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New Correlation for Calculating Critical Pressure of Petroleum Fractions

Sayed Gomaa, PhD[1, 2]

Mining and Petroleum Engineering Department, Faculty of Engineering, Al-Azhar University, Cairo, Egypt[1]

Petroleum Engineering and Gas Technology Department, Faculty of Engineering, British University in Egypt[2]

Abstract: Critical pressure is one of the most important physical properties of the petroleum fractions, which commonly considered in compositional modeling studies and phase behavior calculations. This paper presents a comparison study among ten different correlations used to calculate the critical pressure of undefined petroleum fractions. A new correlation was developed for calculating the critical pressure of petroleum fractions as a function of the number of carbon atoms with an average error of 0.933977 % and correlation coefficient of 0.999585.

Keywords: Critical pressure, petroleum fractions, Compositional Modeling Studies, Phase Behavior Calculations.

INTRODUCTION

Katz and Firoozabadi [1] presented a generalized set of physical properties for the petroleum fractions C6 through C45. The tabulated properties include the critical properties, average boiling point, specific gravity, and molecular weight. The authors generated these properties by analyzing the physical properties of 26 condensates and crude oil samples. These generalized properties are given in Table A-1.

Ahmed [2, 3] correlated Katz-Firoozabadi-tabulated physical properties with the number of carbon atoms of the fraction by using a regression model. The generalized equation has the following form:

$$P_c = a_1 + a_2 n + a_3 n^2 + a_4 n^3 + a_5/n \qquad (1)$$

Where:

$a_1 = 311.2361908$ $\quad a_2 = -14.6869301$

$a_3 = 0.3287671$

$a_4 = -0.0027346$ $\quad a_5 = 1690.9001135$

Undefined Petroleum Fractions

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., C_7 fraction [2, 4].

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, may also be measured for the entire fraction or for various cuts of it [3, 5].

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 adequately characterize these undefined plus fractions in terms of their critical properties and acentric factors has been long recognized in the petroleum industry [3, 5].

Riazi and Daubert [6] developed a simple two-parameter equation for predicting the physical properties of pure compounds and undefined hydrocarbon mixtures. The proposed generalized empirical equation is 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:

$$P_c = aM^b\gamma^c EXP(dM + e\gamma) \qquad (2)$$

Where:

$a = 45203$ $\quad b = -0.8063$ $\quad c = 1.6015$

$d = -0.0018078$ $\quad e = -0.3084$

Edmister [7] proposed a correlation for estimating the acentric factor of pure fluids and petroleum fractions. The equation, widely used in the petroleum industry, requires boiling point, critical temperature, and critical pressure. The proposed expression is given by the following relationship:

$$\omega = \frac{3[\log(p_c/14.7)]}{7[(T_c/T_b) - 1]} - 1 \qquad (3)$$

The Edmister equation can be rearranged to solve for the critical pressure as follows:

$$\log(p_c) = \log(14.7) + \left(\frac{7}{3}\right) * (\omega + 1) * [(T_c/T_b) - 1)] \qquad (4)$$

Cavett [8] proposed correlations for estimating the critical pressure of hydrocarbon fractions. The correlations

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received wide acceptance in the petroleum industry due to their reliability in extrapolating conditions beyond those of the data used in developing the correlations. The proposed correlations were expressed analytically as functions of the normal boiling point in °F and API gravity. Cavett proposed the following expression for estimating the critical pressure of petroleum fractions:

$$\log(p_c) = b_0 + b_1(T_b) + b_2(T_b)^2 + b_3(API)(T_b) + b_4(T_b)^3 + b_5(API)(T_b)^2 + b_6(API)^2(T_b) + b_7(API)^2(T_b)^2 \quad 5)$$

Where:

i	b_i
0	2.8290406
1	0.00094120109
2	-0.30474749E-5
3	-0.20876110E-4
4	0.15184103E-8
5	0.11047899E-7
6	-0.48271599E-7
7	0.13949619E-9

Kesler and Lee [9] proposed a correlation to estimate the critical pressure of petroleum fractions. This relationship use specific gravity boiling point as input parameters for their proposed expressions:

$$ln(p_c) = 8.3634 - 0.0566/\gamma - (0.24244 + 2.2898/\gamma + 0.11857/\gamma^2) \times 10^{-3}\, T_b + (1.4685 + 3.648/\gamma + 0.47227/\gamma^2) \times 10^{-7}\, {T_b}^2 - (0.42019 + 1.6977/\gamma^2) \times 10^{-10}\, {T_b}^3 \quad (6)$$

