Summary Correlations from "Feedstocks & Products"

1. API gravity (G) & specific gravity (γ_o). Higher density $\rightarrow$ lower °API

$$G = \frac{141.5}{\gamma_o} - 131.5 \implies \gamma_o = \frac{141.5}{131.5 + G}$$

2. Watson characterization factor. 12 – 13 (paraffinic) to 10 (aromatic)

$$K_W = \frac{\sqrt[3]{T_b}}{\gamma_o} \quad T_b \text{ in units of °R}$$

3. Blending rules

Volume blending

$$X_{mix} = \sum v_i X_i = \frac{\sum V_i X_i}{\sum V_i}$$

Mass blending

$$X_{mix} = \sum w_i X_i = \frac{\sum m_i X_i}{\sum m_i} = \frac{\sum (v_i \gamma_{oi}) X_i}{\sum (v_i \gamma_{oi})}$$

4. Blend specific gravities – directly by volume

Volume blending

$$\gamma_{o,mix} = \frac{\sum V_i \gamma_{o,i}}{\sum V_i} = \frac{\sum V_i \gamma_{o,i}}{V} = \sum v_i \gamma_{o,i}$$

Alternate blending

$$\frac{1}{\gamma_{o,mix}} = \sum \frac{w_i}{\gamma_{o,i}} \implies \frac{M}{\gamma_{o,mix}} = \sum \frac{x_i M_i}{\gamma_{o,i}}$$

5. Blend API gravities – blend specific gravities & calculate from blended value

6. O'Donnell method to correct liquid specific gravity for temperature

$$\gamma_T^2 = \gamma_o^2 - 0.000601(T - 60) \quad \text{with } T \text{ in °F}$$

7. Method in Chapter 12.3 of API measurement manual to estimate volumetric shrinkage

$$S = 4.86 \times 10^{-8} C (100 - C)^{0.819} (G_L - G_H)^{2.28} \quad \text{where} \quad C \equiv \frac{V_L}{V_H + V_L} \times 100$$

8. Maxwell-Bonnell equations to correct boiling point for pressure (T in °R & P in mmHg)

$$\log_{10} P^{vap} = \begin{cases} \dfrac{3000.538X - 6.761560}{43X - 0.987672} & \begin{array}{c} X > 0.002184346 \\ \left(P^{vap} < 1.7 \text{ mmHg}\right) \end{array} \\[3mm] \dfrac{2663.129X - 5.994296}{95.76X - 0.972546} & \begin{array}{c} 0.001201343 \leq X \leq 0.002184346 \\ \left(1817 \text{ mmHg} \geq P^{vap} \geq 1.7 \text{ mmHg}\right) \end{array} \\[3mm] \dfrac{2770.085X - 6.412631}{36X - 0.989679} & \begin{array}{c} 0.001201343 > X \\ \left(1817 \text{ mmHg} < P^{vap}\right) \end{array} \end{cases}$$

$$X = \frac{\dfrac{1}{T} - 0.0002867}{748.1\left(\dfrac{1}{T_B'} - 0.0002867\right)} \quad \& \quad T_B' = T_B - 2.5 f\left(K_W - 12\right)\log_{10}\left(\frac{P^{vap}}{760}\right)$$

$$f = \begin{cases} 1 & P^{vap} < 760 \text{ mmHg} \\[3mm] \text{Min}\left(1, \text{Max}\left(\dfrac{T_B - 659.67}{200}, 0\right)\right) & P^{vap} \geq 760 \text{ mmHg} \end{cases}$$

9. Interconvert D86 & TBP Temperatures – 1994 *API Technical Data Book* method

$$T_{TBP,50\%} = 0.87180 \cdot T_{D86,50\%}^{1.0258} \quad (T_{TBP,50\%} \ \& \ T_{D86,50\%} \text{ in °F})$$

$$\Delta T_{TBP} = A\left(\Delta T_{D86}\right)^B \quad (\Delta T_{TBP} \ \& \ \Delta T_{D86} \text{ in °F})$$

Vol%	A	B	Max ΔT [°F]
100% to 90%*	0.11798	1.6606	
90% to 70%	3.0419	0.75497	100
70% to 50%	2.5282	0.82002	150
50% to 30%	3.0305	0.80076	250
30% to 10%	4.9004	0.71644	250
10% to 0%*	7.4012	0.60244	100

