# Laboratory Testing of Crude Oils

# True Boiling Point (TBP) Curve

- The composition of any crude oil sample is approximated by a true boiling point (TBP) curve.
- The method for determining this is a batch distillation operation using a large number of stages, usually > 60, and high reflux to distillate ratio (> 5).

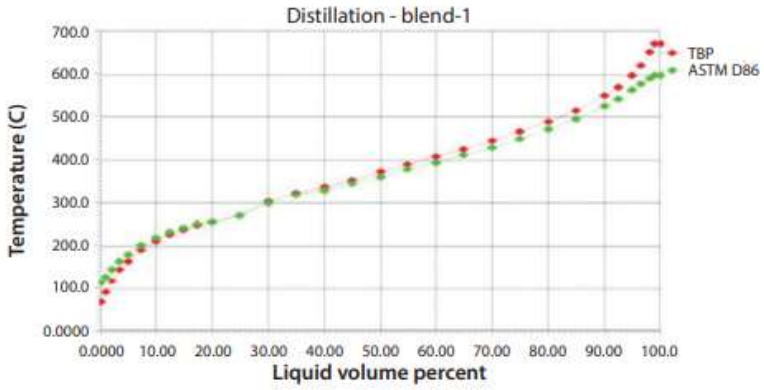
| Test name | Reference | Main applicability |
|---|---|---|
| ASTM (atmosphere) | ASTM D 86 | Petroleum fractions or products, including gasoline turbine fuels, napthas, kerosines, gas oils, distillate fuel oils, and solvents that do not tend to decompose when vaporized at 760 mm Hg |
| ASTM [vacuum often 10 torr (1.3 kPa)] | ASTM D 1160 | Heavy petroleum fractions or products that tend to decompose in the ASTM D86 but can be partially or completely vaporized at a maximum liquid temperature of 750 °F (400 °C) at pressures down to 1 torr (0.13 kPa) |
| TBP [atmospheric or 10 torr (1.3 kPa)] | Nelson*, ASTM D 2892 | Crude oil and petroleum fractions |
| Simulated TBP (gas chromatography) | ASTM D 2887 | Crude oil and petroleum fractions |
| EFV (atmospheric, superatmospheric, or subatmospheric) | Nelson† | Crude oil and petroleum fractions |

# ASTM D86 Distillation

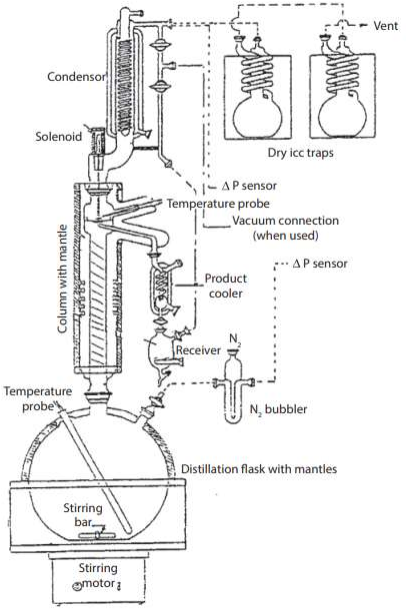
- D86 distillation uses a simple Engler flask containing a calibrated thermometer to measure the temperature of the vapor at the inlet to the condensing tube. An inclined brass condenser in a cooling brass is attached, to remove all distilled vapors; no liquid reflux is returned to the flask. The condenser tube is cooled in an ice water bath to maintain the condensing temperature between 32 and 40 °F (0–4.5 °C). The light components that boil at temperatures lower than the condensing temperature are lost from the distilled product.

# Procedure

100 ml of sample is distilled and the vapor temperature against volume recovered is recorded. The initial boiling point (IBP) is defined as the temperature at which the first drop of liquid leaves the condenser tube. The final boiling point (FBP) or “end point” is the highest temperature recorded during the text. The total volume of the distillate is recorded as the recovery. Any liquid left in the still after the end point temperature is recorded is cooled and measured as the residue. The difference between 100 ml (initial sample volume) and the sum of the recovery and the residue is referred to as the loss. Repeated tests give ±6 °F for the initial boiling and end points. Intermediate distillation points are reproducible within 2 ml of distillate which corresponds to 6–7 °F. Figure beside shows a modern TBP apparatus.




