Select the Right Hydrocarbon Molecular Weight Correlation

By
Donald F. Schneider, P.E.
Chemical Engineer

Stratus Engineering, Inc.
PMB 339
2951 Marina Bay Drive #130
League City, Texas 77573
(281) 335-7138
Fax: (281) 335-8116
E-mail: dfsstratus@aol.com

Introduction

Computer models of systems processing wide boiling range hydrocarbon streams typically employ pseudocomponent representations of distillation fractions. In this method, commonly known bulk properties such as boiling point and gravity distributions are used in correlations to derive physical properties for petroleum fractions (pseudocomponents). These derived characteristics represent the properties of a mixture that is not, or cannot be characterized by its individual chemical species. Even mixtures that can be precisely defined by specific compounds are often represented as a collection of pseudocomponents. Where such an approximation does not materially affect the results obtained, this simplification can greatly reduce the calculational magnitude of a problem.

Because experimental molecular weight determinations of hydrocarbon fractions are difficult, molecular weight is one physical characteristic that is often calculated for pseudocomponents using a correlation. Molecular weight is an important factor in analyzing the performance of hydrocarbon processing systems. It directly impacts chemical equilibrium, reaction kinetics and vapor density calculations. Accurately describing the molecular weight of hydrocarbon fractions is important to proper analysis and design of chemical processing systems.

A variety of mathematical relationships have been developed to predict pseudocomponent molecular weights. These correlations are usually based on boiling point and gravity data, but have also been based on viscosity and UOP K. The numerous equations produce a wide range of molecular weight estimates for heavy hydrocarbon fractions. The continuing growth in the importance of heavy oil processing increases the need for understanding molecular weight prediction methods and their impact on unit operation, process simulation, and design.

Molecular Weight

The importance of molecular weight to a chemical system is observed whenever the kind of molecule present, not just the amount that is present, is critical. Phase equilibrium, reaction kinetics, and vapor densities are three areas where component molecular weight plays an important role.

Thermodynamic phase equilibrium is one of the most important areas where this comes into play. Distillation, absorption, and extraction are some of the processes whose performance is based on phase equilibrium.

Distillation depends on vapor-liquid equilibrium. For a vapor to be in equilibrium with a liquid, the fugacity of each phase must be equal. If the vapor is assumed to be an ideal gas, and the liquid is assumed to be an ideal solution, Raoult's Law (equation 1) results describing vapor-liquid equilibrium. From this simplified expression, the importance of molecular weight can be seen. If the molecular weight of a component is improperly defined, the mole fractions of all components are altered leading to inaccurate equilibrium calculations.

$$y_i P = x_i P^{sat}_i \qquad (1)$$

P = Total system pressure
y_i = Mole fraction of component i in the vapor
x_i = Mole fraction of component i in the liquid
P^{sat}_i = Vapor pressure of component i at the system temperature

When distilling 100,000 lbs/hr of material, it makes a great deal of difference if you have 1,390 moles/hr of 72 average molecular weight material, or 250 moles/hr of 400 average molecular weight material. The impact is felt because equilibrium is established at defined conditions by the type and number of molecules present rather than the mass of material available.

In chemical reactions, the number of molecules present of each type of compound affects every aspect of the reaction. In heavy hydrocarbon processing, this is important to FCC Units, Hydrotreaters, and Cokers. Reactions occur by the type and number of molecules present, not by the weight of reactive mass available. Equation 2 describes a typical hydrotreating reaction. If the molecular weight of a reactant is improperly defined, the required amount of other reactants, in this case hydrogen, is altered. In hydrotreating heavy stocks, this could lead to incomplete conversion or coking.

$$C_{12}H_{24} + H_2 \rightarrow C_{12}H_{26} \qquad (2)$$

Hydrocarbon vapor densities are directly dependent on molecular weights. This is less true of liquids where, by definition, there are strong intermolecular interactions. The simplistic ideal gas expression of Equation 3 has been rearranged in Equation 4 to allow easier identification of the influence of molecular weight on vapor density. If the molecular weight of a species is improperly defined, calculated vapor densities are altered leading to inaccurate vapor dependent calculations such as flow hydraulics and fractionation equipment (e.g. trays) loadings.

$$P V = n R T \tag{3}$$

$$\rho = m / V = P (MW) / R T \tag{4}$$

P = Pressure
V = Volume
n = Number of moles
R = Gas constant
T = Temperature
m = Mass
ρ = Density
MW = Molecular weight

Correlations

Because of the difficulty and cost associated with laboratory molecular weight determinations, heavy hydrocarbon molecular weight estimations are typically made based on known gravity (density) and boiling point data. This information is more easily supplied by laboratory analyses. Curves defining the boiling point versus gravity relationship are produced using standard test methods. These data are then employed in molecular weight prediction. Viscosity versus boiling point data, similarly available from laboratory analyses, may also be used in molecular weight estimation.

Table 1 details ten common methods for estimating the molecular weight of petroleum fractions using known physical properties. Though a theoretical justification for the developed equation is advanced by some of the sources, the wide formula variety is evidence of their empirical nature. Several of the methods are graphical, meaning that more than one equation must be rendered to fit the interpretive graphs. A great number of exponential and power functions are seen. The API 1980, API 1980 Extended, and Riazi-Daubert 1980 methods are very similar in form. Each of the equations may be named differently in other publications.

Specific Gravity @ 60 °F and component boiling point are the two most common parameters used by the correlations to make predictions. API gravity is synonymous with Specific Gravity @ 60 °F. Viscosity is a parameter in two of the presented equations. Given the non-Newtonian nature of heavy hydrocarbons, and the difficulty in ascertaining their viscosities, methods employing viscosity parameters probably are not suited to predicting heavy hydrocarbon molecular weights.

