

CRUDE OIL EVALUATION BY HEMPEL DISTILLATION

UOP Method 77-85

SCOPE

This method is for determining the gasoline and kerosine content of a crude oil, the results of which serve as a guide in operating crude oil topping facilities. Combining this method with UOP Method 109 provides an approximation of the yields of all major fractions generally obtainable from commercial crude fractionation units.

OUTLINE OF METHOD

The sample is charged to a distillation apparatus employing a Hempel column. The sample is distilled at atmospheric pressure in such a manner as to produce results which approximate those obtained from a commercial distillation. Directions are given to obtain gasoline and kerosine fractions of either specified endpoint or API gravity.

APPARATUS

Bath, 316-stainless steel with 25-mm insulation, of sufficient size to completely immerse bulb section of condenser, UOP Inc., or equivalent.

Beaker, 2000-mL

Bottle, two-liter, jug form, flint glass, with molded screw cap, Sargent-Welch Scientific, Cat. No. S-8480A, or equivalent

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

Clamps, for rubber tubing, stainless steel, 6.4-mm minimum, 15.9-mm maximum, Sargent-Welch Scientific, Cat. No. S-73765A, or equivalent

Corks, sizes 10, 14 and 26, Sargent-Welch Scientific, Cat. Nos. S-23025-N, S and FF, or equivalent

Condenser, Allihn; inlet, 25-mm OD, 90-mm long, angled to allow condenser to be placed in a vertical position when attached to the arm of the distillation column; bulbs, approximately spherical, 45-mm OD; drip-tip, 12.5-mm OD, 127-mm long; overall length of condenser, 460-mm, UOP Inc., or equivalent

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).

Cylinder, borosilicate glass, graduated, 500-mL, cut off at the 450-mL mark and annealed, Sargent-Welch Scientific, Cat. No. S-24665-H, or equivalent, modified as stated

Cylinders, borosilicate glass, graduated, 25-mL

Density meter, as specified in ASTM D 4052

Dewar, 1000-mL, SGA Scientific Inc., Cat. No. F-4600, or equivalent

Distillation apparatus, as specified in ASTM D 86

Distillation apparatus, as specified in UOP 1

Dry ice trap, Fig. 2, UOP Inc., or equivalent

Flask, round bottom, short ring neck, 5000-mL, Sargent-Welch Scientific, Cat. No. S-33865M, or equivalent

Hempel fractionation column, consisting of:

Beads, glass 6-mm, Sargent-Welch Scientific, Cat. No. S-39838D, or equivalent. Fill column to a depth of 152-mm.

Distilling column, Pyrex, 300-mm overall length, 25-mm OD, SGA Scientific Inc., Cat. No. D-7505, or equivalent

Wire, 14 gauge nichrome, shaped in two spirals, one to support the beads at the bottom of the column, and one on top of the beads to prevent them from being carried into the vapor outlet tube

Lacquer, black, Panbor Industrial Supply Co., or equivalent

Pan, 316-stainless steel, typical dimensions 356 × 559 × 90-mm, UOP Inc., or equivalent

Ring, compressed cork, Sargent-Welch Scientific, Cat. No. S-23125D, or equivalent

Ring, support, iron, with screw clamp, 152-mm OD, Sargent-Welch Scientific, Cat. No. S-73045E, or equivalent

Ring, base 135 × 225-mm, support rod 600-mm, Sargent-Welch Scientific, Cat. No. S-78306C, or equivalent

Scale, minimum capacity 10-kg, readability, 0.1-g, Sartorius, Model 3808 MP8, Sargent-Welch Scientific, Cat. No. S-2714-21A, or equivalent

Shield, 316-stainless steel, typical dimensions 330 × 318 × 900-mm, with 686-mm door having a safety glass insert, UOP Inc., or equivalent

Stopper, rubber, size 10, two-hole

Thermometer, ASTM low distillation, 7C, Fisher Scientific, Cat. No. 13-481, or equivalent

Thermometer, ASTM high distillation, 8C, Fisher Scientific, Cat. No. 13-482, or equivalent

Tube, glass, bent to form a right angle

Tubing, rubber, red, medium wall, 7.9-mm ID, 11.1-mm OD, 1.6-mm wall, Sargent-Welch Scientific, Cat. No. S-73635E, 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.

