

DISTILLATION RANGE OF HEAVY PETROLEUM OILS AND DETERMINATION OF COKE RESIDUE

UOP Method 1-87

SCOPE

This method is for determining the distillation range of heavy petroleum oils. It is applicable to petroleum products whose boiling range extends above that of kerosine, e.g., crude, gas and fuel oils. The method differs from ASTM D 86 in that a 200-mL flask is used and the distillation apparatus is gas-fired. Coke residue is determined from a separate distillation that is continued past the thermal decomposition point. The test is particularly useful in estimating gasoline, kerosine and/or distillate content, and the coking characteristics of these oils.

OUTLINE OF METHOD

The method is divided into two procedures. Procedure A is for determining the distillation range of the sample. Procedure B is for determining the coke residue. In Procedure A a 100-mL sample is distilled under prescribed conditions. Systematic observations of thermometer readings and volumes of condensate are recorded and a percent bottoms calculated. No corrections are applied to the data. In Procedure B the distillation is performed under the same conditions using a 30-g sample, but no temperature readings are taken. The distillation is continued until all liquid and vapors have been driven over and a dry residue remains. The mass of coke or residue is determined and the percentage calculated.

APPARATUS

Balance, top-loading, 0-600 g, readability 0.01-g, Mettler PE600, Sargent-Welch Scientific, Cat. No. S-2568-25, or equivalent

Burner, Meker type, 2 required, Sargent-Welch Scientific, Cat. No. S-12158, or equivalent

Cheesecloth, double weight, Sargent-Welch Scientific, Cat. No. S-19795, or equivalent

Cork borers, brass-plated, Fisher Scientific, Cat. No. 07-845E, or equivalent

Corks, superior grade, Nos. 4 and 6, Fisher Scientific, Cat. Nos. 07-792C and E, or equivalent

Cylinder, graduated, 100-mL

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Density meter, and support apparatus, as specified in ASTM D 4052 (optional)

Distillation apparatus, as specified in ASTM E 133, Fig. 1, Sargent-Welch Scientific, Cat. No. S-66415, or equivalent

Distilling flask, Engler, 200-mL, as specified in ASTM D 1078, Sargent-Welch Scientific, Cat. No. 33925, or equivalent

Hydrometers, petroleum, and support apparatus, as specified in ASTM D 1298

Thermometer, ASTM 3C (Celsius) or 3F (Fahrenheit), Sargent-Welch Scientific, Cat. No. S-80255C or S-80265C, or equivalent

Wire, copper, Gauge No. 18, Sargent-Welch Scientific, Cat. No. S-85135-C, or equivalent

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

Ice

Methane, natural gas

Water

PROCEDURE

A. Distillation

Fill the condenser bath with a water-and-ice mixture, maintaining a temperature of 4 ± 1 C (40 ± 2 F). Add the minimum amount of ice required to reach and hold this temperature within the prescribed tolerance.

Swab the condenser tube with a piece of cheesecloth attached to a copper wire to remove any liquid remaining from a previous test.

Weigh the distillation flask and record the mass to the nearest 0.01 g. Determine the relative density of the sample at 15.6 C (60 F) according to ASTM D 4052 or D 1298. Multiply the relative density by 100 and weigh this amount to the nearest 0.01 g, directly into the distillation flask. If the sample is viscous, it may be necessary to warm it. Do not permit any of the sample to flow into the vapor tube. If the sample is sufficiently fluid at 15 C, 100 mL may be charged directly into the flask from the 100-mL graduated cylinder.

Fit the thermometer into a cork. The hole in the cork must be of such a size that there will be no leaking, yet loose enough to permit the thermometer to be positioned with gentle pressure. The thermometer bulb is centered in the neck of the flask so that the lower end of the capillary tube is opposite the inside bottom of the vapor tube at its junction with the neck of the flask (refer to Fig. 1 of ASTM D 86). The thermometer should be at room temperature when it is placed in the flask.

Place the flask on the iron ring, and by means of a cork through which the vapor tube has been passed, make a tight connection with the condenser tube. Adjust the position of the flask so that the vapor tube extends into the condenser not less than 2.5, or more than 5 cm (1 - 2 inches).

Place a clean, dry 100-mL graduated cylinder at the outlet of the condenser tube, as a receiver, in such a position that the condenser tube extends into it by at least 2.5 cm, but not below the 100-mL mark. Set the gas burner under the flask. The top of the burner should be approximately 2.5 cm below the bottom center of the flask. Adjust the flame so that it does not spread around the sides of the flask.

Apply sufficient heat to the distillation flask so that the first drop of condensate falls from the condenser in no less than 5, or more than 15 minutes. Record the thermometer reading when the first drop falls. This temperature is the initial boiling point (IBP). Move the receiver so that the tip of the condenser tube touches the side of it. Regulate the heat to cause the distillation to proceed at a uniform rate of not less than 4, or more than 5 mL per minute (see *PRECAUTIONS*).