Snapshot of liquid volume (%) vs. Temperature (oC) of TBP and ASTM D86 plots of distillation blend (Courtesy of Honeywell UniSim software, Honeywell (R) and UniSim (R) are registered trademarks of Honeywell International Inc.).

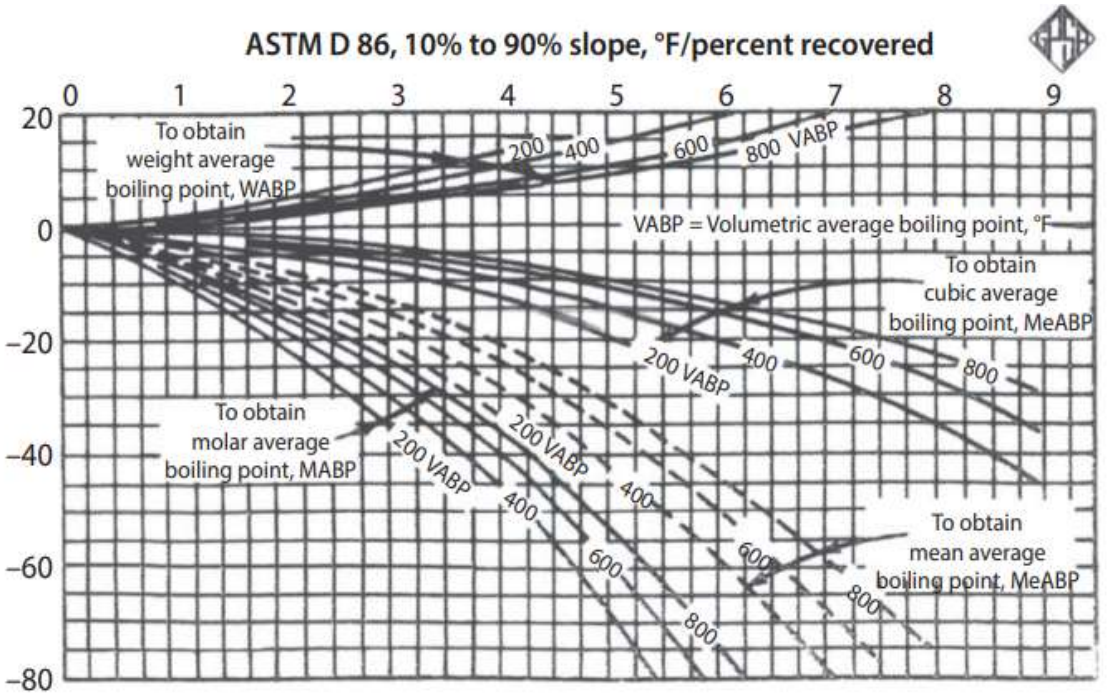


# Boiling Points

- Figure beside illustrates the inter-conversion between ***ASTM D –86*** distillation 10% to 90% slope and ***the different boiling points*** used to characterize fractions of crude oil.
- This is done to determine the properties such as the
  - volumetric average boiling (VABP) point,
  - weight average boiling point (WABP),
  - molal average boiling point (MABP),
  - mean average boiling point (MeABP)
  - and cubic average boiling point (CABP). On the basis of ASTM D-86 distillation data, the VABP is :

