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Novel Correlation for Better Estimation of Pseudo-Critical Pressures and Pseudo-Critical Temeratures of Natural Gas Systems

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Abstract— Critical temperatures (T_{pc}) and pressures (P_{pc}) of hydrocarbon gases are important physical properties used for the calculation of Pseudo reduced properties, which are bases for the application of the corresponding states' theorem, useful in z-factors' determination, which are necessary in several petroleum engineering applications such as compositional modeling studies and phase behavior calculations.
Two simple models which are functions of specific gravity, and having only integers as regressing parameters are presented in this study. One model estimates P_{pc} and the other, T_{pc} of natural gas systems over a wide range of gas specific gravity. The associated parameters were estimated by fitting models to data from over 420 data points obtained from literature using non-linear regression analysis to minimize the sum of squares error employing a trust-region algorithm of BFGS algorithm of a solver add-in program in Microsoft Excel.
The performance of the models in replicating experimentally measured values is compared with four other correlations which have popular industry patronage. The new correlations showed superior accuracy in estimating both the pseudo-critical temperature and pseudo critical pressure for dry and wet natural gas systems in comparison to the other correlations. Average Absolute errors of 0.0565% and 0.2729% for P_{pc} and T_{pc} respectively, and correlation coefficients of 0.992755 and 0.99845097, respectively for P_{pc} and T_{pc} were achieved with the new correlations.
These correlations are recommended in allowable limits of up to $3\%\ H_2S$, $5\%\ N_2$, or a total impurity (non-hydrocarbon) content of 7% .

Index Terms— Pseudo critical pressure, Pseudo critical temperature, Sweet natural gas, Gas Specific gravity, Gaseous petroleum, Reservoir fluid properties, physical constants of natural gas constituents..

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1 Introduction

Natural gas is gaseous petroleum, consisting essentially of hydrocarbons of the paraffin series. Methane is the chief component of natural gas occurring in percentages of over eighty, most of the times, with other hydrocarbons other than methane occurring in smaller fractions. Some non-hydrocarbon components (known as impurities) occur in natural gas, the most common being, carbon dioxide, nitrogen, water vapour and hydrogen sulphide. The composition of natural gas often determines its properties.

Gas composition is usually determined in laboratories and is reported in mole fractions of the gas components. These enable calculation of pseudo critical temperatures and pressures of hydrocarbon gases using Kay's mixing rule, given the critical temperatures and pressures of the pure constituents. Tabulations of physical constants for typical natural gas constituents are often included in some literatures such as is shown in table 1 below.

For example, if y_i is the mole fraction of component *i*, in a gaseous mixture consisting of n number of compounds, the pseudo critical temperature and pseudo - critical pressure of the gas mixture can be calculated using:

$$P_{pc} = \sum_{i=1}^{n} y_i P_{c_i} \quad (1)$$

$$T_{pc} = \sum_{i=1}^{n} y_i T_{c_i} \quad (2)$$

TABLE 1
Physical Constants for Typical Natural Gas Components

Compound	Molecular Weight	Critical Pressure $(psia)$	Critical Temp. $(°R)$	Accentric factor (ω)	Critical Compressibility factor (z_c)
CH_4	16.043	667.8	343.1	0.0115	0.289
C_2H_6	30.070	707.8	549.8	0.0908	0.285
C_3H_8	44.097	616.3	665.7	0.1454	0.281
nC_4H_{10}	58.124	550.7	765.4	0.1928	0.274
iC_4H_{10}	58.124	529.1	734.7	0.1756	0.283
nC_5H_{12}	72.151	488.6	845.4	0.2510	0.262
iC_5H_{12}	72.151	490.4	828.8	0.2273	0.273
nC_6H_{14}	86.178	436.9	913.4	0.2957	0.264
nC_7H_{16}	100.205	396.8	972.5	0.3506	0.263
nC_8H_{18}	114.232	360.6	1023.9	0.3978	0.259
nC_9H_{20}	128.259	332.0	1070.4	0.4437	0.251
$nC_{10}H_{22}$	142.286	304.0	1111.8	0.4902	0.247
N_2	28.013	493.0	227.3	0.0355	0.291
CO_2	44.010	1070.9	547.6	0.2250	0.274
H_2S	34.076	1306.0	672.4	0.0949	0.266
O_2	31.999	737.1	278.6	0.0196	0.292
H_2	2.016	188.2	59.9	−0.2234	0.304
H_2O	18.015	3203.6	1165.1	0.3210	0.230

(*From Edmister and Lee (1984).

