Isobaric specific heat capacity of natural gas as a function of specific gravity, pressure and temperature

3 authors:

Lateef A. Kareem
Cyphercrescent
17 PUBLICATIONS **31** CITATIONS

SEE PROFILE

Tajudeen M. Iwalewa
Harvard University
14 PUBLICATIONS **46** CITATIONS

SEE PROFILE

Omeke James
Federal University of Technology Owerri
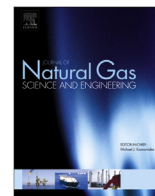**8** PUBLICATIONS **19** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Halley Class solvers for non linear system of equations View project

Multiphase flow in oil and gas wells View project

Isobaric specific heat capacity of natural gas as a function of specific gravity, pressure and temperature

Lateef A. Kareem [a,*], Tajudeen M. Iwalewa [b,1], James E. Omeke [c,2]

[a] Center of Petroleum and Minerals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Eastern Province 31261, Saudi Arabia
[b] Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom
[c] Pioneer-Alpha Petroleum Services Nigeria Limited, Nigeria

ABSTRACT

Natural gas engineering entails production, processing, storage and transportation of natural gas. A good handling of the gas requires a sophisticated understanding of how its density, compressibility, pseudo-pressure and specific heat capacity vary with the gas condition. A variety of methods have been presented in petroleum and gas journals and a host of scholastic materials to evaluate other properties over a wide range of temperatures, however, the available correlation for isobaric specific heat capacity is for only 150 °F. We generated 200 samples of natural gas mixture with methane component ranging from 0.74 to 0.9985 using normally distributed experimental design. The variations of the respective specific heat capacity of the components and the effect of composition on the specific gravity and overall specific heat capacity of the gas were taken into consideration. The developed correlation reads in the specific gravity and temperature to generate the ideal gas specific heat capacity of the sample. The result yielded 99.75% accuracy at 150 °F when compared to experimental data, as against the result from isentropic coefficient method which overestimated the ideal gas specific heat capacity by 25% at the same temperature. The ideal gas specific heat capacity developed compared to 6000 data points generated from mixing rule at different temperatures resulted in correlation regression coefficient of 0.9999. To account for the deviation from ideal gas behaviour, this work presents 99.7% R squared value for dimensionless residual specific heat capacity as a function of reduced temperature and pressure compared to that calculated from Starling Carnahan equation of state. This model is the first explicit correlation for the residual specific heat capacity of natural gas to be derived.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The specific heat capacity of natural gas is the quantity of heat required to raise the temperature of a kilo-mole of natural gas by 1 Kelvin or a Fahrenheit (in field unit). The specific heat capacity is required to calculate the amount of heat energy absorbed or evolved when the temperature of natural gas rises or falls. This requirement makes specific heat capacity vital in the design of intercoolers used between compressors when increasing the pressure of gathered gas to provide the needed energy for transmission through pipelines.

The heat energy accompanying an isobaric (constant pressure) temperature change (Abou-Kassem and Dranchuk, 1982) is given as:

$$\Delta H = n_G \overline{C}_p \Delta T \tag{1}$$

or

$$\Delta H = n_G \int_{T_1}^{T_2} C_p \mathrm{d}T \tag{2}$$

where:

n_G = Number of kilomoles of natural gas
$\overline{C}_p$ = Isochoric average specific heat capacity
ΔT = temperature change

If the temperature change is isochoric (constant volume), the expression becomes:

* Corresponding author. Tel.: +966 138608218; fax: +966 138603989.
  E-mail addresses: adewale@kfupm.edu.sa (L.A. Kareem), tmi21@cam.ac.uk (T.M. Iwalewa), jamitexy2k3@yahoo.com (J.E. Omeke).
  [1] Tel.: +44 7796 722474; fax: +44 (0)1223 333450.
  [2] Tel.: +234 803 206 7676.

$$\Delta H = n_G \overline{C}_v \Delta T \tag{3}$$

or

$$\Delta H = n_G \int_{T_1}^{T_2} C_v dT \tag{4}$$

The expression remains the same except for the isochoric specific heat capacity which replaces its isobaric counterpart. The majority of petroleum and gas journals and textbooks seem to have neglected the necessity of a correlation for specific heat capacity of natural gas. The only available correlation is for isentropic exponent k as a function of specific gravity γ_g at 150 °F from which the isobaric specific heat can be calculated as follows:

$$k^{150°F} = \frac{2.738 - \log\left(\gamma_g\right)}{2.328}, \quad 0.55 < \gamma_g < 1 \tag{5}$$

But,

$$k = \frac{C_p}{C_v} \tag{6}$$

also,

$$C_p = C_v + R \tag{7}$$

Where R is the universal gas constant = 8134 J/kmol K

$$k = \frac{C_p}{C_p - R}$$

$$\frac{1}{k} = 1 - \frac{R}{C_p}$$

$$\frac{R}{C_p} = \frac{k-1}{k}$$

so that,

$$C_p = \frac{kR}{(k-1)} \tag{8}$$

For the fact that Eq. (8) only gives the value of the isobaric specific heat capacity when the temperature is 150 °F, it cannot be used to evaluate the parameter at elevated temperatures. Therefore, there is need for a correlation to that end (Trube, 1957).