10. Interconvert D1160 & TBP Temperatures – temperatures evaluated at 10 mmHg

$$\Delta T_{TBP} = a\left(\Delta T_{D1160}\right) + b\left(\Delta T_{D1160}\right)^2 + c\left(\Delta T_{D1160}\right)^3 + d\left(\Delta T_{D1160}\right)^4$$

Vol% Distilled Range	a	b	c	d
0% - 10%	2.23652561	$-1.39334703 \times 10^{-2}$	3.6358409×10^{-5}	1.433117×10^{-8}
10%-30% 30%-50%	1.35673984	$-5.4126509 \times 10^{-3}$	2.9883895×10^{-5}	-6.007274×10^{-8}

11. Riazi equation to smooth distillation data

$$\frac{T - T_0}{T_0} = \left[\frac{A_T}{B_T} \ln \left(\frac{1}{1-Y} \right) \right]^{\frac{1}{B_T}} \quad \Rightarrow \quad Y = 1 - \exp \left[-\frac{B_T}{A_T} \left(\frac{T - T_0}{T_0} \right)^{B_T} \right]$$

12. Excel functions to interpolate/extrapolate distillation data

Transformed Yield: =NORMSINV(Pct_Yield/100)
From interpolated value: =NORMSDIST(Value) * 100

Functions return errors for the extreme values of 0% & 100%. Typical practice is to use 0.1% & 99.9% instead.

13. Estimate molecular weight of narrow petroleum fraction

$$M = 20.486 T_B^{1.26007} \gamma_o^{4.98308} \exp\left(0.0001165 T_B - 7.78712 \gamma_o + 0.0011582 T_B \gamma_o \right)$$
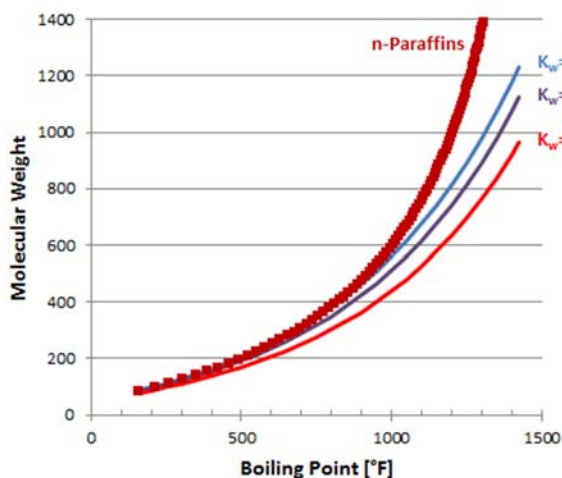
14. Estimate heat of combustion of petroleum fraction (Btu/lb, liquid state @ 60°F)

$$\hat{H}_{LHV} = 16792 + 54.5G - 0.217G^2 - 0.0019G^3$$
$$\hat{H}_{HHV} = 17672 + 66.6G - 0.316G^2 - 0.0014G^3$$

Heating values for the vapor state must take into account the heat of vaporization at the reference temperature.

15. Approximate method to blend individual Watson K factors (by weight)

$$K_{mix} = \sum w_i K_i = \frac{\sum v_i \gamma_{oi} K_i}{\sum v_i \gamma_{oi}}$$

16. 5 definitions for different types of average boiling points:

- Volume average boiling point (VABP) $\quad \left(T_b\right)_v = \sum_{i=1}^{n} v_i T_{b,i}$

-

- Weight average boiling point (WABP) $\quad \left(T_b\right)_w = \sum_{i=1}^{n} w_i T_{b,i}$

-

- Molar average boiling point (MABP) $\quad \left(T_b\right)_M = \sum_{i=1}^{n} x_i T_{b,i}$

-

- Cubic average boiling point (CABP) $\quad \left(T_b\right)_{cubic} = \left(\sum_{i=1}^{n} v_i \sqrt[3]{T_{b,i}} \right)^3$

-

- Mean average boiling point (MeABP) $\quad \left(T_b\right)_{mean} = \frac{\left(T_b\right)_M + \left(T_b\right)_{cubic}}{2}$