Winn [10] developed convenient nomographs to estimate various physical properties including molecular weight and the pseudocritical pressure for petroleum fractions. Sim and Daubert [11] developed analytical relationships that closely matched the monograph graphical data. The authors used specific gravity and boiling point as the correlating parameters for calculating the critical pressure of the undefined petroleum fraction:

$$p_c = 3.48242 \times 10^9 {T_b}^{-2.3177} \gamma^{2.4853} \quad (7)$$

Watansiri et al. [12] developed a set of correlations to estimate the critical properties and acentric factor of coal compounds and other undefined hydrocarbon components and their derivatives. The proposed correlations express the critical and physical properties of the undefined fraction as a function of the fraction normal boiling point, specific gravity, and molecular weight. These relationships have the following forms:

$$ln(p_c) = 6.6418853 + 0.01617283(T_c/V_c)^{0.8} - 8.712(M/T_c)\, 0.08843889(T_b/M) \quad (8)$$

Willman and Teja [13] proposed correlation for determining the critical pressure of the n-alkane homologous series:

$$p_c = (339.0416805 + 1184.157759n)[0.87359 + 0.54285n]^{-1.9265669}$$

Lin and Chao [14] developed a correlation to estimate the critical pressure as a function of molecular weight:

$$p_c = C_1 + C_2 M + C_3(M)^2 + C_4(M)^3 + C_5/M \quad (9)$$

Where:

$C_1 = 6.753444$ $\quad C_2 = -0.010182$ $\quad C_3 = 0.0000251106$

$C_4 = -0.0000000373776$ $\quad C_5 = 3.50737$

Sancet [15] presented a correlation to estimate the critical pressure from the molecular weight. This correlation has the following form:

$$p_c = 653\, exp(-0.007427M) + 82.82 \quad (10)$$

Proposed correlation

A new correlation was developed by use of the linear and nonlinear regression analysis and can be expressed as:

$$P_c = a_0 + a_1\, ln(n) + a_2[ln(n)]^2 + a_3[ln(n)]^3 + a_4 n + a_5 n^2 + a_6 n^3 + a_7/n \quad (10)$$

With the coefficients a_0 through a_7 having the following values:

$a_0 = -50662.795181$ $\quad a_1 = 50832.035066$

$a_2 = -17678.300681$

$a_3 = 3393.832113$ $\quad a_4 = -1991.986187$ $\quad a_5 = 8.395313$ $\quad a_6 = -0.02554$ $\quad a_7 = 53728.166034$

Statistical Error analysis

The statistical error analyses were used to check the accuracy of the critical pressure correlations developed by Ahmed, Reazi- Daubert, Lin, Cavett, Kessler-Lee, Winn-Sim, Watansiri, Willman, Sancet and this study.

The accuracy of correlations relative to the experimental values tabulated by Katz-Firoozabadi-tabulated is determined by various statistical means. The criteria used in this study were average percent relative error, average absolute percent relative error, minimum/maximum absolute percent 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 is given 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:

$$E_i = \left[\frac{\left(p_{c\,exp} - p_{c\,cal}\right)}{p_{c\,exp}}\right]_i \times 100$$

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

Average Absolute Relative Error
This is defined as:

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

and indicates the relative absolute deviation in percent from the tabulated values. A lower value implies a better correlation.

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

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

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:

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

Where

$$p_{c_{avg}} = \left(\sum_{i=1}^{n} p_{ci_{exp}}\right) / n$$

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.

Comparison of Correlations

Statistical Error Analysis
Average relative error, 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 critical pressure calculated from two correlations. The correlation for critical pressure of this study achieved the highest correlation coefficient accuracy of 0.999585, as presented in Table 2.

Table 1 Comparison of critical pressure calculated by correlations from this study and others

Experimental	Reazi	Lin	Cavett	Ahmed	Sayed
483	486.5995	443.6061	474.3079714	516.1762	483.2575
453	459.5854	407.8327	454.7675179	465.1565	452.7127
419	430.0627	379.347	431.8667081	424.7442	417.6729
383	392.9715	347.8725	405.8220313	391.5682	383.6256
351	362.3341	322.5254	378.6496158	363.599	352.8333
325	334.7507	300.1955	354.2682187	339.5392	325.9901
302	309.017	278.8939	331.0501626	318.5184	303.0472
286	286.9266	259.908	312.4320969	299.9291	283.6288
270	266.1019	241.6387	293.8190942	283.3324	267.2419
255	246.1526	224.0397	275.255954	268.4022	253.3796
241	227.6728	207.9795	258.1837004	254.8900	241.5707
230	212.8811	194.0224	243.6370851	242.6017	231.3995
222	199.7345	181.7564	232.2516263	231.3827	222.5123
214	189.6965	171.7151	222.0847588	221.1076	214.6148
207	180.4563	162.033	211.3101072	211.6726	207.4679
200	168.788	149.5843	201.7427904	202.9909	200.8809
193	163.2755	142.7784	193.2726173	194.9881	194.7048
188	155.9749	133.8956	185.7979324	187.6001	188.8262
182	148.9473	125.213	178.6940495	180.7708	183.1615
177	141.5802	116.0197	171.5284832	174.4503	177.6515
173	135.4937	107.7274	165.7204516	168.5939	172.2577
169	130.3144	100.2945	160.6576099	163.1611	166.9576
165	124.7418	92.38068	155.4741815	158.1149	161.7424
161	120.4446	85.95315	151.634223	153.4211	156.6132
158	115.4629	78.45942	147.3897367	149.0478	151.5795
143	111.7754	72.41387	144.1224668	144.9652	146.6569
138	107.6944	65.99212	140.7006346	141.1452	141.8655
134	103.8193	59.82957	137.7846727	137.5609	137.2282