Acetone, 99% minimum purity, Sargent-Welch Scientific Co., Cat. No. SC-10268, or equivalent

Carbon dioxide, solid

Detergent, liquid, commercially available

Ice

Isopar M, isoparaffinic solvent, Exxon Company USA, or equivalent

Methane (natural gas)

Sodium chloride, 99.0% minimum purity

PROCEDURE

Perform a UOP Method 1 distillation on the whole crude. This will indicate the gasoline and kerosine content of the crude.

Wash the flask, Hempel column, condenser, dry ice trap and all receivers with water and detergent. Rinse several times with acetone and dry prior to charging flask and proceeding with the analysis.

Determination of Gasoline Content

Arrange the apparatus as shown in Fig. 1. Maintain the condenser bath temperature between -12 and -1 C by the use of ice, sodium chloride and water, except when otherwise specified. Place the dry ice trap (Fig. 2) in the Dewar and fill the Dewar with dry ice-isopar mixture.

Determine the relative density of the crude oil by ASTM D 4052 and calculate the mass of 4000 mL. Weigh this amount into the 5000-mL round-bottom flask. Never fill a distillation flask to more than 80% of its capacity.

Insert the appropriate thermometer into the Hempel column by means of a cork, positioning the thermometer bulb so that the top of the bulb is in line with the bottom of the vapor outlet tube. Use an ASTM 7C thermometer if determining gasoline content only, and the ASTM 8C thermometer if determining both gasoline and kerosine content.

Insert the Hempel column into the flask with a cork. Place the flask and Hempel column on the ring support inside the shield, connecting the vapor tube of the Hempel column to the condenser inlet with another cork. Adjust the ring stand so that there is no strain on the vapor tube of the flask-and-column assembly.

Seal all connections of the entire distillation assembly made thus far, including cork pores, with lacquer. Use a cut-off 500-mL graduated cylinder for the receiver and place it into a 2000-mL beaker containing ice, sodium chloride and water. Using a 2-hole rubber stopper, connect the receiver to the outlet end of the condenser. Connect the dry ice trap to the receiver, by inserting the right angle glass tube through the remaining hole in the rubber stopper. Do *not* seal these connections or the stopper with lacquer.

Apply heat to the flask at a very low rate initially. Gradually increase the heat so that the first drop will distill over in 15 to 20 minutes. Maintain a 3-mL per minute rate until the column temperature reaches 82-93 C (180-200 F). At this time remove the Dewar with the dry ice trap from the system. Leave a right-angle glass tube in the stopper of the receiver to act as a vapor vent. Close the inlet and outlet of the trap with rubber tubing and clamps, and set trap and contents aside. The dry ice trap should remain in the Dewar with the temperature of the dry ice-isopar mixture maintained.

Increase the distillation rate to 5-mL per minute. When a temperature approximately 16 C below the cut temperature of the gasoline is reached, decrease the rate to 3-mL per minute to ensure more precise fractionation.