17. Estimate average boiling points from ASTM D 86 distillation values (in °F)

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

$$\left(SL\right) = \frac{T_{90} - T_{10}}{90 - 10}$$

$$\left(WABP\right) = \left(VABP\right) + \Delta_1$$

$$\left(MABP\right) = \left(VABP\right) - \Delta_2$$

$$\left(CABP\right) = \left(VABP\right) - \Delta_3$$

$$\left(MeABP\right) = \left(VABP\right) - \Delta_4$$

$$\ln\left(\Delta_1\right) = -3.062123 - 0.01829\left[(VABP) - 32\right]^{0.6667} + 4.45818(SL)^{0.25}$$

$$\ln\left(\Delta_2\right) = -0.563793 - 0.007981\left[(VABP) - 32\right]^{0.6667} + 3.04729(SL)^{0.333}$$

$$\ln\left(\Delta_3\right) = -0.23589 - 0.06906\left[(VABP) - 32\right]^{0.45} + 1.8858(SL)^{0.45}$$

$$\ln\left(\Delta_4\right) = -0.94402 - 0.00865\left[(VABP) - 32\right]^{0.6667} + 2.99791(SL)^{0.333}$$

18. Vapor pressure approximation using acentric factor definition

$$\log_{10}\left(\frac{P_i^{vap}}{P_{ci}}\right) = \frac{7}{3}\left(1 + \omega_i\right)\left(1 - \frac{T_{ci}}{T}\right)$$

19. Volumetric blending with "RVP Blending Indices"

$$\left(RVP\right)_{mix}^{1.25} = \sum v_i \left(RVP\right)_i^{1.25} \quad \Rightarrow \quad \left(RVP\right)_{mix} = \left[\sum v_i \left(RVP\right)_i^{1.25}\right]^{1/1.25}$$

20. Non-linear octane blending equations – Ethyl Corporation models
A is %aromatics (0 to 100) & O is %olefins (0 to 100)

$$R = \bar{R} + a_1\left[\overline{RJ} - \bar{R}\cdot\bar{J}\right] + a_2\left[\overline{\left(O^2\right)} - \bar{O}^2\right] + a_3\left[\overline{\left(A^2\right)} - \bar{A}^2\right]$$

$$M = \bar{M} + b_1\left[\overline{MJ} - \bar{M}\cdot\bar{J}\right] + b_2\left[\overline{\left(O^2\right)} - \bar{O}^2\right] + b_3\left[\frac{\overline{\left(A^2\right)} - \bar{A}^2}{100}\right]^2$$

$$\text{"Road" Octane} = \frac{R+M}{2}$$

$$\text{Sensitivity} = J \equiv R - M$$

$$\text{Volume Average} = \bar{X} \equiv \frac{\sum v_i \cdot X_i}{\sum v_i}$$

	75 Blends	135 Blends
a_1	0.03224	0.03324
a_2	0.00101	0.00085
a_3	0	0
b_1	0.04450	0.04285
b_2	0.00081	0.00066
b_3	-0.00645	-0.00632

21. Driveability Index

$$DI = 1.5\cdot T_{10} + 3\cdot T_{50} + T_{90} + \left(2.4°F\right)\left(EtOH\ vol\%\right)$$

22. Estimate Flash Point
For pure components or well-defined pseudo-components
Method of Lenoir

$$\sum_{i=1}^{N} x_i M_i \gamma_i P_i^{vap} = 1.3 \quad \text{where } \gamma_i \text{ is the liquid activity coefficient}$$

Method of Gmehling & Rasmussen

$$\sum_{i=1}^{N} \frac{x_i \gamma_i P_i^{vap}}{L_i} = 1 \quad \text{with} \quad L_i = L_i(25°C) - 0.182 \left(\frac{T-25}{\Delta H_{c,i}} \right)$$

For petroleum fraction characterized by distillation curve
API Procedure 2B7.1 (using ASTM D86 T10 value)
1987 Version (units of °R)

$$\frac{1}{T_F} = -0.014568 + \frac{2.84947}{T_{10}} + 0.001903 \ln(T_{10})$$

1999 Version (units of °F)

$$T_F = 0.69\, T_{10} - 118.2$$

23. Estimate Cetane index by ASTM D 976 (using ASTM D 86 T50 value in °R)

$$\text{Index} = -420.34 + 0.016G^2 + 0.192G \log(T_{50}) + 65.01 \left[\log(T_{50}) \right]^2 - 0.0001809 T_{50}^2$$

24. Relationship between octane & cetane numbers

$$CN = 60.96 - 0.56(\text{MON})$$
$$CN = 68.54 - 0.61(\text{RON})$$

25. Interrelate SUS viscosity with cSt viscosity (T in °F)

$$\nu_{SUS} = \left[1.0 + 0.000061(T-100) \right] \left[4.6324\nu + \frac{1.0 + 0.03264\nu}{\left(3930.2 + 262.7\nu + 23.97\nu^2 + \nu^3 \right) \times 10^{-5}} \right]$$

