APPENDIX L

Physical Properties of Petroleum Fractions

In the early 1930s, tests were developed that characterized petroleum oils and petroleum fractions so that various physical characteristics of petroleum products could be related to these tests. Details of the tests can be found in *Petroleum Products and Lubricants,* an annual publication of Committee D-2 of the American Society for Testing Materials.[1] These tests are not scientifically exact, and hence the procedure used in the tests must be followed faithfully if reliable results are to be obtained. However, the tests have been adopted because they are quite easy to perform in an ordinary laboratory and because the properties of petroleum fractions can be predicted from the results. The specifications for fuels, oils, and so on are set out in terms of these tests plus many other properties, such as the flash point, the percent sulfur, and the viscosity.

Over the years various phases of the initial work have been extended, and development of a new characterization scheme using the pseudocompound approach is evolving. Daubert[2] summarizes the traditional and new methods insofar as predicting molecular weights, pseudocritical temperature and pressure, acentric factor, and characterization factors.

In this appendix we present the results of the work of Smith and Watson and associates,[3] who related petroleum properties to a factor known as the *characterization factor* (sometimes called the *UOP characterization factor*). It is defined as

$$K = \frac{(T_B)^{1/3}}{S}$$

[1]Report of Committee D-2, ASTM, Philadelphia, annually.
[2]T. E. Daubert, "Property Predictions," *Hydrocarbon Proc.,* 108–10 (March, 1980).
[3]R. L. Smith and K. M. Watson, *Ind. Eng. Chem.,* **29**, 1408 (1937); K. M. Watson and E. F. Nelson. *Ind. Eng. Chem.,* **25**, 880 (1933); K. M. Watson, E. F. Nelson, and G. B. Murphy, *Ind. Eng. Chem.,* **27**, 1460 (1935).

where K = *UOP* characterization factor
T = cubic average boiling point, °R
S = specific gravity at 60°F/60°F

Other averages for boiling points are used in evaluating K and the other physical properties elsewhere on the CD. (Refer to Daubert[4] or Miquel[5] for details.) This factor has been related to many of the other simple tests and properties of petroleum fractions such as viscosity, molecular weight, critical temperature, and percentage of hydrogen, so that it is quite easy to estimate the factor for any particular sample. Furthermore, tables of the UOP characterization factor are available for a wide variety of common types of petroleum fractions, as shown in Table L.1 for typical liquids.

Table L.1 Typical UOP Characterization Factors

Type of Stock	*K*	Type of Stock	*K*
Pennsylvania crude	12.2–12.5	Propane	14.7
Mid-continent crude	11.8–12.0	Hexane	12.8
Gulf Coast crude	11.0–11.8	Octane	12.7
East Texas crude	11.9	Natural gasoline	12.7–12.8
California crude	10.98–11.9	Light gas oil	10.5
Benzene	9.5	Kerosene	10.5–11.5

Refer to the charts of the hydrocarbons that give (a) the specific heats, (b) the vapor pressure, (c) the heat of combustion, (d) the °API, and (e) the heats of vaporization.

[4]M. R. Riazi and T. E. Daubert. *Ind. Eng. Chem. Res.,* **26**, 755–759 (1987).

[5]J. Miquel and F. Castells. *Hydrocarbon Processing,* 101–105 (Dec. 1993).

Table L.2 Information Concerning Charts in Appendix L

1. *Specific heats of hydrocarbon liquids*
   Source: J. B. Maxwell. *Data Book on Hydrocarbons* (p. 93). New York: Van Nostrand Reinhold, 1950 (original from M. W. Kellogg Co.).
   Description: A chart of C_p (0.4 to 0.8) vs. t (0 to 1000ºF) for petroleum fractions from 0 to 120º API.
   Boiling-point basis: Volumetric average boiling point, which is equal to graphical integration of the differential ASTM distillation curve (Van Winkle's "exact method").
   Limitations: This chart is not valid at temperatures within 50ºF of the pseudocritical temperatures.
2. *Vapor pressure of hydrocarbons*
   Source: Maxwell, *Data Book on Hydrocarbons,* p. 42.
   Description: Vapor pressure (0.002 to 100 atm) vs. temperature (50 to 1200ºF) for hydrocarbons with normal boiling points of 100 to 1200ºF (C_4H_{10} and C_5H_{12} lines shown).
   Boiling-point basis: Normal boiling point (pure hydrocarbons).
   Limitations: These charts apply well to all hydrocarbon series except the lowest-boiling members of each series.
3. *Heat of combustion of fuel oils and petroleum fractions*
   Source: Maxwell, *Data Book on Hydrocarbons,* p. 180.
   Description: Heats of combustion above 60ºF (17,000 to 25,000 Btu/lb) vs. gravity (0 to 60ºAPI) with correction for sulfur and inerts included (as shown on chart).
4. *Properties of petroleum fractions*
   Source: O. A. Hougen and K. M. Watson. *Chemical Process Principles Charts* (Chart 3). New York: Wiley, 1946.
   Description: ºAPI(-10 to 90ºAPI) vs. boiling point (100 to 1000ºF) with molecular weight, critical temperature, and K factors as parameters.
   Boiling-point basis: Use cubic average boiling point when using the K values; use mean average boiling point when using the molecular weights.
5. *Heat of vaporization of hydrocarbons and petroleum fractions at* 1.0 *atm pressure*
   Source: Hougen and Watson, *Chemical Process Principles Chart,* Chart 68.
   Description: Heats of vaporization (60 to 180 Btu/lb) vs. mean average boiling point (100 to 1000ºF) with molecular weight and API gravity as parameters.
   Boiling-point basis: Mean average boiling point.