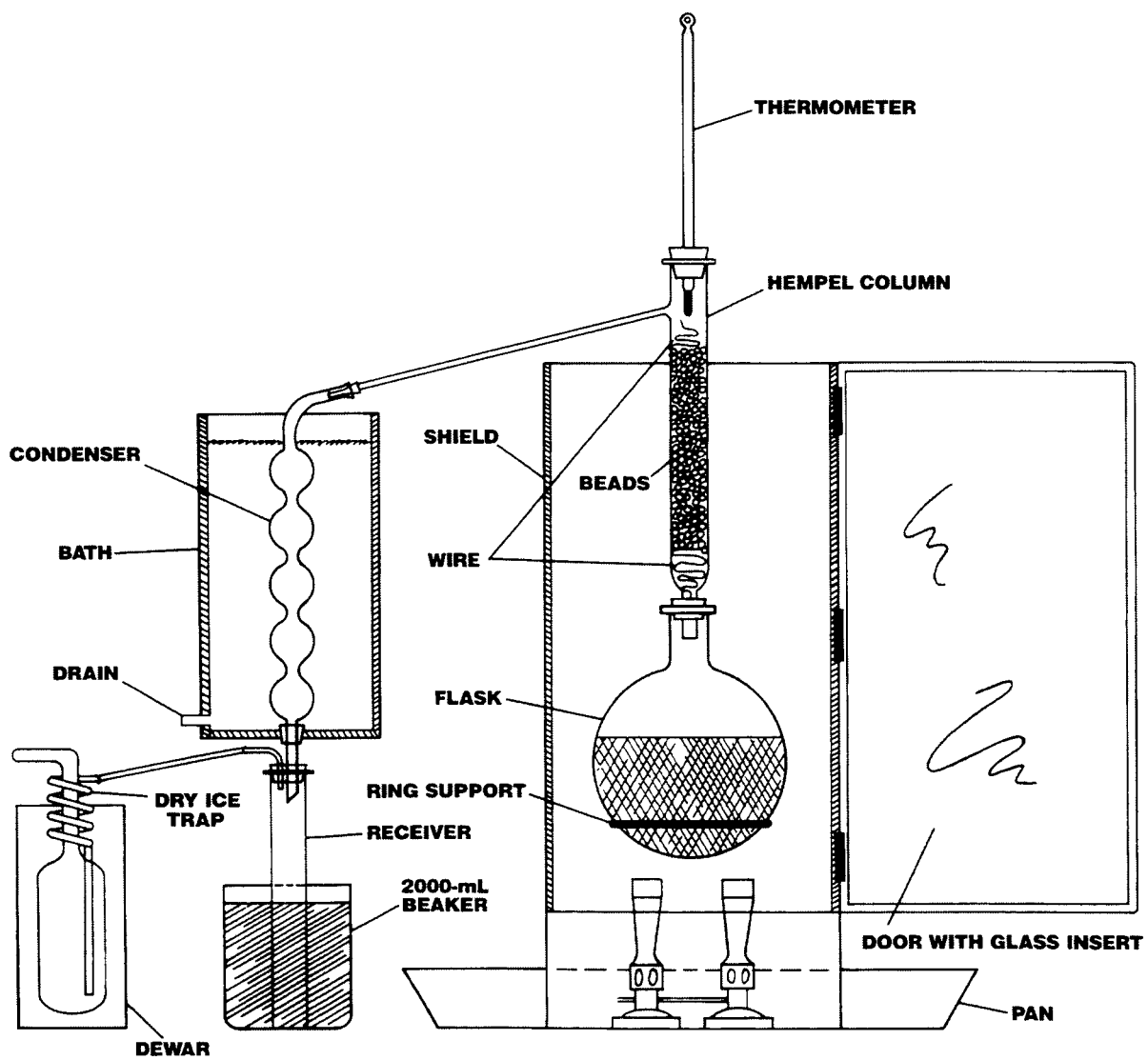


Figure 1

Hempel Distillation Apparatus

Make the initial bulk cut at a temperature 9 C below the desired endpoint of the gasoline fraction. Remove the 500-mL graduate containing the bulk cut and transfer its contents to a bottle that has been pre-cooled to about 5 C. Continue the distillation at the 3-mL per minute rate, removing cuts every 3 C using 25-mL graduates for receivers. Record the volume, temperature, and final vapor temperature of each cut. Continue until a vapor temperature 12 C above the desired endpoint is reached. Discontinue the distillation at this point but leave a receiver in place.

Mix the initial bulk cut well and conduct an ASTM Method D 86 distillation to determine the endpoint. If the endpoint is below that desired, cool the flask and remove the boiling chip. Pour the overhead from the D 86 distillation back into the D 86 flask to rinse out the heavy ends, and return the sample to the bulk cut. Add the first 3 C cut, or more if necessary, to the initial bulk cut. Mix thoroughly and conduct another ASTM D 86 distillation. If the endpoint is still too low, repeat this step until the fraction has the desired endpoint. Make as few D 86 distillations of the bulk cut as possible to get the desired endpoint. Always return the material from the D 86 distillation after it is cooled to the bulk cut.

Very carefully add the contents of the dry ice trap to the endpoint material. Mix thoroughly and conduct a final D 86 distillation to determine the initial boiling point as well as to confirm that the endpoint is as specified.

If a kerosine fraction is not desired, remove the distillation flask and Hempel column from the shield, disconnect the Hempel column and return all unused, higher boiling cuts to the contents of the flask. Weigh this material, determine its relative density, and report it as partially-topped crude.

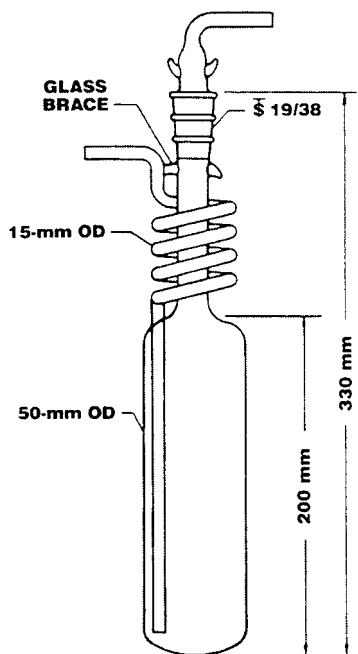


Figure 2

Dry Ice Trap

Determination of Kerosine Content

The kerosine fraction is obtained by continuing the Hempel distillation after the gasoline fraction has been removed. Take a second bulk cut following the same procedure as described for gasoline. Add to it all the 3 C fractions unused in making the endpoint gasoline.