26. Adjust viscosity for temperature using ASTM D341 for viscosities above 0.21 cSt

$$\log\big(\log(Z)\big) = A + B \cdot \log(T)$$
$$Z = v + 0.7 + C - D + E - F + G - H$$
$$C = \exp(-1.14883 - 2.65868v)$$
$$D = \exp(-0.0038138 - 12.5645v)$$
$$E = \exp(5.46491 - 37.6289v)$$
$$F = \exp(13.0458 - 74.6851v)$$
$$G = \exp(37.4619 - 192.643v)$$
$$H = \exp(80.4945 - 400.468v)$$
$$v \approx (Z - 0.7) - \exp\left[-0.7487 - 3.295(Z - 0.7) + 0.6119(Z - 0.7)^2 - 0.3193(Z - 0.7)^3\right]$$

27. Blend viscosities
"log-log" method

$$\log\big(\log(v_{mix} + 0.7)\big) = \sum v_i \log\big(\log(v_i + 0.7)\big) = \frac{\sum V_i \log\big(\log(v_i + 0.7)\big)}{\sum V_i}$$

ASTM D 7152 expansion to be valid for lower viscosities

$$Z_i = v_i + 0.7 + \exp\left(-1.47 - 1.84v_i - 0.51v_i^2\right)$$
$$\mathcal{W}_i = \log\big(\log(Z_i)\big)$$
$$\mathcal{W}_B = \sum v_i \mathcal{W}_i$$
$$Z_B = 10^{10^{\mathcal{W}_B}} - 0.7$$
$$v_B = Z_B - \exp\left[-0.7487 - 3.295 Z_B + 0.6119 Z_B^2 - 0.3193 Z_B^3\right]$$

Chevron Method 2

$$\frac{\ln(v_{mix})}{\ln(1000\,v_{mix})} = \sum v_i \frac{\ln(v_i)}{\ln(1000\,v_i)} \equiv \mathcal{W} \;\Rightarrow\; \ln(v_{mix}) = \ln(1000) \cdot \frac{\mathcal{W}}{1 - \mathcal{W}}$$

28. Relationship of Ramsbottom to Conradson Carbon

$$RCR = \exp\left[-0.236 + 0.883\ln(CCR) + 0.0657\ln^2(CCR)\right]$$

Additional Useful Correlations

29. Critical temperature & pressure for a narrow boiling fraction. Lee & Kesler method also published as Procedures 4D3.1 & 4D4.1 (4th ed., 1987). Temperatures are in °R & pressure is in psia.

$$T_c = 10.6443 \left[\exp\left(-5.1747 \cdot 10^{-4}\, T_b - 0.5444\, \gamma_o + 3.5995 \cdot 10^{-4}\, T_b \gamma_o \right) \right] T_b^{0.81067} \gamma_o^{0.53091}$$