2. Assumption

For simplification, it is assumed that natural gases having the same specific gravity have the same constituents in identical proportions. As would be seen later, this assumption simplifies the situation without impacting the result.

For instance, a mixture of 80% methane and 20% ethane has exactly the same specific gravity (0.651) as a mixture of 90% methane and 10% propane. We might expect the specific heat capacity to be different, but the specific heat capacity turned out to be the same at every temperature. Therefore, the specific gravity gives a good representation of the constituent and can be used along with temperature to express the specific heat capacity of an ideal natural gas.

To illustrate this point, data of isobaric specific heat coefficients extracted from Table 1 were used to construct a plot of the specific

Table 1
Constants of the degree three fit of Cp as a function of temperature (Cengel and Boles, 2002).

Compounds	a	b	c	d
Methane (C_1)	19.89	5.024×10^{-2}	1.269×10^{-5}	-11.01×10^{-9}
Ethane (C_2)	6.900	17.27×10^{-2}	-6.406×10^{-5}	7.285×10^{-9}
Propane (C_3)	−4.04	30.48×10^{-2}	-15.72×10^{-5}	31.74×10^{-9}
n-Butane (C_4)	3.96	37.15×10^{-2}	-18.34×10^{-5}	35.00×10^{-9}
i-Butane (C_4)	−7.913	41.60×10^{-2}	-23.01×10^{-5}	49.91×10^{-9}
n-Pentane (C_5)	6.774	45.43×10^{-2}	-22.46×10^{-5}	42.29×10^{-9}
i-Pentane (C_5)	6.774	45.43×10^{-2}	-22.46×10^{-5}	42.29×10^{-9}
n-Hexane (C_6)	6.938	55.22×10^{-2}	-28.65×10^{-5}	57.69×10^{-9}
Heptane+ (C_{7+})	9.118	73.20×10^{-2}	-37.98×10^{-5}	76.47×10^{-9}
Carbon dioxide (CO_2)	22.26	5.981×10^{-2}	-3.501×10^{-5}	7.469×10^{-9}
Nitrogen (N_2)	28.90	0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}

heat capacities of the two mixtures over a temperature range of 50–1550 °C as shown in Fig. 1.

3. Methodology

Certain properties, including pseudo-critical temperature and pseudo-critical pressure, are calculated as the sum of partial pseudo-critical pressures and temperatures of the components of natural gas sample (Abou-kassem & Dranchuk, 1975; Farzaneh-Gord et al., 2010; George and Brown, 1944). These are elucidated in the following mathematical expressions:

$$P_{pc} = \sum_{i=1}^{n} y_i P_{pci} \tag{9}$$

$$T_{pc} = \sum_{i=1}^{n} y_i T_{pci} \tag{10}$$

Moreover, the specific gravity can be expressed in the same way. For instance, consider:

$$\gamma_g = \frac{MW_{gas}}{MW_{air}} = \frac{1}{MW_{air}} \sum_{i=1}^{n} y_i MW_i = \sum_{i=1}^{n} y_i \left(\frac{MW_i}{MW_{air}}\right)$$

Therefore,

$$\gamma_g = \sum_{i=1}^{n} y_i \gamma_{gi}$$

$$C_p = \sum_{i=1}^{n} y_i C_{pi} \tag{11}$$

where C_p is the heat capacity of the natural gas and C_{pi} is the heat capacity of each constituent gas.