$$VABP = \left(t_{10} + t_{30} + t_{50} + t_{70} + t_{90}\right)/5$$

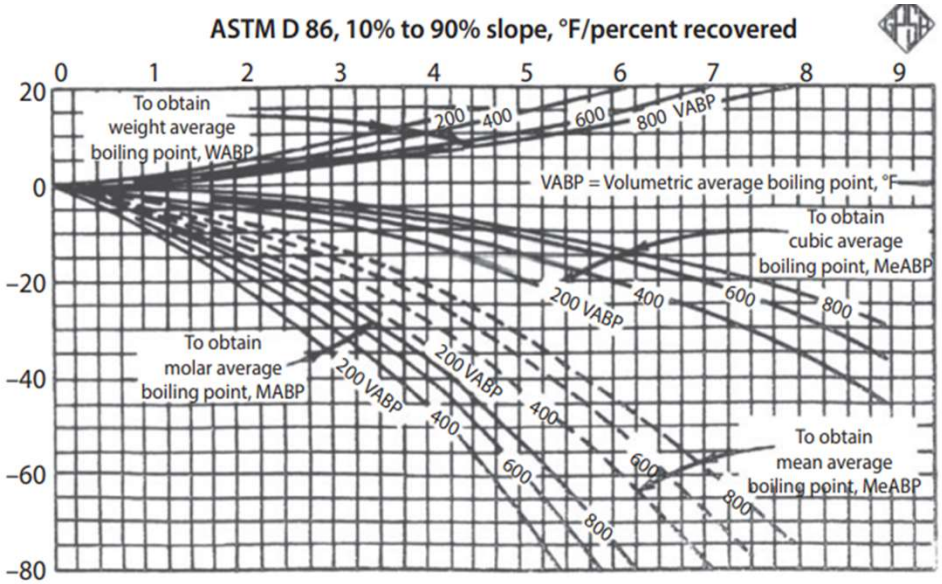
where the subscripts 10, 30, 50, 70 and 90 refer to the volume per cent recovered during the distillation.

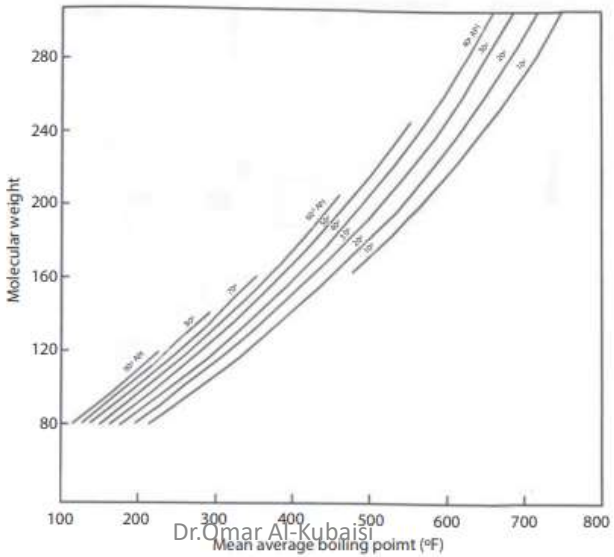



Characterizing Boiling Points of Petroleum Fractions (From API Technical Data Book). Used by permission, Gas Processing Suppliers Association Book Data, 12th ed., v.1 and 2. (2004).

# Uses of Figure

- To locate the curve for the distillation VABP in the appropriate set for the type of boiling point desired.
- For a known 10–90% slope, to read a correction for the VABP from the selected VABP curve.



# Problem

Determine the mean average boiling point (MeABP) and the molecular weight for a 56.8 °API petroleum fraction with the following ASTM distillation data.

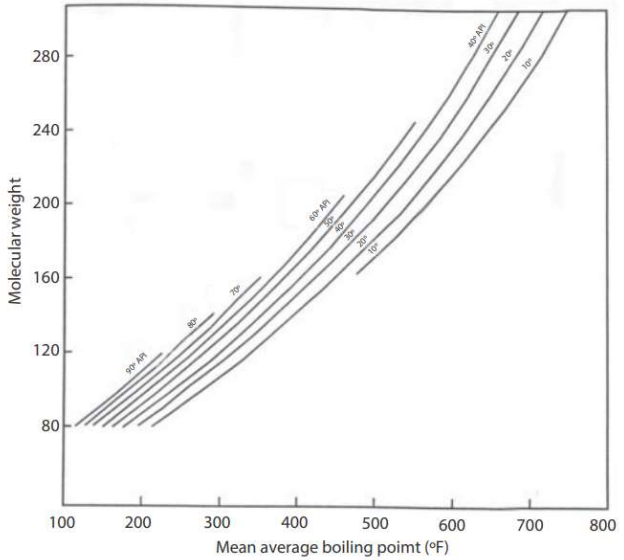
| % Over | Temperature, °F |
|---|---|
| IBP | 100 |
| 5 | 130 |
| 10 | 153 |
| 20 | 191 |
| 30 | 217 |
| 40 | 244 |
| 50 | 280 |
| 60 | 319 |
| 70 | 384 |
| 80 | 464 |
| 90 | 592 |
| EP | 640 |

(Source: *Engineering Data Book*: Gas Processors Suppliers Association, Tulsa, Oklahoma, 12th ed., 2004)