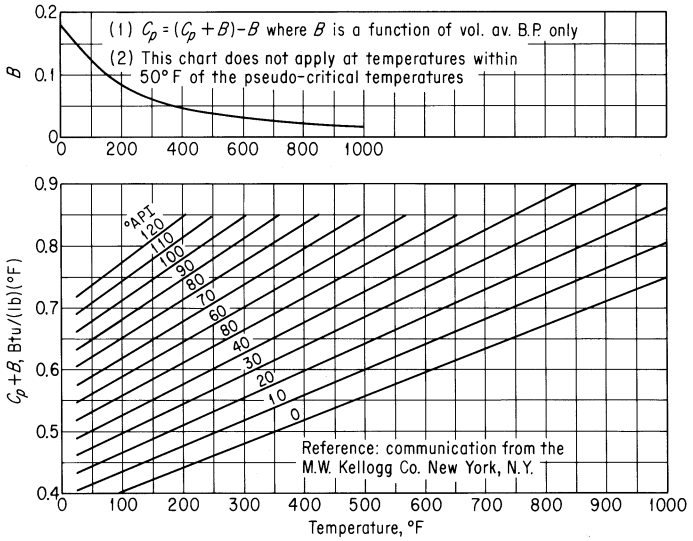


Figure L.1 Specific heats of hydrocarbon liquids.

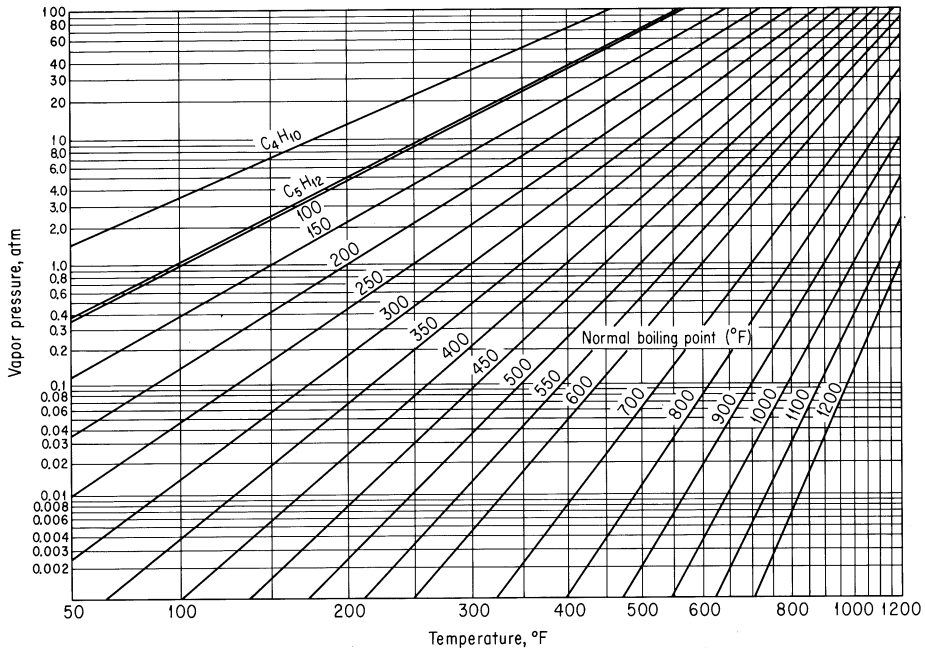


Figure L.2 Vapor pressure of hydrocarbons.