The specific heat capacity of a gas at constant pressure is also expressed as degree-3-function of temperature so that:

$$C_p = a + bT + cT^2 + dT^3 \tag{12}$$

Combining Eqs. (11) and (12) results in:

$$C_p = \sum_{i=0}^{n} y_i a_i + T\left(\sum_{i=0}^{n} y_i b_i\right) + T^2\left(\sum_{i=0}^{n} y_i c_i\right) + T^3\left(\sum_{i=0}^{n} y_i d_i\right) \tag{13}$$

Since the mole fraction is used to calculate the specific gravity, the specific heat coefficients a, b, c, and d can be plotted against the
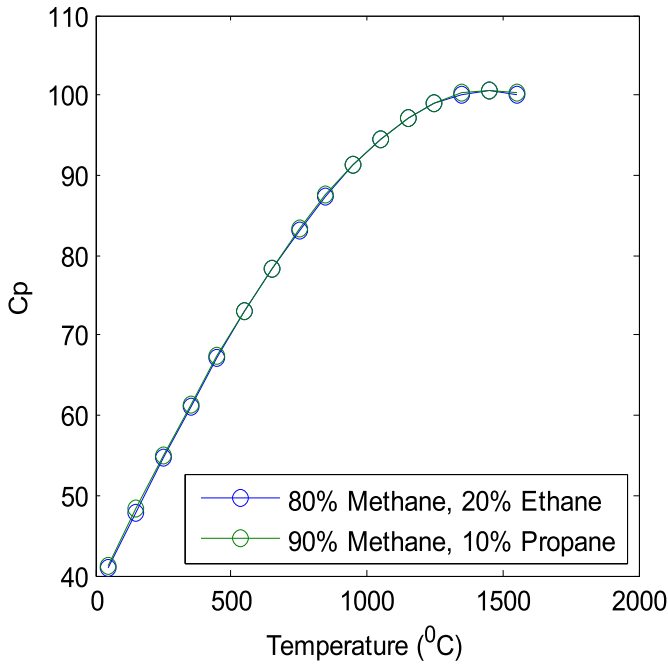
Fig. 1. Comparison of the specific heat capacities of (80% CH$_4$, 20% C$_2$H$_6$) and (90% CH$_4$, 10%C$_3$H$_8$).

specific gravity, because it will carry the information on the mole fraction of the constituent gases.

The following procedures were applied in carrying out this:

1. Qualitative and quantitative analyses of the natural gas samples to identify individual constituents and their respective mole fractions.
2. Evaluation of specific gravity of the natural gas samples.
3. Evaluation of the coefficients (a, b, c and d) of the degree three fit for the samples using the degree three fit coefficients of the constituents and their mole fractions.
4. Generation of linear fit for the coefficients as a function of specific gravity of the samples.
5. Combining the results to form the required expression.

3.1. Results

The linear least square fit for each coefficient gives:

$$a = a_1\gamma_g + a_2 \tag{14}$$

$$b = b_1\gamma_g + b_2 \tag{15}$$

$$c = c_1\gamma_g + c_2 \tag{16}$$

$$d = d_1\gamma_g + d_2 \tag{17}$$

Table 2 gives the estimate of the linear fit for the parameters a, b c and d in terms of the specific gravity, while Figs. 2–5 show the least square linear fits for the parameters a, b, c and d, respectively.

Therefore, Eq. (12) can be rewritten as:

$$C_p = \left(a_1\gamma_g + a_2\right) + \left(b_1\gamma_g + b_2\right)T + \left(c_1\gamma_g + c_2\right)T^2 + \left(d_1\gamma_g + d_2\right)T^3 \tag{18}$$

When these results are combined, then:

Table 2
Constants of linear regression of ideal gas isobaric specific heat capacity degree three coefficients against specific gravity.

Constants	Estimate
a_1	−10.9602
a_2	25.9033
b_1	2.1517×10^{-1}
b_2	-6.8687×10^{-2}
c_1	-1.3337×10^{-4}
c_2	8.6387×10^{-5}
d_1	3.1474×10^{-8}
d_2	-2.8396×10^{-8}

$$
\begin{aligned}
C_p = &\left(-10.9602\gamma_g + 25.9033\right) + \left(2.1517 \times 10^{-1}\gamma_g - 6.8687 \right. \\
&\left. \times 10^{-2}\right)T + \left(-1.3337 \times 10^{-4}\gamma_g + 8.6387 \times 10^{-5}\right)T^2 \\
&+ \left(3.1474 \times 10^{-8}\gamma_g - 2.8396 \times 10^{-8}\right)T^3\left(\frac{kJ}{kmol\ K}\right); \\
&0.55 < \gamma_g < 1 \ \text{and} \ 100\ K < T < 1500\ K
\end{aligned}
\tag{19}
$$

In field units,

$$
\begin{aligned}
C_p = &\left(8.0211\gamma_g + 3.3359\right) + \left(2.0744 \times 10^{-2}\gamma_g - 4.2441 \right. \\
&\left. \times 10^{-3}\right)T + \left(-8.1528 \times 10^{-6}\gamma_g + 4.8536 \times 10^{-6}\right)T^2 \\
&+ \left(1.2887 \times 10^{-9}\gamma_g - 1.1626 \times 10^{-9}\right)T^3 (\text{BTU/lbmol R}); \\
&0.55 < \gamma_g < 1 \ \text{and} \ -280\ {}^\circ F < T < 2240\ {}^\circ F
\end{aligned}
\tag{20}
$$