A summary of each of the Table 1 methods follows.

API 1964. The basis for this familiar nomograph was first published by Winn (1957). For many years carried as Figure 2B2.1 in the API Technical Data Book, it is currently used as Figure 2B6.1 in the API Technical Data Book. This nomograph depicts the interrelationships between many hydrocarbon physical properties.

API 1980. This equation has been replaced by the API 1980 extended equation which is considered to provide more accurate predictions. Both this equation and the API 1980 Extended method are based on the work of M. R. Riazi.

API 1980 Extended. Currently Procedure 2B2.1 in the API Technical Data Book. Both this equation and the API 1980 method are based on the work of M. R. Riazi.

ASTM D2502 & API Figure 2B2.2 (1980). These methods determine the material's molecular weight using its viscosity at 100 °F and 210 °F. These procedures are based on the work of Hirschler (1946). While carried for years as Figure 2B2.2 in the API Technical Data Book, the current API Technical Data Book Figure 2B2.2 is a graphical reformulation of the API 1980 Extended method. The Riazi-Daubert 1987 correlation has been inserted into the current API Technical Data Book as Procedure 2B2.3 for use in molecular weight determinations when viscosities are the basis.

Hariu-Sage. The method of Hariu and Sage (1969) is an equation based description of the Winn nomograph with estimated values for high boiling point fractions added. Predictions by this method appear to track the API 1964 nomograph up to a NBP of approximately 950 °F, after which the Hariu-Sage estimates are slightly higher.

Kessler-Lee. The work of Kessler and Lee (1976) developed a molecular weight correlation based on regression analysis of hydrocarbon data with molecular weights greater than 60 and less than 650. This method appears to track values predicted by the API 1964 method up to a NBP of approximately 1000 °F after which Kessler-Lee estimates are slightly lower.

Maxwell. Maxwell's (1950) graphical representations of an empirical formula.

Riazi-Daubert 1980. The method of Riazi and Daubert (1980) is the simplest of those examined. The development of this equation assumed its characteristic form (the multiplication of two power functions) and then calculated constants by fitting data. This equation also appears to predict smaller molecular weights for heavy hydrocarbons than other procedures. It is very similar to the API 1980 equation (also based on work by Riazi) except that the exponential factors are omitted.

Riazi-Daubert 1987. The method of Riazi and Daubert (1987) differs greatly from their 1980 effort in that the material's viscosity has replaced boiling point as a variable in the equation. Dependence on specific gravity is common to both equations. This method is the current Procedure 2B2.3 in the API Technical Data Book. The Riazi-Daubert 1987 procedure adds a specific gravity term to the Hirschler (1946) viscosity-based estimation methods of ASTM D2502 and API Figure 2B2.2 (1980) and utilizes a large data base to regress equation constants.

Twu. The Twu (1984) method is the most complex examined here. It suggests a theoretical approach where molecular weights are predicted based on their deviation from the molecular weight of an *n*-Alkane at the same boiling point. Experimental data were regressed to determine the constants. Note that the set of equations proposed is not explicit in the required corresponding *n-Alkane* molecular weight (MW°) leading to a trial-and-error solution. Explicit equations for MW° are easily generated from *n-Alkane* data simplifying calculations by eliminating the trial-and-error solution.

The Twu MW° equation is implicit in molecular weight. An iterative process is required to obtain MW°. During this work the author developed an Alternative MW° equation that is explicit in molecular weight:

$$MW^\circ = 3.3955E\text{-}15T_{bF}^{6} -1.2416E\text{-}11T_{bF}^{5} +1.8256E\text{-}08T_{bF}^{4} -1.3234E\text{-}05T_{bF}^{3} +0.0052285T_{bF}^{2} -0.741692T_{bF} +116.19.$$

Valid for *n*-Alkane molecular weights from 86 to 1400. This correlation gives values within 2% of the Twu correlation through a molecular weight of 1100, and within 5% of the Twu correlation above that. Even simpler relations may be found with similar or better accuracy.

A correlation used for any purpose should not be extended beyond the limits for which it is valid without caution. Knowing this, there are still occasions when an extrapolation beyond these limits is made because no other tool is available. Or, in the case of a process modeling package, the molecular weight assumptions that are being made may not be obvious to the user. Software may make an extrapolation automatically without a warning.

A number of simulation vendors have developed their own molecular weight correlations. These are often modifications of published methods. An investigation into what method is employed and the values it is producing is recommended when using simulation packages or other estimating software.

Prediction Comparison

All of the Table 1 molecular weight correlations have been compared to experimental data by their authors with varying yet similar conclusions; all appear very accurate. To better assess the relationship of the predictions produced by so many different methods taking so many different forms, two crudes were selected for which most of the presented equations were used to generate molecular weight estimates. Standard assay gravity and boiling point data along with viscosity data (where available) were used. Typically heavy ends viscosity data were limited. Therefore the Riazi-Daubert 1987 method was not plotted, and few points for the ASTM D2502 method were plotted. Alaska North Slope Crude °API 30.0, and Venezuela Bachaquero Crude °API 13.0 were chosen for study.

Figures 1 and 1A illustrate the molecular weight predictions for the North Slope Crude. Figures 2 and 2A illustrate the molecular weight predictions for the Bachaquero Crude. On both plots, *n*-Alkane boiling point and molecular weight data are plotted for reference. Note that at the highest NBP's and molecular weights several of the correlations are being extrapolated beyond their recommended range.