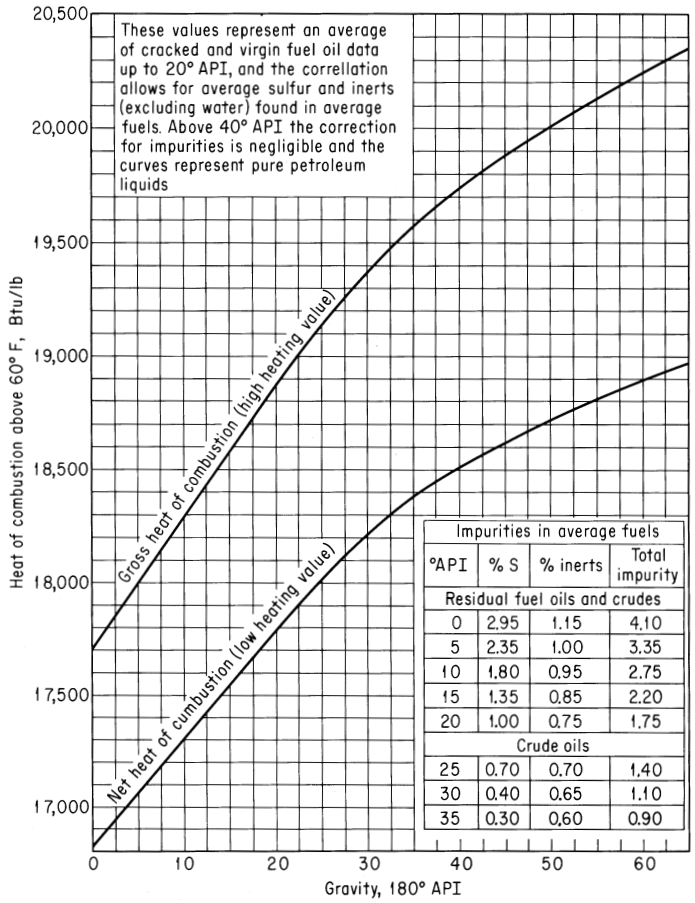


Figure L.3 Heat of combustion of fuel oils and petroleum fractions.

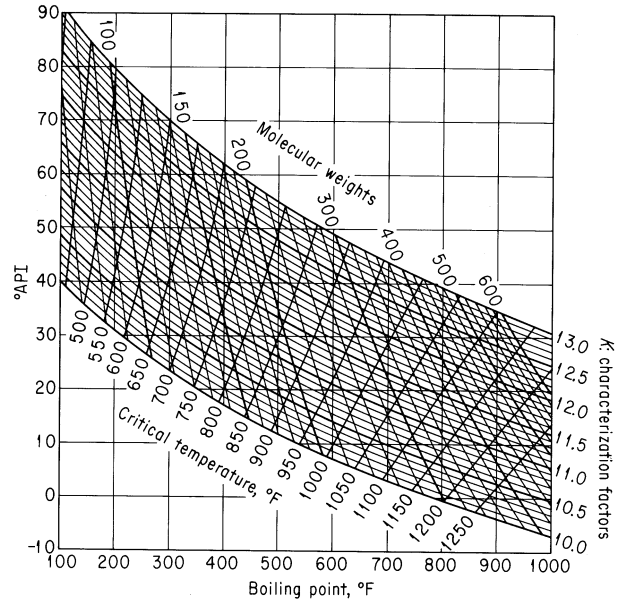


Figure L.4 Properties of petroleum fractions.

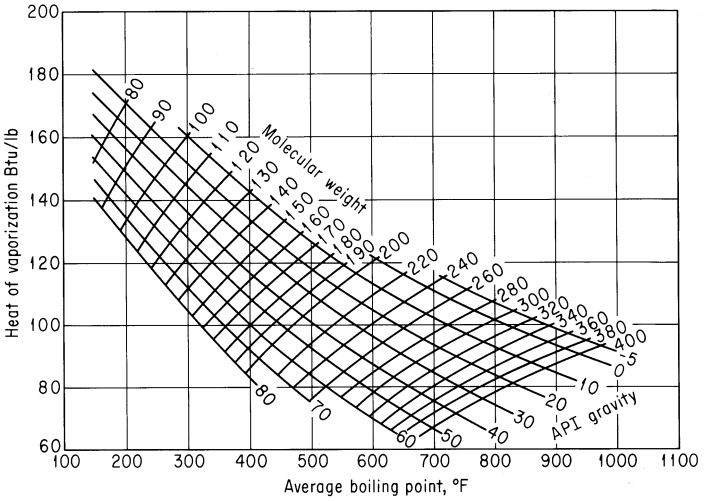


Figure L.5 Heats of vaporization of hydrocarbon and petroleum fractions at 1.0 atmosphere pressure.