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130	99.99206	53.94648	134.9703598	134.1870	132.7701
127	97.54432	49.85437	132.9233977	130.9988	128.5172
124	94.02806	44.49788	130.474535	127.9728	124.4954
121	91.77916	40.8066	128.9424617	125.0862	120.7303
118	88.53959	36.02199	127.0247512	122.3169	117.2463
115	86.04582	32.36387	125.4438954	119.6434	114.0663
112	83.07149	28.2116	123.8322733	117.0444	111.2112
110	81.3324	25.75291	122.8347137	114.4997	108.6998
108	78.72571	22.48766	121.4980115	111.9888	106.5483
105	76.58938	19.79505	120.5610443	109.4920	104.7704
103	74.28081	17.07123	119.4965043	106.9898	103.377
101	72.53922	15.08983	118.908402	104.4628	102.3759

Table 1 Cont.: Comparison of critical pressure calculated by correlations from this study and others

Kessler	Winn-Simm	Edmister	Watansiri	Willman	Sancet
475.7941	490.6552	484.968823	494.0948601	484.1689	432.7416
455.7638	463.3941	448.3040413	463.6339024	442.3843	402.9045
427.4347	429.512	420.5805151	434.4403965	407.108	377.7943
396.4306	394.5733	384.0602243	396.2830547	377.015	348.6641
366.3598	362.547	350.0630266	364.8704104	351.0822	324.1968
341.0123	336.6751	326.0504211	336.9122923	328.5233	301.9813
318.1025	314.0271	303.4746434	310.1766626	308.7307	280.3381
300.6279	297.1088	284.9497729	286.4527956	291.2303	260.8322
283.8007	281.2067	268.887675	264.1577419	275.6485	242.0655
267.3945	266.1107	255.6445822	242.9863424	261.6873	224.2232
252.27	252.5976	241.5604987	222.8809163	249.1068	208.3799
239.7186	241.507	230.9518626	206.9204758	237.7118	195.1429
229.7009	232.8445	221.1620973	192.1894556	227.3419	184.0505
220.7771	225.2051	213.9721549	181.3967283	217.8645	175.4188
211.1687	217.092	205.7912628	171.65114	209.1686	167.5231
202.5909	209.9168	199.8857102	158.7385351	201.1609	158.0327
194.9432	203.5703	192.8457201	153.3087592	193.7624	153.1696
188.1387	197.961	187.8318369	145.5723076	186.9058	147.171
181.3904	192.4708	181.9426756	138.0179495	180.5331	141.684
174.2314	186.7235	177.9829364	130.413171	174.5947	136.2663
168.4868	182.1078	172.870038	123.8364352	169.0471	131.7091
163.3878	178.0275	169.4158311	118.4605784	163.8528	127.8738
157.8294	173.634	165.1475023	112.5653569	158.9788	124.0322
153.6697	170.3481	160.8962772	107.9064729	154.3961	121.0822
148.8598	166.575	158.4226723	102.7690901	150.0791	117.8197
145.1926	163.6818	143.6578274	98.98044296	146.0052	115.3144
141.0457	160.4491	138.5137221	94.69497994	142.1542	112.7653
137.3853	157.6011	134.8857603	90.68844035	138.5081	110.4161
133.6109	154.6899	130.4651316	86.63458303	135.0509	108.2512
130.8394	152.5374	127.2683332	84.2220399	131.7681	106.7842
127.2556	149.7861	123.3277198	80.55322596	128.6467	104.9043
124.9567	148.0047	121.4809425	78.399966	125.6749	103.6303
121.8599	145.6341	117.8412754	74.96735094	122.8422	101.9978
119.152	143.5625	115.2558872	72.50478695	120.139	100.7578
116.2044	141.3132	111.9798104	69.40769228	117.5564	99.35058
114.221	139.7958	110.5923539	67.8061103	115.0864	98.51313
111.4857	137.7213	107.5755948	65.1006677	112.7219	97.38983
109.3013	136.0562	105.442655	62.97507318	110.456	96.44778
106.6034	134.0058	102.5297079	60.70537044	108.2828	95.47231
104.793	132.6266	100.6609292	58.97903267	106.1965	94.74246