Reviewing the figures, all the correlations give similar estimates up through a NBP of approximately 600 °F. Beyond this, the correlation results diverge until at the end points the highest and lowest predictions differ by large amounts. The curves illustrate the typically high molecular weight estimates generated by the API 1980 and API 1980 Extended methods. Below these is a large middle group of correlation results. While the lowest estimates are predicted by Riazi-Daubert 1980, it is substantially beyond its recommended upper limit of 850 °F at high NBP's. Clearly there is a choice of correlations to be made. The importance of these variances must be seen in the predicted physical properties of the material in order to judge their significance.

Molecular Weight Prediction Effects

The impact of molecular weight estimates can be seen in the thermodynamic calculations associated with process design, process trouble shooting, and process operations. Figure 3 illustrates the computer model employed to examine the effects of molecular weight prediction differences. A Crude Unit Atmospheric and Vacuum tower simulation maintaining constant side-draw rates, constant overflash, and constant column bottoms 5% TBP point was used. Vapor-Liquid phase equilibrium and vapor density effects are observed in this model. As has been discussed, molecular weight predictions affect calculations associated with many systems and processes. The Crude Unit simulation is used here because the effects are clearly illustrated.

Table 2 details Bachaquero Crude simulation results for analyses performed with four different molecular weight correlations spanning the range of estimates at high NBP. The Riazi-Daubert 1980 vs API 1980 comparison is the largest molecular weight gap while Hariu-Sage vs API 1980 comparison is a smaller gap. Note the large absolute, and in some cases percentage, differences in the thermodynamic calculation results. The molecular weight correlation selected impacts engineering calculations to a significant degree. Most important in this case are the vapor-liquid equilibrium effects evidenced by the column flash zone temperatures and heater duties listed in Table 2. Flash zone temperature variations of 10 to 30 °F, and heater duty differences of 5 to 10 percent are large enough to make process design and trouble-shooting inaccurate.

One way to assess which molecular weight correlation is appropriate for a system is to match thermodynamic calculations, such as process simulator results, to existing operating data. In this way, an existing process can be modeled accurately and the resulting physical property basis can be used for other work. Based on comparisons of this kind, the higher molecular weight predictions appear to result in more accurate thermodynamic representations for these two Crudes. The API 1980 and API 1980 Extended molecular weights are perhaps a little high for these Crudes, while the Hariu-Sage and Maxwell molecular weights are a little low. Understanding the impact of the selected molecular weight method allows a knowledgeable assessment of the conservatism of calculations.

Summary

Molecular weight is a key physical property in phase equilibria, reaction kinetics, and vapor density calculations. Molecular weight prediction of wide boiling range hydrocarbons is necessitated by the difficulty and expense of obtaining experimental molecular weight data. Many estimating methods have been proposed for this purpose. They differ greatly in approach and form. Care should be taken to examine which approach provides the most accurate system representation.

References

"*Molecular Weight and Watson Characterization Factor of Petroleum Fractions*," API Technical Data Book Figure 2B2.1 (1964).

"*Molecular Weight of Petroleum Fractions*," API Technical Data Book Procedure 2B2.1 (1980).

"*Molecular Weight of Petroleum Fractions*," API Technical Data Book Procedure 2B2.1 (1982).

"*Molecular Weight of Heavy Petroleum Fractions*," API Technical Data Book Figure 2B2.2 (1980).

"*Molecular Weight of Heavy Petroleum Fractions*," API Technical Data Book Figure 2B2.3 (1982).

"*Standard Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils from Viscosity Measurements*," ASTM D 2502,

Brule, M. R., et. al.,"Multiparameter Corresponding-States Correlation of Coal-Fluid Thermodynamic Properties," AIChE Journal, Vol. 28, No. 4 (1982), pp. 616-625

Chung, K. H., et. al., "Supercritical Fluid Extraction Reveals Resid Properties," Oil & Gas Journal, Jan. 20, 1997, pp. 66-69.

"*CRC Handbook of Chemistry & Physics*," CRC Press, 61st Edition.

Hariu, O. H., Sage, R. C., "*Crude Split Figured by Computer*," Hydrocarbon Processing, April, 1969, pp. 143-148.

Hirschler, A. E., "*Molecular Weights of Viscous Hydrocarbon Oils: Correlation of Density with Viscosities*," Journal of the Institute of Petroleum, Vol. 32 1946, pp. 133-161.

Kesler, M. G., Lee, B. I., "*Improve Prediction of Enthalpy of Fractions*," Hydrocarbon Processing, March, 1976, pp. 153, 158.

Mathur, B. C., et. al., "*New, Simple Correlation Predicts Critical Temperature*," Chemical Engineering, March 24, 1969, pp. 182, 184.

Maxwell, J. B., *Data Book on Hydrocarbons - Application to Process Engineering*, Van Nostrand, Princeton, New Jersey, 1950, pp. 19-23.

Riazi, M. R., Daubert, T. E., "*Simplify Property Predictions*," Hydrocarbon Processing, March, 1980, pp. 115, 116.

Riazi, M. R., Daubert, T. E., "*Molecular Weight of Heavy-Oil Fractions from Viscosity*," Oil & Gas Journal, Dec. 28, 1987, pp.110-112 (Equation error corrected O&GJ, Feb. 15, 1988, p. 40)

Twu, C. H., "*Prediction of Thermodynamic Properties of Normal Paraffins Using Only Normal Boiling Point*," Fluid Phase Equilibria, 11 (1983), pp. 65-81.

Twu, C. H., "*Boiling Point as a Third Parameter for Use in a Generalized Equation of State*," Fluid Phase Equilibria, 13 (1983), pp. 189-194.