It is important to note that Eq. (19) has been presented in graphical form in Fig. 6 and this has made it easier than calculation for a quick estimate.
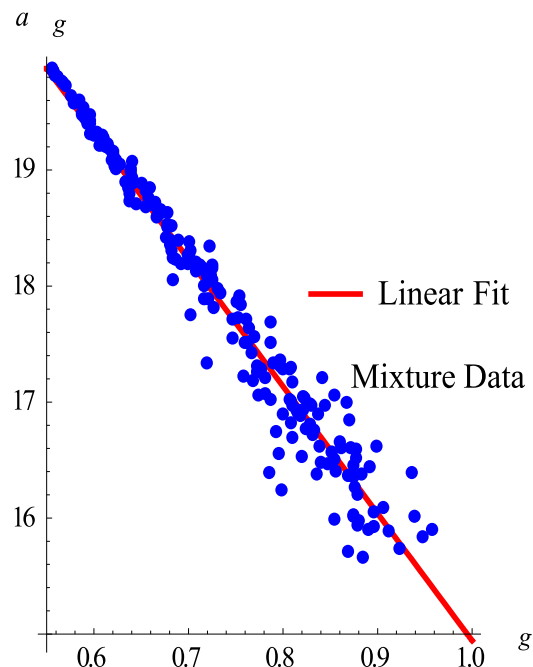

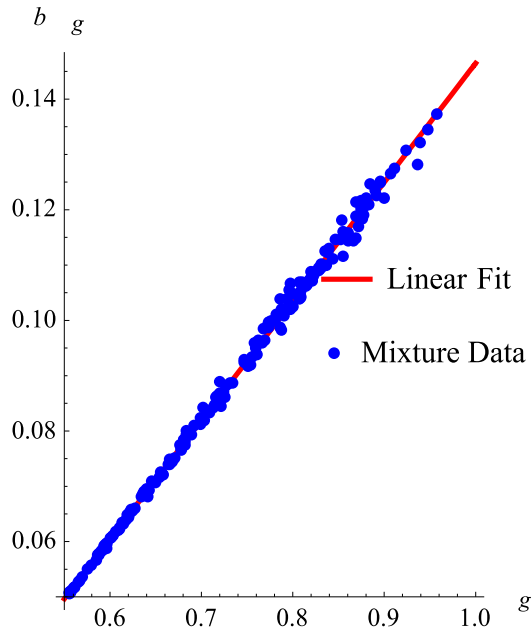**Fig. 2.** Least square fit for specific heat capacity constant a.

Fig. 3. Least square fit for specific heat capacity constant b.

To test the validity of the result, the C_p obtained at 150 °F using the correlation in Eq. (19) was compared with the result obtained from Eq. (13) for the test sample shown in Table 3.

The specific gravity of the sample is evaluated thus:

$$\gamma_g = \frac{MW_{gas}}{MW_{air}} = \frac{1}{MW_{air}} \sum_{i=1}^{n} y_i MW_i = 0.708451$$

The constants (a, b, c and d) of the ideal gas isobaric specific heat capacity are calculated as follows:
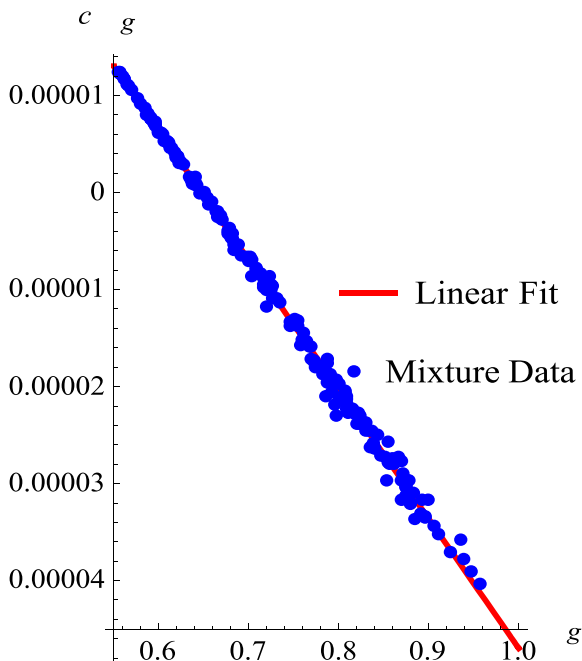
$$a = \sum_{i=0}^{n} y_i a_i = 18.126, \quad b = \sum_{i=0}^{n} y_i b_i = 8.3407 \times 10^{-2}$$

