

New Correlation Predicting Molecular Weight of Petroleum Fractions

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Abstract

A proper description of the physical properties of the petroleum fractions in hydrocarbon mixtures is essential in performing reliable phase behavior calculations and compositional modeling studies. This paper presents a comparison study among nine different correlations used to calculate the molecular weight of undefined petroleum fractions. A new correlation was developed for calculating the molecular weight of undefined petroleum fractions as a function of boiling point with an average error of 0.4 %, standard deviation of 0.6 % and correlation coefficient of 0.99991.

Keywords: Molecular Weight; Boiling Point; Specific Gravity; Critical Pressure; Critical Temperature

Introduction

Petroleum fractions are complex mixtures of thousands of hydrocarbon compounds and can be categorized roughly into several special fractions, e.g. liquefied petroleum gas (LPG), straight run gasoline, naphtha, gas oil, diesel etc., according to their boiling range [1]. In order to obtain the detailed molecular composition distribution in the petroleum fractions, during the past decade several modern analytical techniques such as gas chromatography (GC), gas chromatography-mass spectrometry (GS-MS), nuclear magnetic resonance (NMR) have been developed. However, all these straightforward methods are time-consuming, so rarely applied in simulation process [1]. Several empirical modelling and correlations developed to predict molecular weight of petroleum fractions as a function of

critical and pseudo properties. Katz and Firoozabadi presented a generalized set of physical properties for the petroleum fractions C6 through C45 [2]. The tabulated properties include the average boiling point, specific gravity, molecular weight and critical properties. These tabulated properties generated by analyzing the physical properties of 26 condensates and crude oil samples as given in Appendix-1. Ahmed correlated Katz-Firoozabadi physical properties with the number of carbon atoms of the fraction by using a regression model [3, 4]. The generalized concluded mathematical model has the following form:

$$M = a_1 + a_2n + a_3n^2 + a_4n^3 + a_5/n \quad (1)$$

where:

$$a_1 = -131.11375a_2 = 24.96156a_3 = -0.34079022$$

$$a_4 = 0.002494118a_5 = 468.32575$$

Nearly all naturally occurring hydrocarbon systems contain a quantity of heavy fractions that are not well defined and are not mixtures of discretely identified components. These heavy fractions are often lumped together and identified as the plus fraction, e.g., C7+ fraction [3,5]. A proper description of the physical properties of the plus fractions and other undefined petroleum fractions in hydrocarbon mixtures is essential in performing reliable phase behavior calculations and compositional modeling studies. Frequently, a distillation analysis or a chromatographic analysis is available for this undefined fraction. Other physical properties, such as molecular weight and specific gravity can be measured for the entire fraction or some cuts [6,7]. To use any of the thermodynamic property-prediction models, e.g., equations of state, to predict the phase and volumetric behavior of complex hydrocarbon mixtures, one must be able to provide the acentric factor, along with the critical temperature and critical pressure, for both the defined and undefined (heavy) fractions in the mixture. The problem of how to characterize these undefined plus fractions in terms of their critical properties and acentric factors has been long recognized in the petroleum industry [4,7]. Riazi and Daubert [8] developed a simple two-parameter equation for predicting the physical properties of pure compounds and undefined hydrocarbon mixtures. The proposed generalized empirical equation based on the use of the molecular weight and specific gravity of the undefined petroleum fraction as the correlating parameters. Their mathematical expression has the following form:

$$M = aT_b^b \gamma^c \text{EXP}(dT_b + e\gamma + fT_b\gamma) \quad (2)$$

where:

$$a=581.96 \quad b=-0.97476 \quad c=6.51274 \\ d=0.000543076 \quad e=9.53384 \quad f=0.00111056$$

Kesler and Lee proposed a correlation to estimate the molecular weight of petroleum fractions [7]. This relationship uses specific gravity boiling point as input parameters for their proposed expressions:

$$M = -12272.6 + 9486.4\gamma + (4.6523 - 3.3287\gamma)T_b \\ + (10^7/T_b)(1 - 0.77084\gamma - 0.02058\gamma^2) \left(1.3437 - \frac{720.79}{T_b}\right) \\ + (10^{12}/T_b^3)(1 - 0.80882\gamma - 0.02226\gamma^2) \left(1.8828 - \frac{181.98}{T_b}\right) \quad (3)$$