**Solution**

IBP = initial boiling EP = end point
Slope (592–153)/80 = 5.49
VABP = (153 + 217 + 280 + 384 + 592)/5 = 325 °F
From Figure 3.6, Read down from a slope of 5.49 on the x-axis to the interpolated curve closest to 325 °F,

in the set drawn with the dashed lines (MeABP). Read across to obtain a correction value of –54 on the ordinate.
MeABP = 325–54 = 271 °F.
At °API = 56.8, the molecular weight is 198 from




Correlations between MeABP. SpGr and Mol. Wt

# Conversion Between ASTM and TBP Distillation

The True Boiling Point distillation determination of petroleum crudes can often be time consuming and tedious as compared to the ASTM method. Therefore, a correlation between ASTM and TBP distillation is employed that achieves the separation of TBP with little effort of the ASTM distillation

$$\text{TBP} = a\left(\text{ASTM D86}\right)^{b}$$

- where a and b are constants varying with percent of liquid sample distilled as shown in Table 3.10. TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90 and 95 volume percent distilled, in degrees Rankine (°R).

| Volume% distilled | a | b |
|---|---|---|
| 0 | 0.9167 | 1.0019 |
| 10 | 0.5277 | 1.0900 |
| 30 | 0.7429 | 1.0425 |
| 50 | 0.8920 | 1.0176 |
| 70 | 0.9490 | 1.0110 |
| 90 | 0.9490 | 1.0110 |
| 95 | 0.8008 | 1.0355 |

## Watson's Characterization Factor:

The MeAPB is used in the determination of Watson characterization factor as expressed by:

$$K = \frac{\left(\text{MeABP}\right)^{1/3}}{\text{SpGr}}$$

where MeAPB is in degrees Rankin(°R).

# Example

A petroleum cut has the following ASTM data

| Volume% distilled | 0 | 10 | 30 | 50 | 70 | 90 | 95 |
|---|---|---|---|---|---|---|---|
| Temperature °C | 36.5 | 54 | 77 | 101.5 | 131 | 171 | 186.5 |

Convert these data to TPB data using the API method. Plot the result and compare. If the API gravity of this fraction is 62, Calculate the Watson's characterization factor.

- 1- VAPB

$$VABP = \left(t_{10} + t_{30} + t_{50} + t_{70} + t_{90}\right)/5$$

  - VAPB= 224.2 °F (106.9 °C)
- Slope

$$Slope = \frac{\left(t_{90} - t_{10}\right)}{\left(90 - 10\right)}$$

  - Slope =2.6325
- MeAPB= VAPB-lnΔ
- lnΔ

$$\ln \Delta = -0.94402 - 0.00865\left(\mathrm{VABP} - 32\right)^{0.6667} + 2.9979\left(\mathrm{Slope}\right)^{0.333}$$

MEABP = VABP = 224.4–18.3 = 206.1 °F (96.8 °C)

°API = 62 Specific gravity = 141.5/(62+131.5) = 0.731

Watson characterization factor from Equation is:

$$K = \frac{(\text{MeABP})^{1/3}}{\text{SpGr}}$$

$$K = \frac{(206.1 + 460)^{1/3}}{0.731} = 11.92$$

| Index number, i | Volume% distilled | a | b | Temp D86 °C | Temp D86 °F | TBP °R | TBP °F | TBP °C (Eq 3.8) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0.9167 | 1.0019 | 36.5 | 97.7 | 517.4 | 57.4 | 14.1 |
| 2 | 10 | 0.5277 | 1.09 | 54 | 129.2 | 552 | 92 | 33.3 |
| 3 | 30 | 0.7429 | 1.0425 | 77 | 170.6 | 616.1 | 156.1 | 68.9 |
| 4 | 50 | 0.892 | 1.0176 | 101.5 | 214.7 | 674.9 | 214.9 | 101.6 |
| 5 | 70 | 0.8705 | 1.0226 | 131 | 267.8 | 735.3 | 275.3 | 135.2 |
| 6 | 90 | 0.949 | 1.011 | 171 | 339.8 | 816.9 | 356.9 | 180.5 |
| 7 | 95 | 0.8008 | 1.0355 | 186.5 | 367.7 | 841.4 | 381.4 | 194.1 |