$$P_c = 6.162 \cdot 10^6 \left[\exp\left(-4.725 \cdot 10^{-3}\, T_b - 4.8014\, \gamma_o + 3.1939 \cdot 10^{-3}\, T_b \gamma_o \right) \right] T_b^{-0.4844} \gamma_o^{4.0846}$$
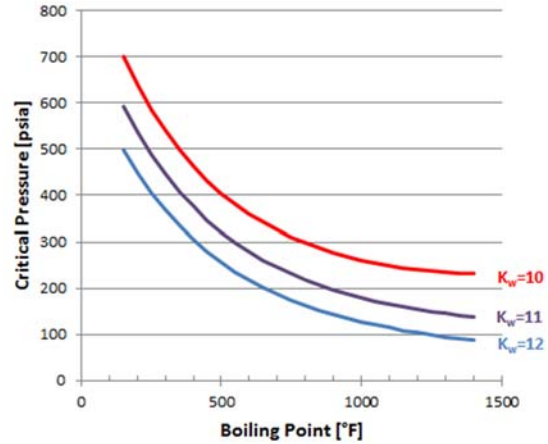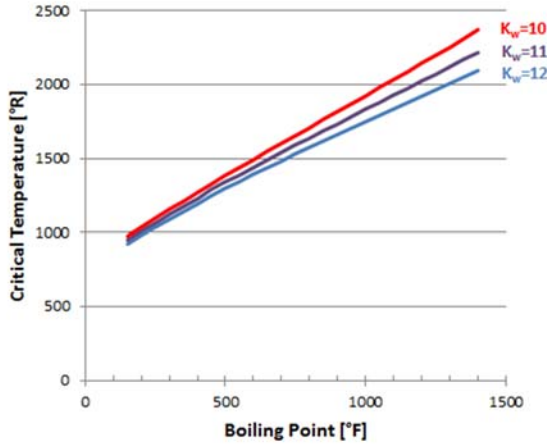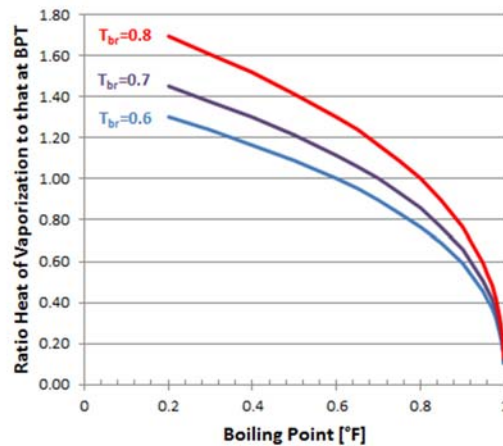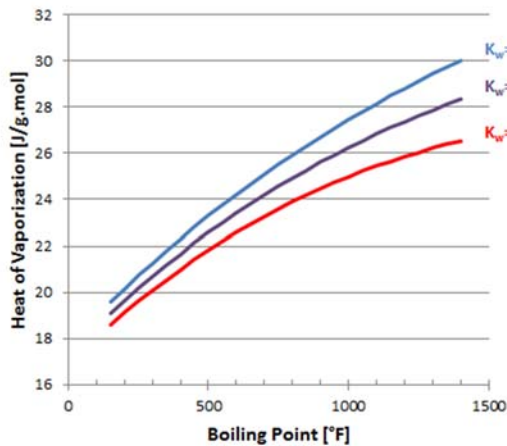

30. Heat of Vaporization. Kistiakowsky equation (*The Properties Of Gases And Liquids*, 3rd ed., p 215):

$$\Delta H_{vb} = \frac{T_b}{T_c}\left(8.75 + R \log(T_b)\right)$$

where temperatures are in units of K & the heat of vaporization are in units of J/g.mol. The effect of temperature can be estimated using the Watson method (*The Properties Of Gases And Liquids*, 4th ed., p 228):

$$\Delta H_{v2} = \Delta H_{v1} \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38}$$

31. Prediction of kinematic viscosities @ 100 & 210°F. Correlation by Abbott included in old editions the API *Technical Data Book*:

$$\log\left(\nu_{100°F}\right) = 4.39371 - 1.9473\,K_W + 0.12769\,K_W^2$$
$$+ 3.2629\cdot10^{-4}\,G^2 - 1.18246\cdot10^{-2}\,K_W G$$
$$+ \frac{0.171617\,K_W^2 + 10.9943G + 9.50663\cdot10^{-2}\,G^2 - 0.860218\,K_W G}{G + 50.3642 - 4.78231\,K_W}$$

$$\log\left(\nu_{210°F}\right) = -0.463634 - 0.166532G + 5.13447\cdot10^{-4}\,G^2 - 8.48995\cdot10^{-3}\,K_W G$$
$$+ \frac{8.0325\cdot10^{-2}\,K_W + 1.24899G + 0.19768\,G^2}{G + 26.786 - 2.26296\,K_W}$$

where the units on kinematic viscosity is cSt. However, <u>*this technique does not extrapolate well & is only valid for boiling points 600- 700°F or so.*</u>

Once these values are known then the temperature dependency can be determined from:

$$\log\log\left(\nu + 0.7 + c_T\right) = A_1 + B_1 \log\left(T\right)$$
$$c_T = \begin{cases} 0.085\left(\nu_T - 1.5\right)^2 & \text{if } \nu_T < 1.5 \text{ cSt} \\ 0 & \text{if } \nu_T \geq 1.5 \text{ cSt} \end{cases}$$