Winn developed convenient nomographs to estimate various physical properties including molecular weight and the pseudocritical temperature for petroleum

fractions [9]. Sim and Daubert developed analytical relationships that closely matched the monograph graphical data [10]. The authors used specific gravity and boiling point as the correlating parameters for calculating the molecular weight of the undefined petroleum fraction:

$$M = 1.4350476 \times 10^{-5} T_b^{2.3776} \gamma^{-0.9371} \quad (4)$$

Hall and Yarborough proposed a correlation for determining the molecular weight as follows [11];

$$M = (40v_c \gamma^{0.7935})^{1/1.15} \quad (5)$$

Silva and Rodriguez proposed a correlation for determining the molecular weight with the following formula [12]

$$M = 64.2576 \text{EXP} \left(\frac{T_b - 460}{447.08723} \right) \quad (6)$$

Sancet presented the following expression to estimate the molecular weight of petroleum fractions [13]:

$$M = 4.075 + \text{EXP} \left(\frac{T_c + 778.5}{383.5} \right) \quad (7)$$

Sancet presented the following expression to estimate the molecular weight of petroleum fractions [13]:

$$M = 0.01077 T_b^x / \rho_{20} \quad (8) \\ x = 1.52869 + 0.06486 \ln(T_b / (1078 - T_b))$$

In this study, a new correlation was developed for calculating the molecular weight of undefined petroleum fractions as a function of boiling point with an average error of 0.4%, standard deviation of 0.6% and correlation coefficient of 0.99991, where the proposed mathematical formula is represented as follows:

$$M = \frac{a}{(1 + \exp(b - cT_b))^{1/d}} \quad (9)$$

$$a=2238.880249 \quad b=0.836856 \quad c=-0.001215 \\ d=0.225397$$

Statistical Error Analyses

The statistical error analyses were used to check the accuracy of the developed molecular weight correlations and the published one. The accuracy of correlations relative to the experimental values tabulated by Katz-Firoozabadi determined by various statistical means. The criteria used in this study were average absolute relative error, standard deviation, and the correlation coefficient.

Average Relative Error

This is an indication of the relative deviation in percent from the experimental values and expressed by:

$$\left(\sum_{i=1}^n E_i \right) / n$$

E_i is the relative deviation in percent of an estimated value from an experimental value and is defined by:

$$E_i = \left[\frac{(M_{exp} - M_{cal})}{M_{exp}} \right] \times 100$$

The lower the value of E_i the more equally distributed are the errors between positive and negative values.

Average Absolute Relative Error

It indicates the relative absolute deviation in percent from the tabulated values. A lower value implies a better correlation, and expressed mathematically as follow;

$$\sum_{i=1}^n |E_i| / n$$

Standard Deviation

Standard deviation s_x is a measure of dispersion and is expressed as:

$$s_x^2 = \left(\sum_{i=1}^n E_i^2 \right) / (n - 1)$$

A lower value of standard deviation means a smaller degree of scatter.

Correlation Coefficient

The correlation coefficient, r , represents the degree of success in reducing the standard deviation by regression analysis. It is defined as:

$$r^2 = 1 - \left[\frac{\sum_{i=1}^n (M_{cal} - M_{exp})^2}{\sum_{i=1}^n (M_{cal} - M_{avg})^2} \right]$$

where

$$M_{avg} = \left(\sum_{i=1}^n M_{i_{exp}} \right) / n$$

The correlation coefficient lies between 0 and 1. A value of 1 indicates a perfect correlation, whereas a value of 0 implies no correlation at all among the given independent variables.

Evaluation of the Developed Correlation

Average absolute relative error, standard deviation, and correlation coefficient were computed for each correlation. Table 1 presents the comparison of errors relative to the experimental molecular weight calculated from two correlations. The correlation for molecular weight of this study achieved a high correlation coefficient accuracy of 0.99991 with absolute average relative error of 0.4 % and standard deviation of 0.6 % as presented in Table 2.

Experimental	Ahmed	Riazi	Kesler	Win	Hall	Silva	Sancet	Goossense	This Study
84	84.98018	160.0781	-64.6297	84.17638	1.75187	89.27263	181	2.101526	82.49
96	94.67761	324.9857	-32.9812	97.10382	1.789958	100.0597	207.92	2.591884	95.09
107	106.5859	493.3227	-4.23043	110.1388	1.820842	110.4079	233.05	3.070802	107.13
121	119.7907	708.1217	24.71852	125.1073	1.851046	122.3725	260.04	3.623509	120.94
134	133.7495	926.6575	51.33385	140.4904	1.878169	134.7266	286.29	4.201221	135.03
147	148.1225	1147.633	74.33009	155.0289	1.90109	146.6784	311.69	4.761669	148.47
161	162.6882	1423.758	96.79857	170.2492	1.923225	159.6904	338.58	5.367884	162.86
175	177.2976	1766.512	116.367	184.1934	1.942681	172.3082	364.52	5.945137	176.57
190	191.8489	2194.964	136.6396	199.1452	1.962086	186.3393	393.32	6.588405	191.52
206	206.2712	2680.466	157.3627	214.8717	1.980897	201.513	424.4	7.294062	207.32
222	220.5152	3095.054	176.4675	229.7399	1.996983	215.9812	451.83	7.988802	222.05
237	234.5466	3641.447	194.8083	244.261	2.012244	230.9711	481.03	8.703864	236.95
251	248.3421	4042.259	209.3778	255.9942	2.023714	243.1641	503.04	9.304619	248.81
263	261.8865	4486.749	223.3939	267.4059	2.03464	255.4288	526.05	9.91449	260.5
275	275.1706	4988.433	238.9952	280.2669	2.04613	269.5152	551.35	10.63199	273.66
291	288.1898	5545.487	254.051	292.8042	2.057072	283.743	577.86	11.3686	286.65