Twu, C. H., "*An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal Tar Liquids*," Fluid Phase Equilibria, 16 (1984), pp. 137-150.

Winn, F. W., "*Physical Properties by Nomogram*," Petroleum Refiner, Vol. 36 No. 2 (1957), pp. 157-159.

Table 1 - Molecular Weight Correlation Summary

Source	Equation	Function of Specific Gravity	UOP K	NBP	MeABP	Viscosity	Comments & Limits
API 1964 (Winn)	Nomograph	✓			✓		Limit: $80 \le MW \le 600$ (Current API Figure 2B6.1)
API 1980	$MW=204.38\ e^{(0.00218\ Tm)}e^{(-3.07\ S)}T_m^{0.118}S^{1.88}$	✓			✓		Limit: 97 °F $\le$ NBP $\le$ 1500 °F
API 1980 Extended	$MW = 20.486\ e^{(1.165\text{ E-04 }Tm\ -\ 7.78712\ S\ +\ 1.1582\text{ E-03 }Tm\ S)}T_m^{1.26007}S^{4.98308}$	✓			✓		Limit: 90 °F $\le$ NBP $\le$ 1500 °F (Current API Procedure 2B2.1)
ASTM D2502 and API Figure 2B2.2(1980)	Graphical					✓	Limit: $200 \le MW \le 700$ (Hirschler)
Hariu-Sage	$\log 10(MW) = \sum_{j=0}^{2}\sum_{i=0}^{2}(a_{ij}\ T_{bF}^{\ i}\ K^{j})$ $a_{00} = 0.6670202$ $a_{10} = 0.004583705$ $a_{20} = -2.698693\text{E-}06$ $a_{01} = 0.1552531$ $a_{11} = -5.755585\text{E-}04$ $a_{21} = 3.875950\text{E-}07$ $a_{02} = -0.005378496$ $a_{12} = 2.500584\text{E-}05$ $a_{22} = -1.566228\text{E-}08$		✓	✓			Extrapolated surface fit of Winn Nomograph with additional data Limit: 80 °F $\le$ NBP $\le$ 1500 °F
Kesler-Lee	$MW = -12{,}272.6 + 9{,}486.4\ S + (4.6523-3.3287S)\ T_b + (1 - 0.77084\ S - 0.02058\ S^2)\ (1.3437 - 720.79 / T_b)\ 10^7 / T_b + (1-0.80882\ S + 0.02226\ S^2)\ (1.8828 - 181.98 / T_b)\ 10^{12} / T_b^3$	✓		✓			Regression analysis on hydrocarbons with $60 \le MW \le 650$
Maxwell	Graphical	✓			✓		
Riazi-Daubert 1980	$MW = 4.5673\text{E-}05\ T_b^{2.1962}\ S^{-1.0164}$	✓		✓			Limit: 100 °F $\le$ NBP $\le$ 850 °F
Riazi-Daubert 1987	$MW=233.56\ S^{-0.6665}\ \nu_{100}^{(-1.2435\ +\ 1.1228\ S)}\ \nu_{210}^{(3.4758\ -\ 3.038\ S)}$	✓				✓	$200 \le MW \le 800$ (Current API Procedure 2B2.3)
Twu	$\ln(MW) = \ln(MW^\circ)\ [(1+2fm)/(1-2fm)]^2$ $fm = \Delta SG_m[\ \lvert x\rvert + (-0.0175691 + 0.193168 / T_b^{0.5})\ \Delta SG_m]$ $\lvert x\rvert = \lvert 0.0123420 - 0.328086 / T_b^{0.5}\rvert$ $\Delta SG_m = e^{[5\ (S^\circ\ -\ S)]} - 1$ $T_c^\circ = T_b/(0.533272+0.191017\text{E-}03T_b + 0.779681\text{E-}07\ T_b^2-0.284376\text{E-}10\ T_b^3 + 0.959468\text{E }28 / T_b^{13})$ $S^\circ = 0.843593 - 0.128624\ \alpha - 3.36159\ \alpha^3 - 13{,}749.5\ \alpha^{12}$ $\alpha = 1 - T_b / T_c^\circ$ $T_b = e^{(5.71419\ +\ 2.71579\ \theta\ -\ 0.286590\ \theta\ *\ \theta\ -\ 39.8544\ /\ \theta\ -\ 0.122488\ /\ \theta\ /\ \theta)} - 24.7522\ \theta + 35.3155\ \theta^2$ $\theta = \ln(MW^\circ)$	✓		✓			Perturbation Expansion from *n*-Alkanes