Where,

P_{pc} is pseudo - critical pressure of the gas mixture,
T_{pc} is pseudo- critical temperature of the gas mixture,
P_{c_i} is critical pressure for pure component i,
T_{c_i} is critical temperature for pure component i; and
y_i is the mole fraction of component *i*, in a gaseous mixture.

If the gas composition is not known, but gas-specific gravity is available or can be calculated, the pseudo-critical pressure and pseudo critical temperature can be estimated using various charts or correlations developed empirically from various laboratory measurements. Most correlations of P_{pc} and T_{pc} are functions of the gas specific gravity. Gas specific gravity is defined as the ratio of the density of the gas to the density of air at standard conditions (60^oF, temperature and $14.7\ psia$, average pressure). Since at atmospheric pressure and temperature the densities of gases are directly proportional to the molecular weight, the specific gravity of the gas mixture may be defined as the molecular weight of the gas to the molecular weight of air, usually taken as 28.97. Gas gravities for natural gases range from 0.6 to 1.1, depending on the relative concentration of the heavier hydrocarbons present in the gas. (Amyx et al. (1988)).

Thus, mathematically, gas specific gravity is,

$$\gamma = M/M_{air} = M/28.97 \quad (3)$$

2.0 REVIEW OF LITRATURE

Many correlations which estimate pseudo-critical properties have been reported in the literature. The accuracy of these correlations varies widely and depends on the nature of the compositions of fluid sample (e.g. percentage of different hydrocarbon and non-hydrocarbon components, and other impurities), and the gas specific gravity. Some correlations for estimating gas pseudo critical properties for sweet natural gas systems containing minor amounts of carbon dioxide and nitrogen with no hydrogen sulfide or a total impurity (non-hydrocarbon) content of $7\ mol\ \%$, are as follows:

2.1 Standing's Correlation (1981):

Based on work on light molecular weight California natural gases presented two sets of correlations: one for dry hydrocarbon gases and one for wet gas mixtures, Standing in 1981 proposed the following correlations for dry and wet gases**:**

Dry hydrocarbon gases ($\gamma_g < 0.75$):

$$T_{pc} = 168 + 325\gamma_g - 12.5{\gamma_g}^2 \quad (4)$$

and $$P_{pc} = 667 + 15.0\gamma_g - 37.5{\gamma_g}^2 \quad (5)$$

Wet gas mixtures ($\gamma_g \geq 0.75$):

$$T_{pc} = 187 + 330\gamma_g - 71.5{\gamma_g}^2 \quad (6)$$

and $$P_{pc} = 706 - 51.7\gamma_g - 11.1{\gamma_g}^2 \quad (7)$$

Standing indicated that his correlation works only when there is no non-hydrocarbon gases present in the natural gas mixture.

2.2 Sutton's (1985) Correlation:

Sutton, working with PVT reports of high molecular weight, mainly sweet gases rich in Heptane-plus fractions, used regression analysis on the raw data to obtain the following second-order fit for the pseudo critical properties of hydrocarbon mixtures:

$$P_{pc} = 756.8 - 131.07\gamma_g - 3.6{\gamma_g}^2 \quad (8)$$

and $$T_{pc} = 169.2 + 349.5\gamma_g - 74.0{\gamma_g}^2 \quad (9)$$

Sutton developed his correlation using gases which had minor amounts of carbon dioxide and nitrogen with no hydrogen sulfide. The range of the gas gravities were $0.57 < \gamma_g < 1.68$. Thomas et al. (1970), recommended the use of these equations in allowable limits of up to $3\%\ H_2S$, $5\%\ N_2$, or a total impurity (non-hydrocarbon) content of $7\ mol\ \%$, beyond which errors in critical pressures exceed 6%.

