC method from distillation may be due to sample-GC column packing interactions and differences between the calibration standards and tested samples.

ACKNOWLEDGMENTS

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Table I Results of tetralin distillation

| Distillation Run No. | Boiling Point °C | Recovery wt% | Residue wt% | Loss wt% |
|----------------------|------------------|--------------|-------------|----------|
| 1 | 207.8 | 98.7% | 0.7% | 0.6% |
| 2 | 207.7 | 99.1% | 0.5% | 0.4% |
| 3 | 207.8 | 98.9% | 0.5% | 0.6% |
| Literature value | 207.6 | - | - | - |

Table II Results of the seven liquid fuel distillations

| Sample | IBP °C | BP @50wt% °C | FBP °C | Recovery wt% | Residue wt% | Loss wt% |
|--------|--------|--------------|--------|--------------|-------------|----------|
| A | 206.1 | 278.5 | 316.4 | 95.3% | 3.2% | 1.5% |
| B | 169.4 | 285.6 | 334.9 | 90.5% | 8.6% | 0.9% |
| C | 84.3 | 285.6 | 346.2 | 89.7% | 9.8% | 0.5% |
| D | 194.1 | 272.7 | 350.8 | 96.1% | 3.5% | 0.4% |
| E | 105.1 | 365.7 | 378.2 | 59.9% | 35.1% | 5.0% |
| F | 209.6 | 342.0 | 353.8 | 71.9% | 23.3% | 4.8% |
| G | 198.1 | 280.6 | 348.5 | 95.5% | 3.9% | 0.6% |

Table III Comparison of SimDis GC with TG

| Distillation Method | IBP °C | BP @40wt% °C | BP @50wt% °C | FBP °C | Recovery wt% | Residue wt% | Loss wt% |
|-----------------------------|--------|--------------|--------------|--------|--------------|-------------|----------|
| Sample: Crude oil | | | | | | | |
| TG (1st) | 56.3 | - | 301.5 | 314.7 | 71.9% | 22.0% | 6.1% |
| TG (2nd) | 55.8 | - | 297.6 | 314.9 | 72.6% | 21.1% | 6.3% |
| SimDis GC | 95.6 | - | 431.1 | 720.0 | 91.0% | - | - |
| Sample: Decanted oil | | | | | | | |
| TG (1st) | 244.1 | 363.7 | - | 364.6 | 42.5% | 50.2% | 7.3% |
| TG (2nd) | 244.9 | 368.7 | - | 373.6 | 46.8% | 45.5% | 7.7% |
| SimDis GC | 215.6 | 383.9 | - | 705.0 | 99.5% | - | - |