Properties of Petroleum Fractions

Heat capacity of hydrogen vapor[1]

$$C_p = (0.0450K - 0.233) + (0.440 + 0.0177K)(10^{-3}t) - 0.1520(10^{-6}t^2)$$

where C_p = specific heat of vapor, Btu/(lb_m)(°F)
t = temperature, °F
K = characterization factor

Heat capacity of hydrocarbon liquids[1]

$$C_p = [(0.355 + 0.128 \times 10^{-2}\text{API}) + (0.503 + 0.117 \times 10^{-2}\text{API})(10^{-3}t)] \times (0.05K + 0.41)$$

where API = gravity degrees API and the other units are the same as for vapor heat capacity.

Specific gravity

$$\text{sp gr} = \frac{141.5}{131.5 + °\text{API}}$$

where sp gr = specific gravity, 60/60°F
°API = degrees API

Pseudo critical temperature [2]

$$t'_c = a_0 + a_1T + a_2T^2 + a_3AT + a_4T^3 + a_5T^2 + a_6A^2T^2$$

where t'_c = pseudo-critical temperature, °R
T = molal average boiling point, °F
A = degrees API
a_i = constants in the correlation (see Table K.3)

Pseudo critical pressure [2]

$$p'_c = b_0 + b_1T + b_2T^2 + b_3AT + b_4T^3 + b_5AT^2 + b_6A^2T + b_7A^2T^2$$

where p'_c = pseudo-critical pressure psia
T = mean average boiling point, °F
A = degrees API
b_i = constants in the correlation

Constants for Cavett Correlations

i	a_i	b_i
0	768.07121	2.8290406
1	(0.17133693) (10)	(0.94120109) (10^{-3})
2	(−0.10834003) (10^{-2})	(−0.30474749) (10^{-5})
3	(−0.89212579) (10^{-2})	(−0.20876110) (10^{-4})
4	(0.38890584) (10^{-6})	(0.15184103) (10^{-8})
5	(0.53094920) (10^{-5})	(0.11047899) (10^{-7})
6	(0.32711600) (10^{-7})	(−0.48271599) (10^{-7})
7		(0.13949619) (10^{-9})

Enthalpy. Calculated as

$$\Delta H = \int_{T_{ref}}^{\bar{T}_1} C_{P\text{liq}}\, dt + \Delta H_{\text{vaporization at } \bar{T}_1} + \int_{\bar{T}_1}^{T} C_{P\text{vap}}\, dt$$

where $\overline{T_1}$ is the mean average boiling point.

Heat of vaporization[1]

$$\Delta H_{vap} = 2.303\ \{(z_g - z_l)R(T_c)[A + 40T_r^2(T_r - b)e^{-20(T_r - b)^2}]\}$$

where H_{vap} = latent heat of vaporization, Btu/lb_m
$z_g - z_l$ = pressure correction (see Fallon and Watson for table of values)
R = universal gas constant
T_c = critical temperature, °R

T_r = reduced temperature
A, b = constants (see Fallon and Watson for ways to calculate values)

or (a somewhat less accurate equation) [3]

$$\Delta H_{vap} = 0.95RT_B\left(\frac{T_B}{T_B - 43}\right)^2\left(\frac{1 - T_r}{1 - T_{rB}}\right)^{0.38}$$

where T_B = molal average boiling point, °R
T_r = reduced temperature
T_{rB} = reduced T_B

Boiling-point relations

(a) $$\bar{t}_v = \sum_{i=1}^{n} X_{vi} t_{bi}$$

where X_{vi} = volume fraction of the ith component of the petroleum fraction
t_{bi} = normal boiling point of the midpoint of the ith volume fraction, °F or °R
n = number of volume fractions in the distillation curve to characterize the petroleum product

(b) $$\bar{t} = (V_1 t_1^{1/3} + V_2 t_2^{1/3} + \cdots + V_n t_n^{1/3})^3$$

where $\bar{t}$ = cubic average boiling point, °F
V_i = volume fraction i of a petroleum product having a normal boiling point of t_i
t_i = temperature, °F

(c) $$\bar{t}_x = x_1 t_1 + x_2 t_2 + \cdots + x_n t_n$$

where $\bar{t}_x$ = molar average boiling point, °F
x_i = the mole fractions of the narrow boiling range with normal boiling points t_i
t_i = temperature, °F

(d)
$$\bar{t}_M = \frac{\bar{t}_x + \bar{t}}{2}$$

where $\bar{t}_M$ is the mean average boiling point, °F.

Sources of Equations

1. J.F. Fallon and K.M. Watson, "Thermal Properties of Hydrocarbons," *Nat. Pet. News (Tech. Sec.),* p. R-372 (June 7, 1944).
2. R.H. Cavett. "Physical Data for Distillation Calculations-Vapor-Liquid Equilibria," *Proc. Am. Pet. Inst. Div. Refining,* v. 42. p. 351 (1962).
3. K.M. Watson, "Thermodynamics of the Liquid State," *Ind. Eng. Chem*. V. 35, p. 398 (1943).