Figure 1 - North Slope Crude Molecular Weight Correlation Comparison

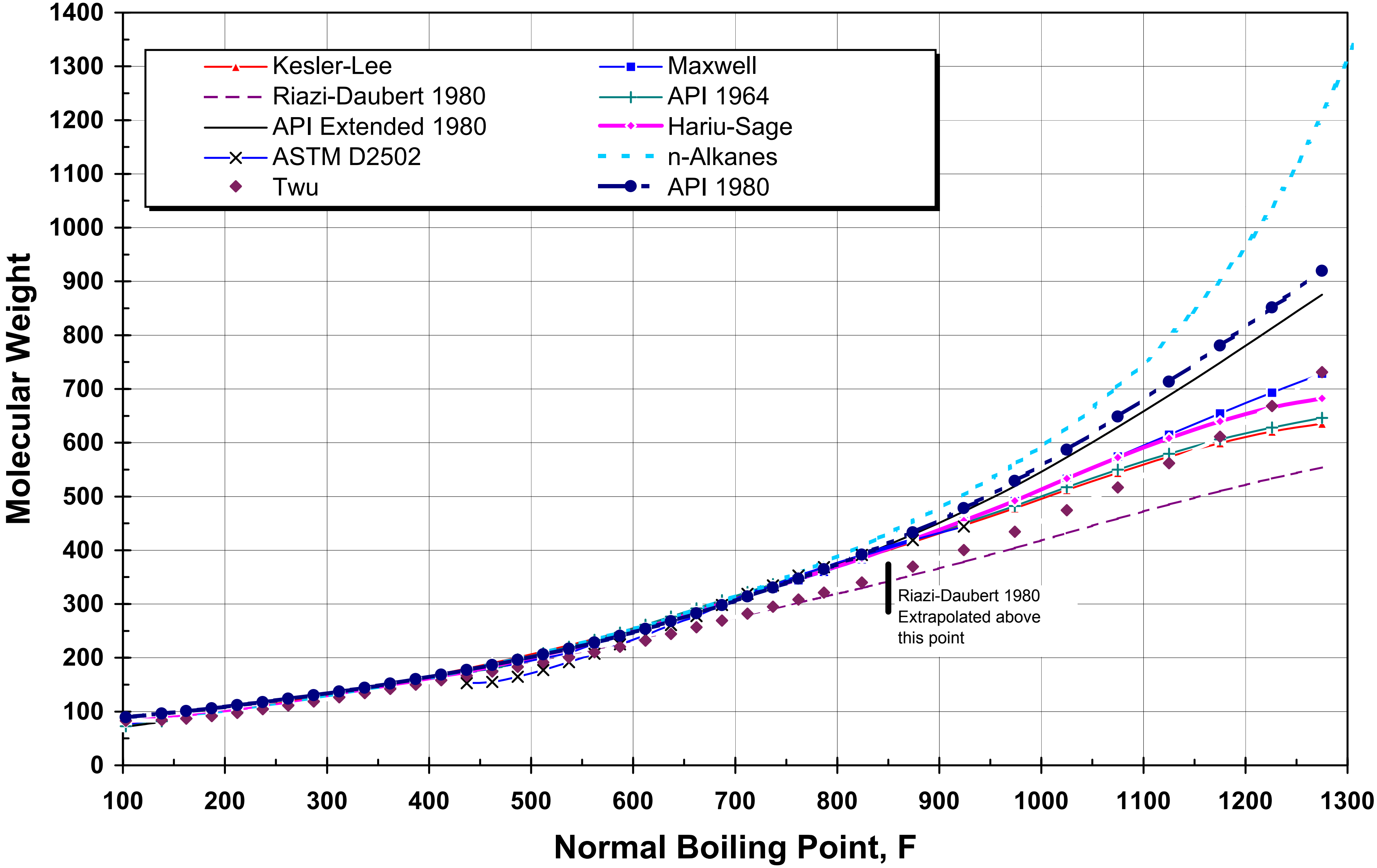
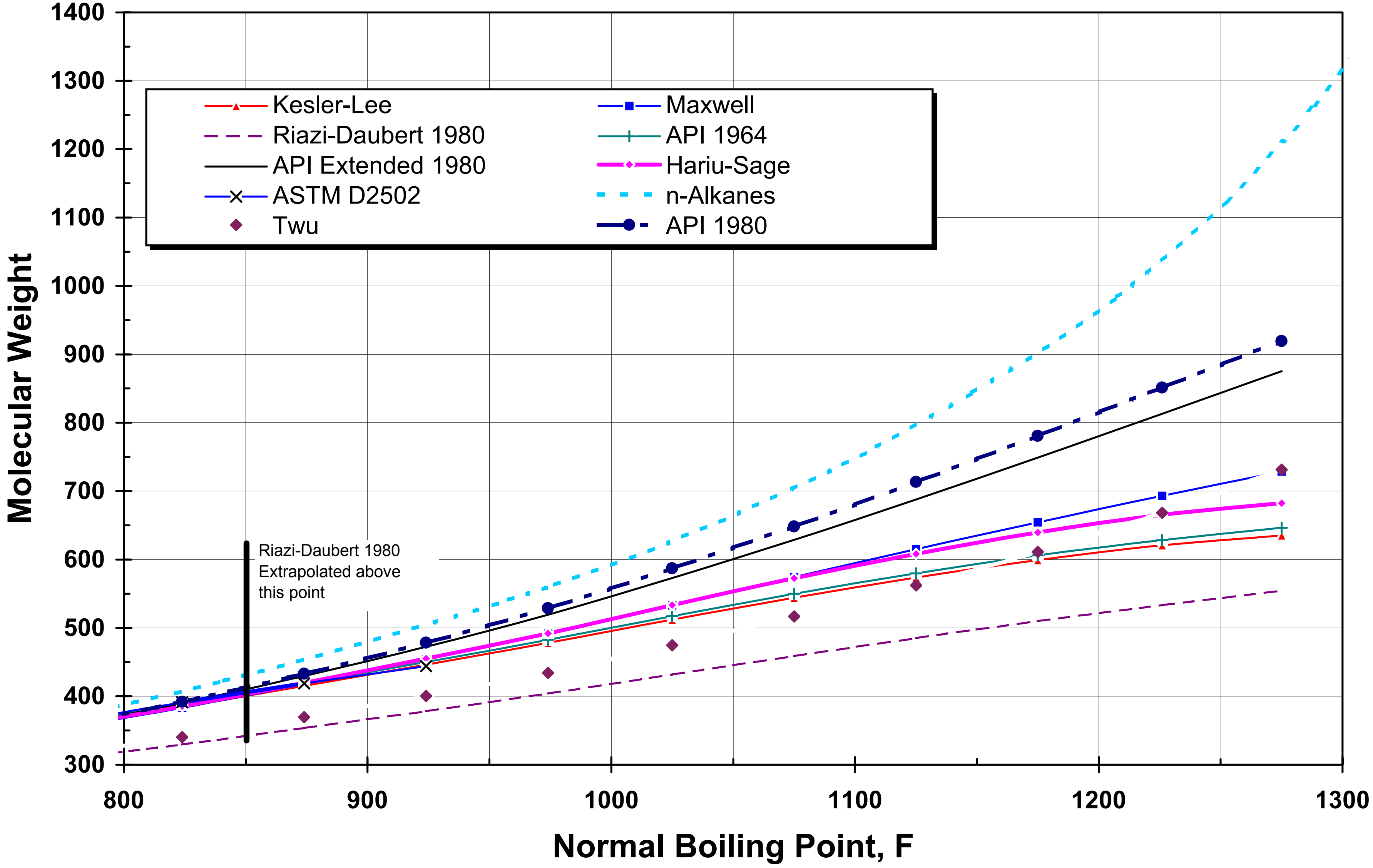