2.3 Elsharkawy et al.'s (2004) Correlation:

Elsharkawy with his research team developed a correlation for critical properties using a large data bank of retrograde gas condensates with minor amounts of hydrogen sulfide. The correlation has the form:

$$P_{pc} = 787.06 - 147.34\gamma_g - 7.916{\gamma_g}^2 \quad (10)$$

and $$T_{pc} = 149.18 + 358.14\gamma_g - 66.976{\gamma_g}^2 \quad (11)$$

2.4 Menon, El Shashi's (2015) Correlation:

$$P_{pc} = 709.604 - 58.718\gamma_g \quad (12)$$

$$T_{pc} = 170.491 + 307.344\gamma_g \quad (13)$$

Proposed correlations

A: Pseudo-Critical Temperature:

$$T_{pc} = 160 + 350\gamma_g - 30{\gamma_g}^2 \quad (14)$$

B: Pseudo-Critical Pressure

$$P_{pc} = 695 - 35\gamma_g - 7{\gamma_g}^2 \quad (15)$$

RESULTS

Results for estimation of P_{pc} and T_{pc}, by the various correlations are as shown in tables 2 and 3, respectively, and the performances of the various correlations in comparison to values obtained from the graph of G. G. Brown et al of specific gravity versus pseudo-critical temperature and pseudo-critical pressure. The graph was developed on the basis of over 480 experimentally derived data points. The comparative performances for the estimated values of P_{pc} and T_{pc}, are shown graphically in figures 1 and 2, respectively.

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TABLE 2
PSEUDOCRITICAL PRESSURES OF MODELS COMPARED TO MEASURED VALUES

	P_{pc} Measured	THIS STUDY	Menon's	Elsharkawy et al.'s	Sutton's	Standing's
$\gamma_g = 0.6$	**672**	671.48	674.373	695.80624	676.862	662.50
$\gamma_g = 0.63$	**670**	670.1717	672.612	691.09394	672.797	661.566
$\gamma_g = 0.65$	**669**	669.2925	671.437	687.94449	670.084	660.906
$\gamma_g = 0.68$	**668**	667.9632	669.676	683.20844	666.008	659.86
$\gamma_g = 0.7$	**667**	667.07	668.501	680.04316	663.287	659.125
$\gamma_g = 0.73$	**666**	665.7197	666.74	675.28336	659.20	657.966
$\gamma_g = 0.75$	**665**	664.8125	665.566	672.10225	656.473	660.981
$\gamma_g = 0.78$	**664**	663.4412	663.804	667.31871	652.375	658.921
$\gamma_g = 0.8$	**663**	662.52	662.63	664.12176	649.64	657.536
$\gamma_g = 0.83$	**662**	661.1277	660.868	659.31447	645.532	655.442
$\gamma_g = 0.85$	**660**	660.1925	659.694	656.10169	642.79	654.035
$\gamma_g = 0.88$	**659**	658.7792	657.932	651.27065	638.671	651.908
$\gamma_g = 0.90$	**658**	657.83	656.758	648.04204	635.921	650.479
$\gamma_g = 0.93$	**657**	656.3957	654.996	643.18725	631.791	648.319
$\gamma_g = 0.95$	**655**	655.4325	653.822	639.94281	629.035	646.867
$\gamma_g = 0.98$	**654**	653.9772	652.06	635.06427	624.489	644.674
$\gamma_g = 1.00$	**653**	653.00	650.886	631.804	622.13	643.20
$\gamma_g = 1.03$	**652**	649.256	649.124	626.902	617.9787	640.973
$\gamma_g = 1.05$	**650**	648.09	647.950	623.626	615.2075	639.477
$\gamma_g = 1.08$	**649**	646.334	646.189	618.6996	611.0454	637.217
$\gamma_g = 1.10$	**647**	645.16	645.014	615.4076	608.267	633.699