$$c = \sum_{i=0}^{n} y_i c_i = -7.9480 \times 10^{-6}, \quad d = \sum_{i=0}^{n} y_i d_i = -6.1263 \times 10^{-9}$$

$$T = 150\,°F = 324.33\,K$$

$$C_p = a + bT + cT^2 + dT^3$$

$$\begin{aligned}
C_p &= (18.126) + \left(8.3407 \times 10^{-2}\right)(324.33) \\
&\quad + \left(-7.9480 \times 10^{-6}\right)(324.33)^2 + \left(-6.1263 \times 10^{-9}\right)(324.33)^3 \\
&= 44.133 \left(\frac{kJ}{kmol K}\right)
\end{aligned}$$

For gravity gas value of 0.708451, Eq. (7) gives:

$$\begin{aligned}
k^{150°F} &= \frac{2.738 - \log\left(\gamma_g\right)}{2.328} = \frac{2.738 - \log(0.708451)}{2.328} \\
&= 1.17612
\end{aligned}$$

Therefore,

$$\overline{C}_p = \frac{kR}{k-1} = \frac{1.17612 \times 8.314}{1.17612 - 1} = 55.499 \left(\frac{kJ}{kmol\ K}\right)$$

Substituting 0.708451 for γ_g and 324.333 K for T in Eq. (19), therefore:

$$C_p = 44.242 \left(\frac{kJ}{kmol\ K}\right)$$

This result implies an error of 0.25%.

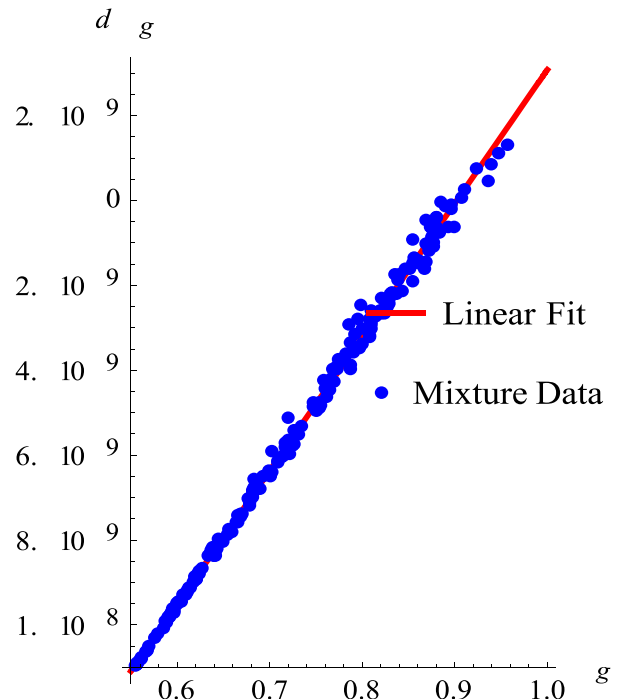**Fig. 4.** Least square fit for specific heat capacity constant c.

Fig. 5. Least square fit for specific heat capacity constant d.

Table 3
Test sample data.

Compounds	Mole fraction
Methane (C_1)	0.8833
Ethane (C_2)	0.0270
Propane (C_3)	0.0203
n-Butane (C_4)	0.0174
i-Butane (C_4)	0.0106
n-Pentane (C_5)	0.0096
i-Pentane (C_5)	0.0087
n-Hexane (C_6)	0.0082
Heptane+ (C_{7+})	0.0068
Carbon dioxide (CO_2)	0.0052
Nitrogen (N_2)	0.0029

By using the chart in Fig. 6, the specific heat capacity of the ideal gas is also estimated as 44 (kJ/kmol K).