When the endpoint of the kerosine is specified, the procedure of making several 3 C cuts before and after reaching the desired endpoint is also followed. Blend these back in the order taken until the fraction has the desired endpoint as determined by ASTM D 86.

When a kerosine of specified API gravity is requested, usually 41-43 or 42-44, make a bulk cut at 260 C, mix well, and determine the relative density by ASTM D 4052. Convert the relative density to API gravity by using the ASTM-IP Petroleum Measurement Tables. Should the API gravity be too high, continue the Hempel distillation. Take several 1 vol-% cuts and reserve them in the order taken. Blend the first 1% cut into the bulk kerosine cut and determine the gravity. If still too high, blend in the next, repeating this procedure until the required gravity has been secured. If the gravity of the original bulk cut is too low, cool the distillation flask, return the bulk cut, and redistill the kerosine fraction taking the bulk cut at a lower temperature.

When the desired kerosine fraction has been produced, add all unused 1% kerosine cuts back to the distillation flask. Weigh the mixture and report this material as fully-topped crude. Determine the API gravity of this fraction.

If further evaluation of the crude is required, the residue is subjected to vacuum distillation.

CALCULATIONS

Using ASTM D 1250 (Vol. II), correct the volumes of the bulk cut and small cuts to 15.6 C (60 F).

Convert the mass of both the original charge and the bottoms fraction to volumes at 15.6 C (60 F) using the following equation:

$$V = \frac{M}{D}$$

where:

D = relative density, g/mL at 15.6 C (60 F)

M = mass, g

V = volume, mL

Calculate the bottoms fraction as follows:

$$R = \frac{100 S}{C}$$

where:

C = volume of the original charge, mL

R = bottoms fraction, vol-%

S = volume of the bottoms fraction, mL

100 = percentage constant

Calculate the gasoline and kerosine fractions as follows:

$$F = \frac{100 (A + B)}{C}$$

where:

A = volume of the bulk cut, mL

B = combined volume of all small cuts used to make the specified fraction, mL

C = volume of the original charge, mL

F = gasoline (or kerosine) fraction, vol-%

100 = percentage constant

Calculate the distillation loss as follows:

$$L = 100 - (F_g + F_k + R)$$

where:

F_g = gasoline fraction, vol-%

F_k = kerosine fraction, vol-%

L = distillation loss, vol-%

R = bottoms fraction, vol-%

100 = percentage constant

PRECAUTIONS

Keep the total crude oil sample in a well-sealed container from the time it is drawn until charged into the distillation flask to avoid losses of light fractions. It is desirable to store the sample under refrigeration except when in actual use for the same reason.

If the presence of water in the oil is suspected, the Hempel column and the neck of the distillation flask should be warmed sufficiently before starting the distillation to prevent condensation of moisture. In this case apply heat with special caution, starting at the oil level and slowly lowering the burner until it is in the normal position underneath the flask. An auxiliary burner may be used for this purpose before lighting the main burner, if desired, and for warming the neck of the flask and the column. Also, the temperature of the condenser bath should be held between 0 and 4 C.

The pan under the shield is specified for safety reasons. In the event of a break or a spill, an oil fire may be prevented from spreading.

PRECISION

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.

TIME FOR ANALYSIS

The time required to perform the distillation varies according to the sample. The elapsed time may be from 4 to 16 hours with a similar labor requirement.

REFERENCES

ASTM Methods D 86, D 1250, D 1298 and D 4052, www.astm.org

ASTM-IP Petroleum Measurement Tables, Applied Publishers, Ltd., Ripple Road, Barking, Essex, England

UOP Methods 1 and 109

SUGGESTED SUPPLIERS

Exxon Company USA, 600 Enterprise Dr., Oak Brook, IL 60521

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143

Panbor Industrial Supply Co., 4046 Tugwell, Franklin Park, IL 60131

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

SGA Scientific Inc., 188 Industrial Drive, Elmhurst, IL 60126

UOP Inc., Box 5017, Des Plaines, IL 60017-5017