Figure 1A - North Slope Crude Molecular Weight Correlation Comparison - Expanded



Riazi-Daubert 1980 Extrapolated above this point

Figure 2 - Bachaquero Crude Molecular Weight Correlation Comparison

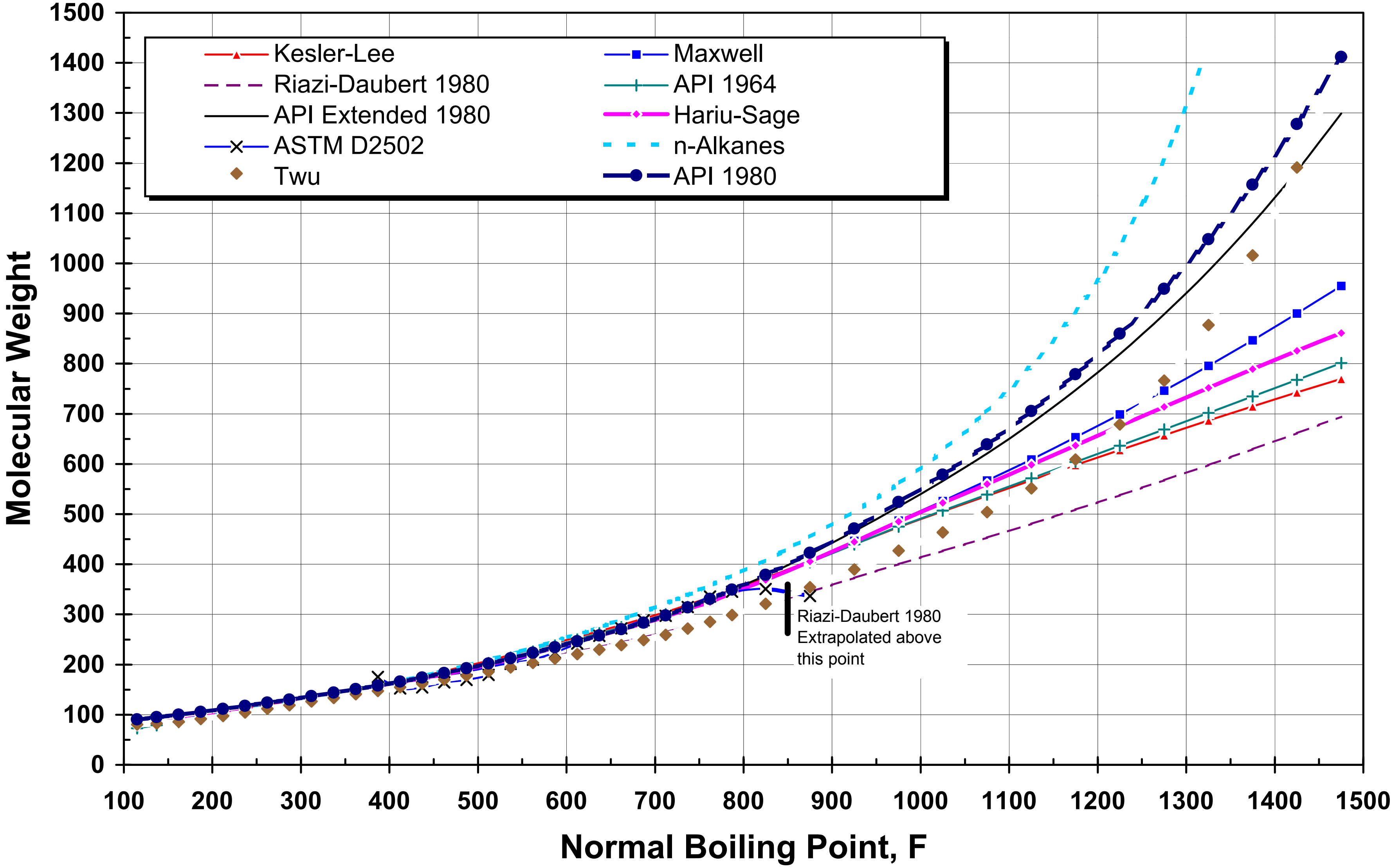


Figure 2A - Bachaquero Crude Molecular Weight Correlation Comparison - Exploded

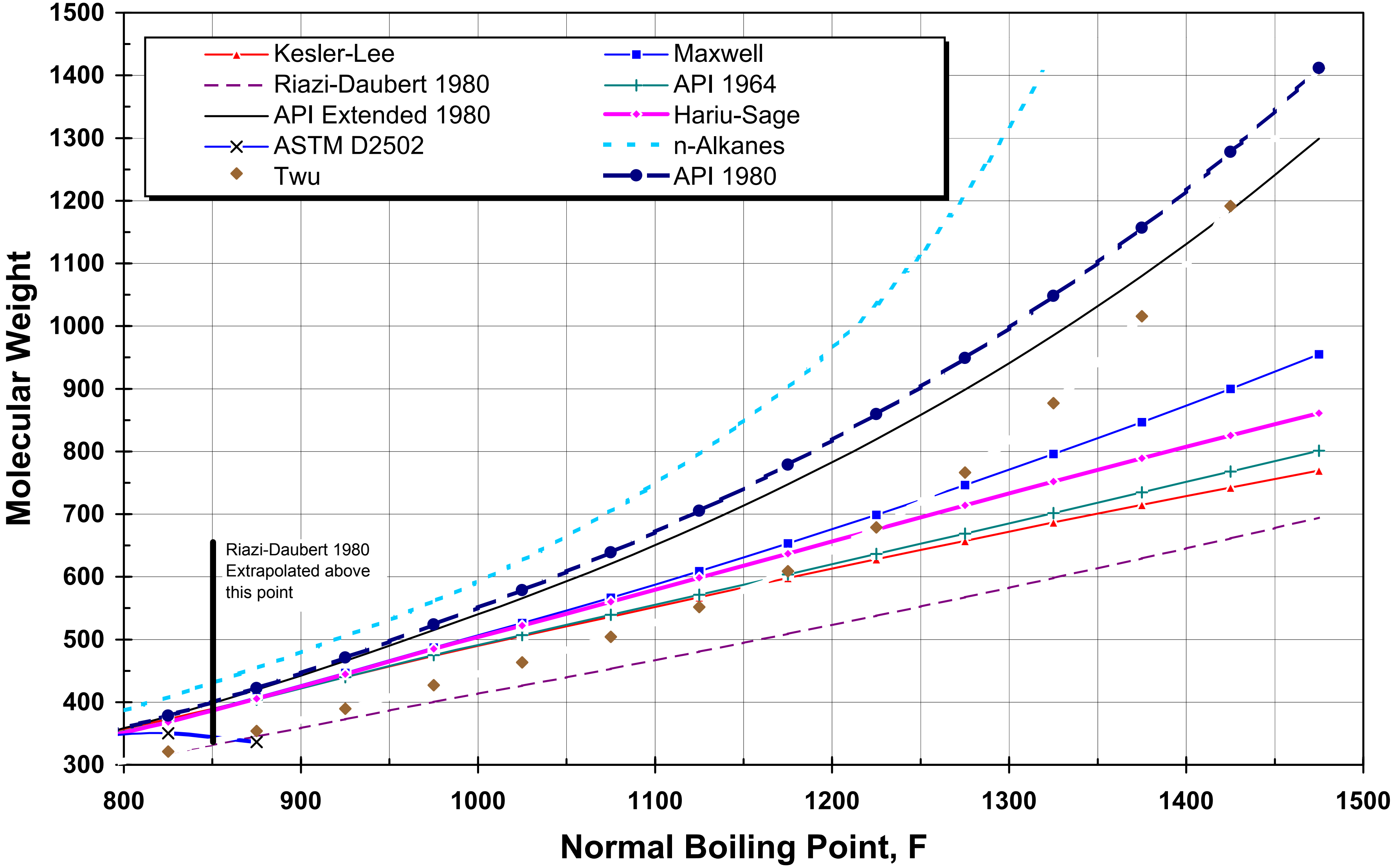


Figure 3 - Process Simulation

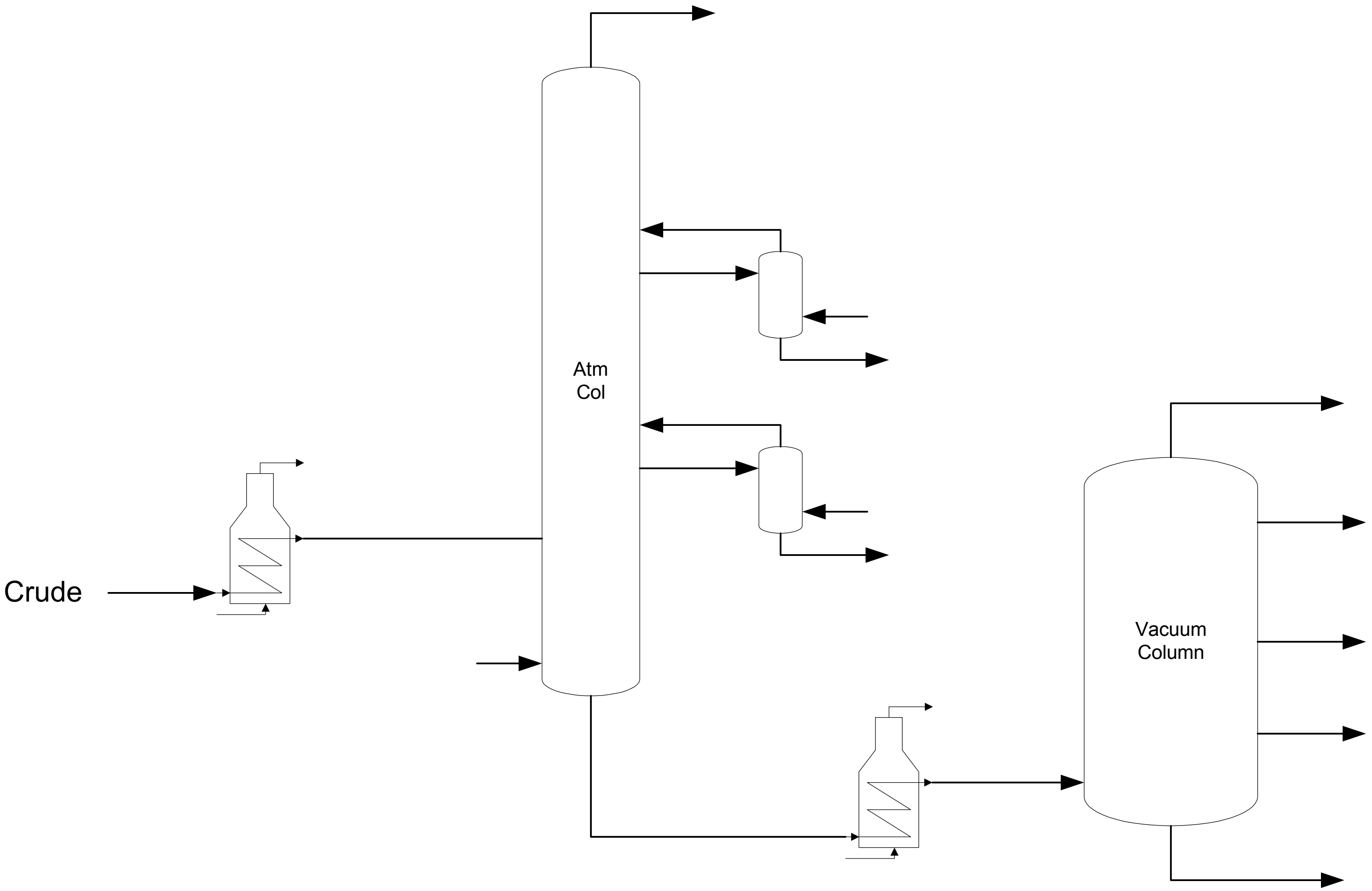


Table 2 - Impact of Molecular Weight Predictions

80,000 bpsd Bachaquero Crude feed, Constant side-draw product rates, constant bpsd overflash, constant column bottoms TBP 5% point.

	Riazi-Daubert 1980	Kessler-Lee	Hariu-Sage	API 1980	Difference Riazi-Daubert & API 1980		Difference Hariu-Sage & API 1980	
					Absolute	%	Absolute	%
Crude Average MW	337	384	386	417	80	24	31	8
Vacuum Residue Average MW	507	590	626	766	259	58	140	22
Atmospheric Flash Zone Temperature, °F	696	682	680	669	27	4	11	2
Atmospheric Heater Duty, MMBtu/hr	236	220	218	207	29	12	11	5
Atmospheric Heater Vapor Outlet Density, lb/ft3 (Constant T & P for all cases)	0.490	0.537	0.530	0.554	0.064	13	0.024	5