4. Validation of the ideal gas specific heat capacity correlation

To validate this correlation, the plot of the ideal isobaric specific heat capacity obtained from the mixing rule shown in Fig. 7 was compared with that obtained from Eq. (19) shown in Fig. 8. In Fig. 9, a cross plot of isobaric specific heat capacity by mixing and correlation shows the nearly unit correlation of the regression coefficient. The statistical analyses in Table 4 denote that the standard deviations of the constants are of 10^2 order less than the value of the constant. The narrow 95% confidence intervals and the P-values indicate that the probabilities that these constants could have been
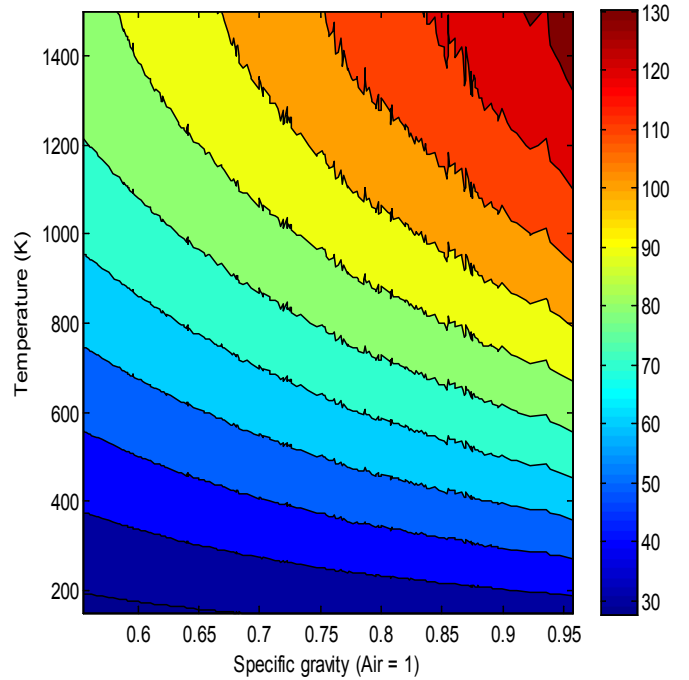

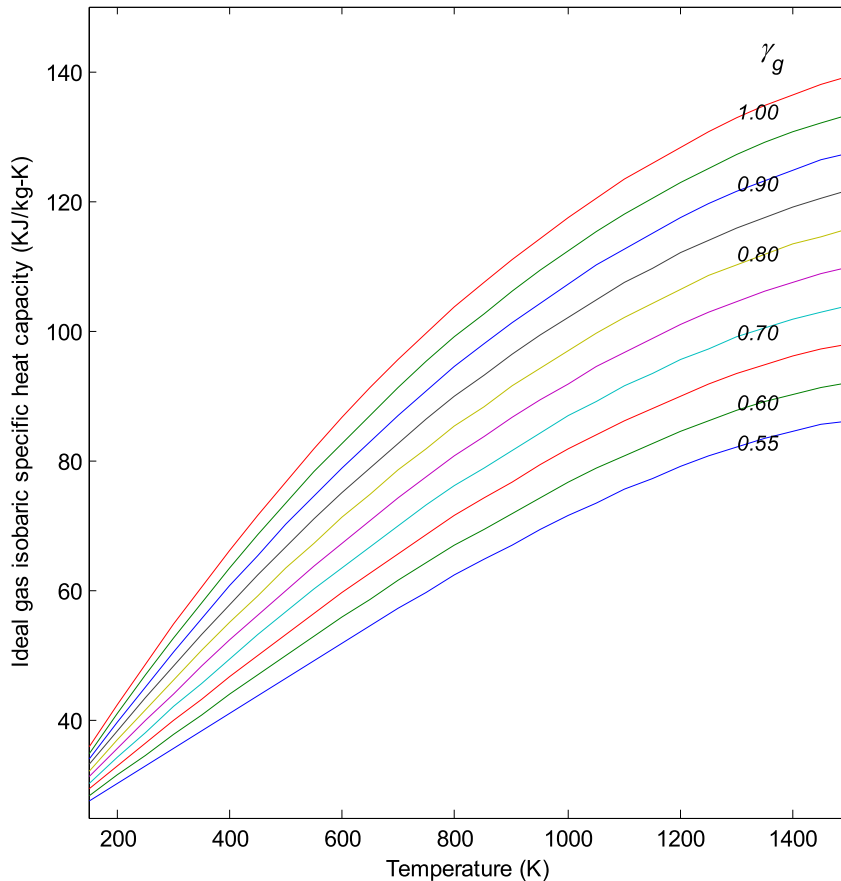**Fig. 7.** Contour plot of the specific heat capacity by mixture law.

Fig. 6. Specific heat capacity chart as a function of temperature and specific gravity.
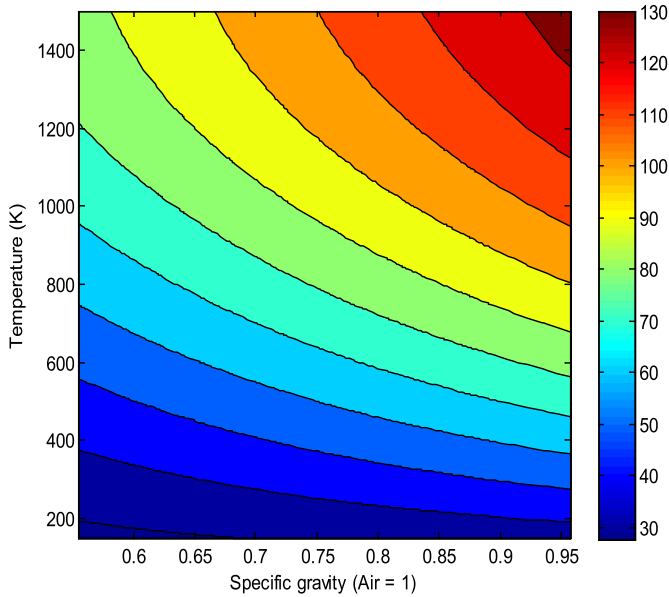
Fig. 8. Contour plot of the specific heat capacity by Eq. (19).