The latest API Technical Data Book (10th ed.) has a better Procedure 11.A4.2:

$$\log_{10}\left(\nu_{ref}\right) = -1.35579 + 8.16059\cdot10^{-4}\,T_b + 8.38505\cdot10^{-7}\,T_b^2$$
$$\log_{10}\left(\nu_{cor}\right) = A_1 + A_2\,K_W$$
$$A_1 = 34.9310 - 8.84387\cdot10^{-2}\,T_b + 6.73513\cdot10^{-5}\,T_b^2 - 1.01394\cdot10^{-8}\,T_b^3$$
$$A_2 = -2.92649 + 6.98405\cdot10^{-3}\,T_b - 5.09947\cdot10^{-6}\,T_b^2 + 7.49378\cdot10^{-10}\,T_b^2$$
$$\nu_{100°F} = \nu_{ref} + \nu_{cor}$$
$$\log_{10}\left(\nu_{210°F}\right) = -1.92353 + 2.41071\cdot10^{-4}\,T_b + 0.511300\log_{10}\left(T_b\,\nu_{100°F}\right)$$

where the boiling point is in units of °R. The recommended equation to modify these viscosities with respect to temperature is:

$$\frac{\log_{10}\left(\nu_T\right) + 0.86960}{\log_{10}\left(\nu_0\right) + 0.86960} = \left(\frac{T_o}{T}\right)^S \quad \text{where } S = 0.28008\log_{10}\left(\nu_0\right) + 1.8616.$$

This procedure gives viscosity curves those shown below.
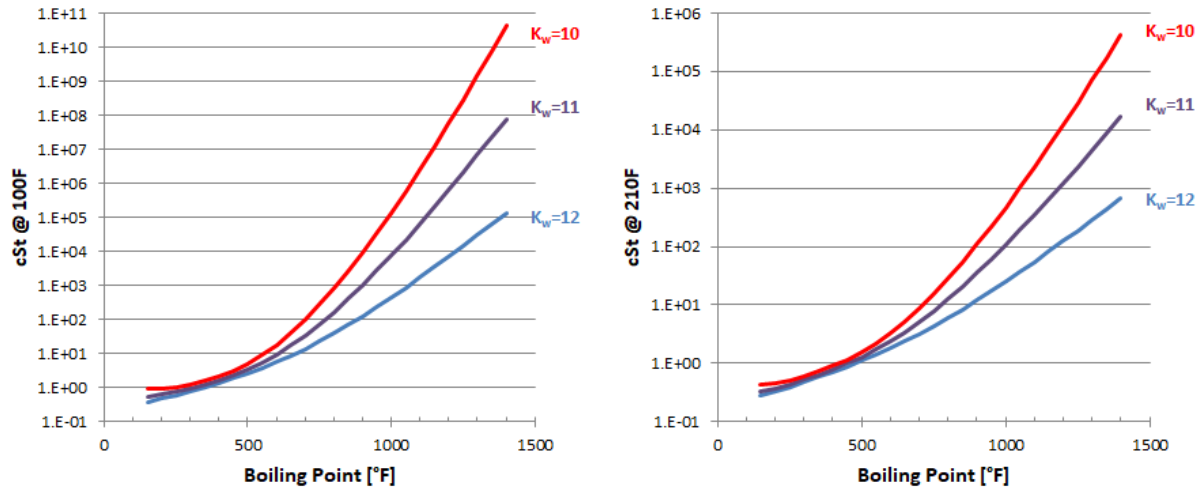
32. Freezing point, pour point, & cloud point. If kinematic viscosities are not known then Procedures 2C5.1, 2C2, & 2C6.1, respectively (10th ed. API Technical Data Book) can be used:

$$T_{FPT,°R} = -2390.42 + 1826\gamma_o + 122.49 K_W - 0.135(\text{MeABP}).$$

$$T_{pour,°R} = 3.85 \cdot 10^{-8} (\text{MeABP})^{5.49} \, 10^{-\left(0.712(\text{MeABP})^{0.315} + 0.133\gamma_o\right)} + 1.4.$$

$$\log_{10}\left(T_{CPT,°R}\right) = -7.41 + 5.49 \log_{10}(\text{MeABP}) - 0.712(\text{MeABP})^{0.315} - 0.133\gamma_o.$$

If kinematic viscosity is known:

$$T_{pour,°R} = 753 + 136\left[1 - e^{-0.15\nu_{100°F}}\right] - 572\gamma_o + 0.0512\nu_{100°F} + 0.139(\text{MeABP}).$$

If cloud point is known then (Procedure 2C8.2):

$$T_{pour,°R} = 0.9895 \, T_{CPT,°R} + 1.4.$$

The curves are shown below. Note:
- You would not expect the pour & cloud points to max out with increasing boiling point temperature. The curves imply that the correlations are probably only good to about 700 – 800°F.
- The freezing point expression is probably better at higher boiling points but not as good at lower boiling points where the pour point values are at colder temperatures than the freezing points .