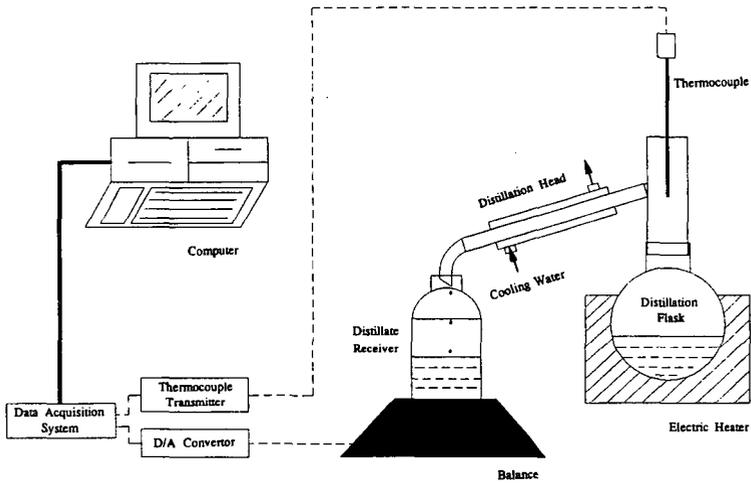


Figure 1 Schematic diagram of a custom built TG for distillation

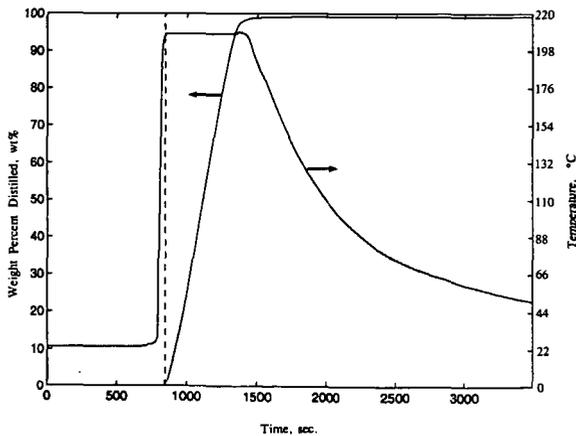


Figure 2 Temperature-mass-time plot for tetralin distillation

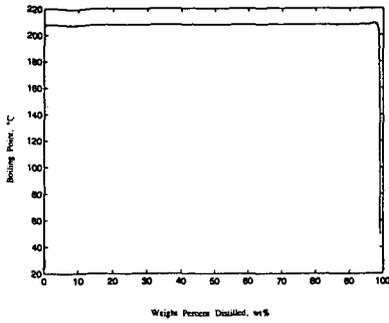


Figure 3 wt% vs T_b of tetralin

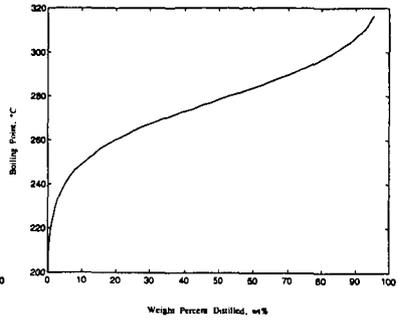


Figure 4 wt% vs T_b of Sample A

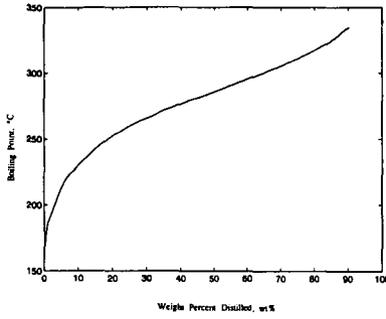


Figure 5 wt% vs T_b of Sample B

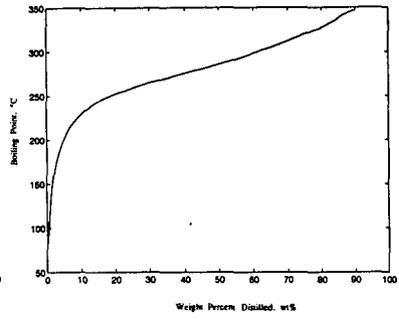


Figure 6 wt% vs T_b of Sample C

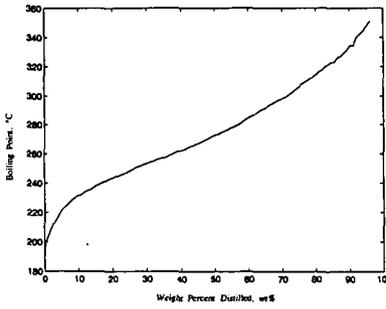


Figure 7 wt% vs T_b of Sample D

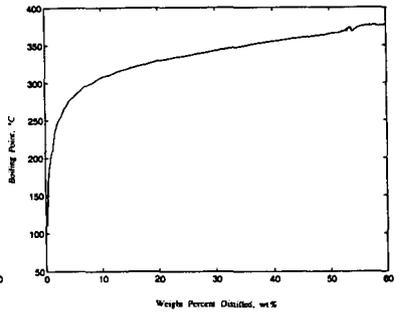


Figure 8 wt% vs T_b of Sample E

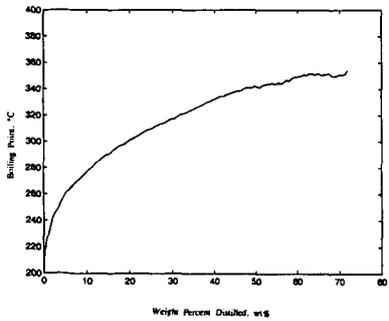


Figure 9 wt% vs T_b of Sample F

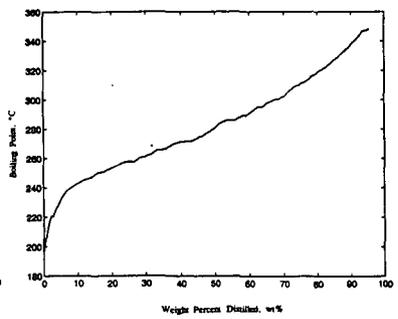


Figure 10 wt% vs T_b of Sample G

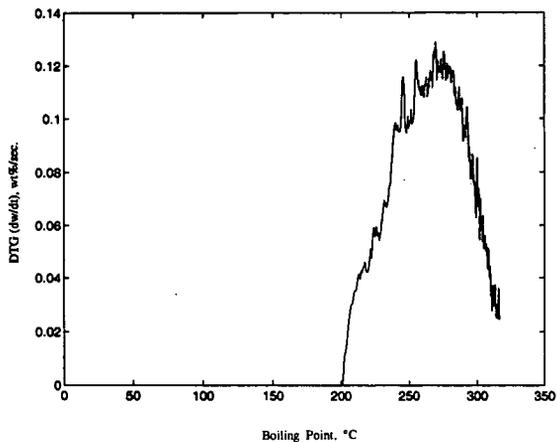


Figure 11 DTG vs T_b of Sample A

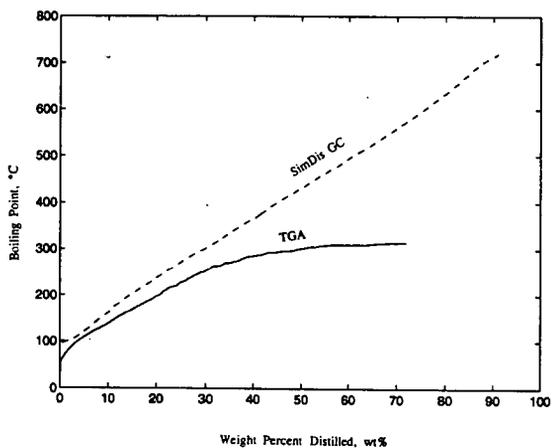


Figure 12 wt% vs T_b of a crude oil determined by TG and SimDis GC

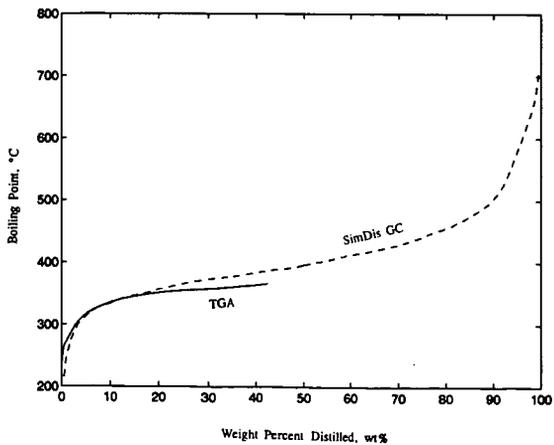


Figure 13 wt% vs T_b of a decanted oil determined by TG and SimDis GC