derived by chance are almost zero (Wolberg, 2006). The reliability of this correlation is further confirmed by the analyses in Table 5 such that 6000 data points generated from the mixing rule at different temperatures were utilized for comparison. The result shows a regression coefficient of 99.98% and a very small maximum percentage error.

5. Correction for the effect of pressure

An ideal gas maintains a constant specific heat capacity regardless of its pressure as long as temperature is constant. But natural gas is far from ideal (Abou-kassem & Dranchuk, 1975; Abou-Kassem and Dranchuk, 1982; Dranchuk and Quon, 1964; Farzaneh-Gord et al., 2010; George and Brown, 1944; Goodwin, 1961; Dranchuk et al., 1976; Seifarthi and Joffe, 1952; Weissl and Joffe, 1957; Yorizane et al., 1983). Therefore, the deviation is accounted for by the residual specific heat capacity which is the temperature derivative of the residual enthalpy. To obtain the residual specific heat capacity, the widely accepted Hall and Yarborough z factor
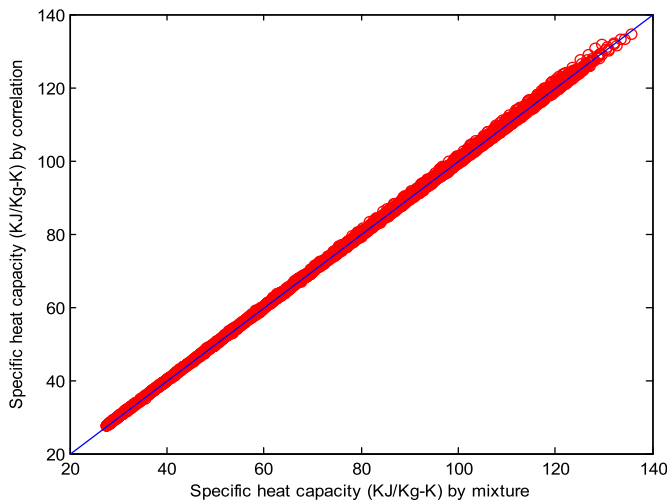

Fig. 9. Cross plot of the mixture C_p against the correlation C_p for an ideal gas.

correlation which is a product of Starling Carnahan equation of state was applied. The mathematical description of the process is as follows:

$$C_{p,\,\text{real}} = \frac{\partial H_{\text{real}}}{\partial T}$$

$$H_{\text{real}} = H_{\text{ideal}} + H_{\text{residual}}$$

$$\begin{aligned}
C_{p,\,\text{real}} &= \frac{\partial (H_{\text{ideal}} + H_{\text{residual}})}{\partial T} \\
&= \frac{\partial H_{\text{ideal}}}{\partial T} + \frac{\partial H_{\text{residual}}}{\partial T} \\
&= C_{p,\,\text{ideal}} + \frac{\partial H_{\text{residual}}}{\partial T}
\end{aligned}$$

$$C_{p,\,\text{residual}} = \frac{\partial H_{\text{residual}}}{\partial T}$$

From thermodynamics of residual properties, we know that:

$$\frac{H_{\text{residual}}}{R} = -T^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right) \frac{\mathrm{d}P}{P}$$

$$\frac{C_{p,\,\text{residual}}}{R} = -\frac{\partial}{\partial T} \left(T^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right) \frac{\mathrm{d}P}{P} \right)$$

The ratio of the residual specific heat capacity to the molar gas constant is the dimensionless residual specific heat capacity.