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Table 2 Statistical accuracy of critical pressure correlations

	AARE, %	SD	R^2
This study(sh4)	0.933977	1.317814	0.999585
Ahmed	3.475806	3.838117	0.991964
Reazi	16.22215	19.16977	0.946263
Lin	39.34908	47.73011	0.773554
Cavett	6.191865	7.612793	0.981904
Kesler	3.169919	3.518671	0.99421
Winn-Simm	11.5529	15.28577	0.962153
Edmister	0.322695	0.387337	0.999887
Watansiri	22.71815	27.04131769	0.910100284
Willman	2.809648	0.032314	0.996947
Sancet	15.12048	16.41881	0.896163

CONCLUSIONS

From this paper, one may conclude that:

1. This paper presents a comparison among nine different correlations used to calculate the critical pressure of undefined petroleum fractions.
2. New correlation was developed for calculating the critical pressure of undefined petroleum fractions.
3. Deviations from experimental values of critical pressure indicated as average percent relative errors, average absolute percent relative errors, and the standard deviations, were lower for this study than for calculated values based on Ahmed, Reazi- Daubert, Lin, Cavett, Kessler-Lee, Winn-Sim, Watansiri and Willman, Sancet correlations.
3. The developed correlation is more practical than Edmister correlation, which is a function of critical temperature and acentric factor that in turn need two correlations to be calculated.
4. The correlation coefficient of the correlations of this study are closer to one than that of other correlations.

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, ft^3/lb-mol
n = no of carbon atoms

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Appendix 1:

Table A-1

C	Tb	SG	K	M	Tc	Pc	ω	Vc
6	607	0.69	12.27	84	923	483	0.25	0.06395
7	658	0.727	11.96	96	985	453	0.28	0.06289
8	702	0.749	11.87	107	1,036	419	0.312	0.06264
9	748	0.768	11.82	121	1,085	383	0.348	0.06258

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10	791	0.782	11.83	134	1,128	351	0.385	0.06273
11	829	0.793	11.85	147	1,166	325	0.419	0.06291
12	867	0.804	11.86	161	1,203	302	0.454	0.06306
13	901	0.815	11.85	175	1,236	286	0.484	0.06311
14	936	0.826	11.84	190	1,270	270	0.516	0.06316
15	971	0.836	11.84	206	1,304	255	0.55	0.06325
16	1,002	0.843	11.87	222	1,332	241	0.582	0.06342
17	1,032	0.851	11.87	237	1,360	230	0.613	0.0635
18	1,055	0.856	11.89	251	1,380	222	0.638	0.06362
19	1,077	0.861	11.91	263	1,400	214	0.662	0.06372
20	1,101	0.866	11.92	275	1,421	207	0.69	0.06384
21	1,124	0.871	11.94	291	1,442	200	0.717	0.06394
22	1,146	0.876	11.95	300	1,461	193	0.743	0.06402
23	1,167	0.881	11.95	312	1,480	188	0.768	0.06408
24	1,187	0.885	11.96	324	1,497	182	0.793	0.06417
25	1,207	0.888	11.99	337	1,515	177	0.819	0.06431
26	1,226	0.892	12	349	1,531	173	0.844	0.06438
27	1,244	0.896	12	360	1,547	169	0.868	0.06443
28	1,262	0.899	12.02	372	1,562	165	0.894	0.06454
29	1,277	0.902	12.03	382	1,574	161	0.915	0.06459
30	1,294	0.905	12.04	394	1,589	158	0.941	0.06468
31	1,310	0.909	12.04	404	1,603	143	0.897	0.06469
32	1,326	0.912	12.05	415	1,616	138	0.909	0.06475
33	1,341	0.915	12.05	426	1,629	134	0.921	0.0648
34	1,355	0.917	12.07	437	1,640	130	0.932	0.06489
35	1,368	0.92	12.07	445	1,651	127	0.942	0.0649
36	1,382	0.922	12.08	456	1,662	124	0.954	0.06499
37	1,394	0.925	12.08	464	1,673	121	0.964	0.06499
38	1,407	0.927	12.09	475	1,683	118	0.975	0.06506
39	1,419	0.929	12.1	484	1,693	115	0.985	0.06511
40	1,432	0.931	12.11	495	1,703	112	0.997	0.06517
41	1,442	0.933	12.11	502	1,712	110	1.006	0.0652
42	1,453	0.934	12.13	512	1,720	108	1.016	0.06529
43	1,464	0.936	12.13	521	1,729	105	1.026	0.06532
44	1,477	0.938	12.14	531	1,739	103	1.038	0.06538
45	1,487	0.94	12.14	539	1,747	101	1.048	0.0654