Vacuum Flash Zone Temperature, °F	753	752	746	733	20	3	13	2
Vacuum Heater Duty, MMBtu/hr	97	98	96	92	5	5	4	4
Vacuum Heater Vapor Outlet Density, lb/ft3 (Constant T & P for all cases)	0.0197	0.0228	0.0225	0.0236	0.0039	20	0.0011	5

Nomenclature

NBP = Normal Boiling Point

a, b, c, d = constants

T_b = Normal Boiling Point, degrees R

T_{bF} = Normal Boiling Point, °F

T_m = Mean Average Boiling Point, degrees R

T_c = Critical Temperature, degrees R

S = Specific Gravity, 60 °F/60 °F

K = UOP K

ν_{100} = Kinematic Viscosity @ 100 °F, cSt

ν_{210} = Kinematic Viscosity @ 210 °F, cSt

° denotes the properties of an *n*-Alkane with the same NBP as the component under study.

Author Biography

Donald F. Schneider

Donald F. Schneider is President of Stratus Engineering, Inc., Houston, TX (281-335-7138; Fax: 281-335-8116; e-mail: dfsstratus@aol.com). Previously he worked as a senior engineer for Stone & Webster Engineering, and as an operating and project engineer for Shell Oil Co. He holds a B.S. from the University of Missouri-Rolla, and an M.S. from Texas A&M University, both in chemical engineering. Don is a registered professional engineer in Texas.