300	300.943	6163.412	268.5339	304.9742	2.06746	298.0545	602.95	12.12328	299.42
312	313.432	6848.169	282.4147	316.7357	2.077287	312.3883	629.13	12.89472	311.93
324	325.6608	7468.978	296.0141	328.3975	2.086334	326.6799	653.51	13.69696	324.13
337	337.635	8001.685	310.0939	340.6244	2.095179	341.6254	680.36	14.57886	336.61
349	349.3618	8726.249	323.1698	352.0257	2.103675	356.4565	705.15	15.46498	348.72
360	360.8494	9511.829	335.5645	362.9137	2.111605	371.1005	730.84	16.36888	360.41
372	372.1072	10183.77	348.4284	374.3491	2.119622	386.346	755.77	17.36831	372.32
382	383.1451	10880.29	359.0181	383.8148	2.125932	399.528	776.33	18.25933	382.41
394	393.9739	11644.82	371.249	394.8443	2.133389	415.0121	802.82	19.36342	394.01
404	404.6048	12683.85	382.3224	404.8744	2.140179	430.1332	828.36	20.47309	405.1
415	415.0494	13569.38	393.8678	415.446	2.14678	445.8052	852.8	21.71491	416.36
426	425.32	14507.23	404.6534	425.3959	2.153095	461.016	877.96	22.99312	427.05
437	435.4289	15220.6	415.1257	435.1399	2.158945	475.6805	899.83	24.33042	437.15
445	445.3889	16249.67	424.349	443.7711	2.164106	489.715	922.24	25.66864	446.64
456	455.2129	17053.15	434.8991	453.721	2.169964	505.2925	945.22	27.30938	456.96
464	464.9142	18194.41	443.3339	461.7363	2.174834	519.0384	968.76	28.84152	465.9
475	474.5061	19081.89	453.1145	471.0857	2.180117	534.352	990.67	30.75133	475.68
484	484.0021	19997.11	462.089	479.7247	2.184821	548.8885	1013.08	32.75248	484.79
495	493.416	20976.96	471.9244	489.2532	2.189818	565.0829	1036	35.26358	494.74
502	502.7615	21947.6	479.2556	496.4163	2.193941	577.8645	1057.06	37.48333	502.46
512	512.0526	22572.81	487.9962	504.96	2.198198	592.2584	1076.15	40.37904	511.01
521	521.3033	23642.09	496.1993	513.0671	2.202325	607.0109	1098.03	43.79877	519.62
531	530.5277	24809.68	506.1166	522.9186	2.207332	624.9202	1122.87	48.91041	529.88
539	539.74	25964.92	513.484	530.316	2.211167	639.0552	1143.14	53.99257	537.83

Table 1: Comparison of molecular weight calculated by correlations from this study and others

	AARE, %	SD	R ²
This study	0.40	0.60	0.99991
Ahmed	0.42	0.60	0.98921
Reazi	2394.56	2790.46	0.013
Kessler	24.18	45.08	0.90
Win	1.79	2.45	0.978
Hall	99.22	100.48	-0.17
Silva	6.18	8.39	0.94
Sancet	106.94	108.42	0.29
Goossense	95.09	96.32	-0.16

Table 2: Statistical accuracy of molecular weight correlations

Conclusions

From this paper, one may conclude that:

1. This paper presents a comparison among eight different correlations used to calculate the molecular weight of undefined petroleum fractions.

2. New correlation was developed for calculating the molecular weight of undefined petroleum fractions.

3. Deviations from experimental values of molecular weight indicated as average absolute percent relative error, and the standard deviation were lower for this

study than for calculated values based on the other correlations except Ahmed correlation.

- The developed correlation has high accuracy where the correlation coefficient of the proposed correlation in this study is closer to one.

Nomenclature

p_c = critical pressure, psia

T_c = critical temperature, °R

T_b = boiling point, °R

ω = acentric factor

M = molecular weight

γ = specific gravity

v_c = critical volume, ft³/lb-mol

n = no of carbon atoms

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