When a temperature of 274 C (525 F) has been reached, allow the water to drain from the condenser bath as quickly as possible to prevent the distillate from solidifying in the condenser tube. Keep the condenser tube warm with a second Meker burner during the remainder of the distillation. When approximately 90% of distillate has been collected, adjust the gas-regulating valve to obtain maximum heat output and watch the thermometer carefully for the highest temperature reached. Record this temperature as the endpoint (EP). In cases where the mercury rises above 400 C (760 F), record the endpoint as “above 400 C (760 F).”

Heat the condenser tube with the gas flame until all material that may have solidified during the distillation has drained into the receiver. Allow the distillate to cool to 15 ± 3 C (60 ± 5 F). Read and record the volume of distillate collected as the percent recovered.

B. Determination of Coke Residue

Swab the condenser tube with a piece of cheesecloth attached to a copper wire to remove any liquid remaining from a previous test. Do not fill the condenser bath with water.

Weigh the distillation flask and record the mass to the nearest 0.01 g. Weigh nominally 30 ± 0.01 g of sample directly into the distillation flask. Do not permit any of the sample to flow into the vapor tube. If the sample is viscous, it may be necessary to warm it.

Place a solid cork (without thermometer) in the neck of the distillation flask. Place the flask on the iron ring, and by means of a cork through which the vapor tube has been passed, make a tight connection with the condenser tube. Adjust the position of the flask so that the vapor tube extends into the condenser not less than 2.5, or more than 5 cm (1-2 inches).

Place a clean, dry 100-mL graduated cylinder at the outlet of the condenser tube, as a receiver, in such a position that the condenser tube extends into it by at least 2.5 cm, but not below the 100-mL mark. Set the gas burner under the flask. The top of the burner should be approximately 2.5 cm below the bottom center of the flask.

Apply sufficient heat to the distillation flask to produce a steady drip from the tip of the condenser (see *PRECAUTIONS*). Keep the condenser tube warm with a second Meker burner during the course of the distillation. When most of the liquid has distilled over and fuming begins, adjust the gas-regulating valve to obtain maximum heat output. Continue heating the entire surface of the flask until all the vapors tending to

hang over the coking mass have been driven off. The length of time for this superheating varies with the amount of residue in the flask. Heating for fifteen minutes is usually sufficient.

Allow the flask to cool, remove both corks, and weigh the flask.

CALCULATIONS

Calculate the percent bottoms determined by Procedure A as follows:

$$\text{Percent bottoms, LV-\%} = 100 - R$$

where:

R = percent recovered, LV-%

100 = percentage constant

Calculate the mass-percent coke or residue determined by Procedure B as follows:

$$\text{Coke or residue, mass-\%} = \frac{100 C}{W}$$

where:

C = mass of coke or residue, g

W = mass of sample, g

100 = percentage constant

PRECAUTIONS

Oils containing more than traces of water are very difficult to distill. When water is present, heat the flask evenly over its top and bottom surfaces. Do *not* concentrate heat on the bottom of the flask. Keep the top of the flask hot enough to prevent water vapor from condensing there. After all the water has been distilled over, allow time for the temperature to return to ambient before continuing the distillation. Do not include water in the percentages reported for the temperatures named. The IBP obtained in this manner on samples containing water may, or may not, be a true IBP *owing* to the possibility of superheating the vapors when the flame is applied to the top surface of the flask.

Decomposition or cracking can result when oils containing material boiling above 329 C (625 F) are distilled at atmospheric pressure. Characteristic indications of decomposition are evolution of fumes and erratic temperature readings. When a sample is cracking, efforts to maintain the specified distillation rate will result in a gradual drop in temperature. Therefore, when there are signs that decomposition is occurring, continue the distillation at whatever rate is required to ensure a steady rise in temperature.

When coal tar products and certain other heavy oils are being distilled, frothing sometimes occurs early in the distillation or near the end. Care must be taken to prevent the boiling mass of coke and very high-boiling liquid from entering the condenser. When frothing occurs, remove the flame and allow the froth to subside. Resume gentle heating so that frothing will be slight. Here, also, disregard the 4 - 5 mL per minute rate of distillation. When frothing is extreme or uncontrollable, discontinue the distillation and begin again using a 500-mL distillation flask.

PRECISION

Procedure A: An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least 4 degrees of freedom. Because this method uses the same apparatus and distillation rates as ASTM Method D 86, the precision cited for that method should be comparable.

Procedure B: The estimated standard deviation (esd) for coke is shown below. Duplicate results by the same operator should not be considered suspect unless they differ by more than the amount shown under “allowable difference” (95% probability).

Coke Level, mass-%	Number of Duplicates	esd, mass-%	Allowable Difference, mass-%
4 to 18	8	0.18	0.60

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.44 hour (Procedure A) to 1.3 hours (Procedures A & B). The labor requirement is 0.44 hour (Procedure A) to 1.5 hours (Procedures A & B).

REFERENCES

ASTM Standard Test Methods D 86, D 1078, D 1298, D 4052 and Specifications E 1 and E 133,
www.astm.org

SUGGESTED SUPPLIERS

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143
 Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077