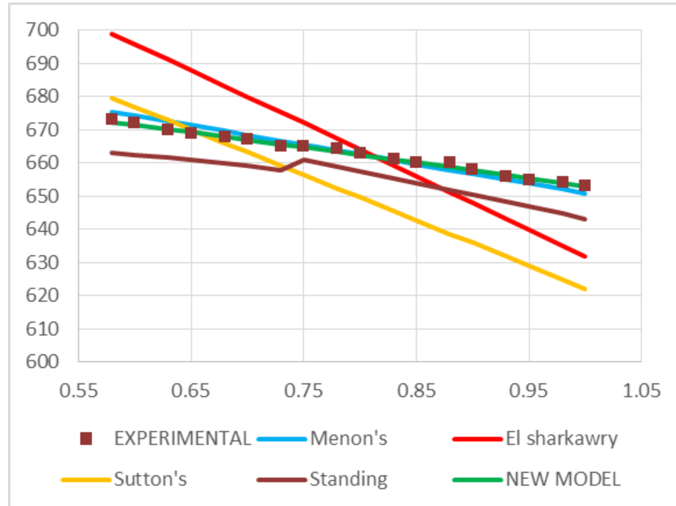

Figure 1: Comparison of Pseudo critical temperatures versus Specific gravity

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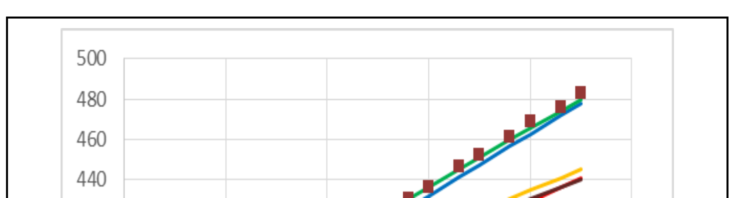
$\gamma_g = 1.03$	**494**	488.673	487.055	451.386	450.678	451.046
$\gamma_g = 1.05$	**500**	494.425	493.202	457.850	454.590	454.671
$\gamma_g = 1.08$	**508**	503.008	502.423	487.850	460.346	400.002
$\gamma_g = 1.10$	**515**	508.7	508.569	462.093	464.110	463.485



PERFORMANCE COMPARISON OF CORRELATIONS:

The performance of the new correlations for Pseudo critical pressure and pseudo critical temperature relative to those of Standing's (1981), Sutton, R. P.'s, (1984), Menon's, (2015), and El Sharkawy et al.s' (2004) were compared and the errors of estimation against the measured values read from the graph of specific gravity versus pseudo critical temperature and pseudo critical pressure developed by G. G. Brown et al. The error analysis criteria used in this study are Average percent Relative Error (ARE), Average Absolute percent Relative Error (AARE), Standard Deviation (SD), and the Correlation coefficient (R^2), as contained in

Results for error analyses for pseudo critical temperature

TABLE 4
STATISTICAL ACCRACY OF PSEUDO CRITICAL TEMPERATURE CORRELATIONS

ARE, %	*AARE*, %	*SD*, %	R^2
$\sum_{i=1}^{n} E_i/n$ Where, $E_i = \left[\frac{X_{avg}-X_{calc}}{X_{avg}}\right]_i * 100$	$\sum_{i=1}^{n} \lvert E_i \rvert/n$	$S_x^2 = \frac{\left(\sum_{i=1}^{n} E_i^2\right)}{(n-1)}$	$r^2 = 1 - \left[\sum_{i=1}^{n}(X_{calc}-X_{avg})^2 \Big/ \sum_{i=1}^{n}(X_{calc}-X_{avg})^2\right]$ Where, $X_{avg} = \left(\sum_{i=1}^{n} X_{i_{calc}}\right)/n$

calculated from the various correlations are shown as table 5 and that for pseudo critical pressure are as tabulated in table 6

TABLE 5
STATISTICAL ACCRACY OF PSEUDO CRITICAL TEMPERATURE CORRELATIONS

	ARE, %	*AARE*, %	*SD*, %	R^2
This study	**-0.0294**	**0.2729**	**0.0014**	**0.998451**
Standing	-4.0193	4.1077	0.2981	0.393194
Sutton	-4.5055	4.5055	0.2600	0.616887
El Sharkawy	-6.6678	6.6678	0.4871	0.537263
Menon	-1.0057	1.0057	0.0111	0.988158

TABLE 6
STATISTICAL ACCRACY OF PSEUDO CRITICAL PRESSURE CORRELATIONS

	ARE, %	AARE%	SD	R^2
This study	**-0.0162**	**0.0565**	**0.0001**	**0.992755**
Standing	-1.1408	1.1408	0.0144	0.374308
Sutton	-1.8299	2.0831	0.0690	0.386013
El Sharkawy	0.3746	1.9384	0.0533	0.48915
Menon	0.0348	0.2217	0.0007	0.951546

*X *is the estimated parameter,* (T_{pc}) *or* $(\boldsymbol{P_{pc}})$

CONCLUSIONS

The proposed correlation showed the best performance for the data analyzed. New correlations have been developed for calculating the pseudo critical pressures and pseudo critical temperatures of sweet natural gas systems with no impurities to a great degree of accuracy. Deviations from experimental values of pseudo critical pressures and pseudo critical temperatures 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 Standings' El Sharkawy's, Sutton's and Menon's correlations. The correlation coefficients of the correlations of this study are closer to one than those of other correlations.

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