Previous publications:

"*How to Calculate Purge Gas Volumes,*" D. Schneider, Hydrocarbon Processing, November, 1993.

"*Analysis of Alky Unit DIB Exposes Design, Operating Considerations*," D. Schneider, J. Musumeci, R. Chavez, Oil & Gas Journal, September 30, 1996.

"*Deep Cut Vacuum Tower Incentives for Various Crudes*," D. Schneider, J. Musumeci, L. Suarez, Presented @ the AIChE 1997 Spring Nat'l Mtg.

"*Debottlenecking Economics - Maximizing Profitability with Minimum Capital*," D. Schneider, Presented @ the NPRA 1997 Annual Mtg.

"*Process Simulation: Matching the Computer's Perception to Reality*," D. Schneider, Presented @ the AIChE 1997 Spring Nat'l Mtg.

"*Programming It's not Just for Programmers Anymore*," D. Schneider, Chemical Engineering, May, 1997.

"Debottlenecking Options and Optimization," D. Schneider, Petroleum Technology Quarterly, Autumn 1997.

"*Deep Cut Vacuum Tower Processing Provides Major Incentives,*" D. Schneider, J. Musumeci, Hydrocarbon Processing, November, 1997.

"*Build a Better Process Model,*" D. Schneider, Chemical Engineering Progress, April, 1998.