Using change of variable by putting:

$$P = P_{pc} P_{pr}$$

Therefore,

$$\frac{C_{p,\,\text{residual}}}{R} = -\frac{\partial}{\partial T} \left(T^2 \int_0^{P_{pr}} \left(\frac{\partial Z}{\partial T}\right) \frac{\mathrm{d}P_{pr}}{P_{pr}} \right)$$

Performing the derivative, we have:

$$\frac{C_{p,\,\text{residual}}}{R} = -2T \int_0^{P_{pr}} \left(\frac{\partial Z}{\partial T}\right) \frac{\mathrm{d}P_{pr}}{P_{pr}} - T^2 \int_0^{P_{pr}} \left(\frac{\partial^2 Z}{\partial T^2}\right) \frac{\mathrm{d}P_{pr}}{P_{pr}}$$

Using change of variable by putting:

$$T = T_{pc} T_{pr}$$

Therefore,

$$\frac{C_{p,\,\text{residual}}}{R} = -2T_{pr} \int_0^{P_{pr}} \left(\frac{\partial Z}{\partial T_{pr}}\right) \frac{\mathrm{d}P_{pr}}{P_{pr}} - T_{pr}^2 \int_0^{P_{pr}} \left(\frac{\partial^2 Z}{\partial T_{pr}^2}\right) \frac{\mathrm{d}P_{pr}}{P_{pr}} \quad (21)$$

Using Hall and Yarborough correlation for z factor such that:

$$z = \frac{AP_{pr}}{y}$$

where $A = 0.06125 t e^{-1.2(1-t)^2}$ and y is the root of:

Table 4
Statistical parameters of the constants of correlation of the ideal gas isobaric specific heat capacity.

	Estimate	Standard error	95% Confidence interval	t Statistic	P Value	R^2
P_{pc}	−10.960	1.516×10^{-1}	{−11.259, −10.661}	−72.289	8.849×10^{-144}	0.9637
a_2	25.903	1.123×10^{-1}	{25.681, 26.125}	230.617	1.294×10^{-241}	
b_1	2.151×10^{-1}	7.779×10^{-4}	{2.136×10^{-1}, 2.167×10^{-1}}	276.144	5.567×10^{-257}	0.9974
b_2	-6.869×10^{-2}	5.772×10^{-4}	{-6.983×10^{-2}, -6.755×10^{-2}}	−118.991	1.970×10^{-185}	
c_1	-1.333×10^{-4}	5.033×10^{-7}	{-1.344×10^{-4}, -1.324×10^{-4}}	−264.539	2.564×10^{-253}	0.9972
c_2	8.639×10^{-5}	3.727×10^{-7}	{8.565×10^{-5}, 8.712×10^{-5}}	231.286	7.329×10^{-242}	
d_1	3.147×10^{-8}	1.343×10^{-10}	{3.121×10^{-8}, 3.174×10^{-8}}	234.249	6.028×10^{-243}	0.9964
d_2	-2.839×10^{-8}	9.953×10^{-11}	{-2.859×10^{-8}, -2.820×10^{-8}}	−285.275	9.315×10^{-260}	

$$-AP_{pr} + \frac{y + y^2 + y^3 - y^4}{(1-y)^3} - By^2 + Cy^D = 0 \tag{22}$$

where

$$B = 14.76t - 9.76t^2 + 4.58t^3, \quad C = 90.7t - 242.2t^2 + 42.4t^3,$$
$$D = 2.18 + 2.82t$$

$$t = \frac{T_{pc}}{T}$$

$$\frac{C_{p,\,\text{residual}}}{R} = -t^2 \int_0^{P_{pr}} \left(\frac{\partial^2 Z}{\partial t^2} \right) \frac{dP_{pr}}{P_{pr}}$$

We have:

$$\frac{\partial Z}{\partial t} = \left(\frac{\frac{dA}{dt} y - A \frac{\partial y}{\partial t}}{y^2} \right) P_{pr}$$

$$\frac{\partial^2 Z}{\partial t^2} = \left(\frac{\left(\frac{d^2 A}{dt^2} y^2 + 2A \left(\frac{\partial y}{\partial t} \right)^2 \right) - y \left(A \frac{\partial^2 y}{\partial t^2} - 2 \frac{dA}{dt} \frac{\partial y}{\partial t} \right)}{y^3} \right) P_{pr}$$

Hence,

$$\frac{C_{p,\,\text{residual}}}{R} = -t^2 \int_0^{P_{pr}} \left(\frac{\left(\frac{d^2 A}{dt^2} y^2 + 2A \left(\frac{\partial y}{\partial t} \right)^2 \right) - y \left(A \frac{\partial^2 y}{\partial t^2} + 2 \frac{dA}{dt} \frac{\partial y}{\partial t} \right)}{y^3} \right) dP_{pr} \tag{23}$$

It is impossible to compute the integral analytically; hence, the numerical method was used. At any value of P_{pr} at which the integrand is to be computed, the following procedures were utilized:

1. Compute y from:

$$-AP_{pr} + \frac{y + y^2 + y^3 - y^4}{(1-y)^3} - By^2 + Cy^D = 0 \tag{24}$$

2. Using the value of y from Eq. (24), $\partial y / \partial t$ is computed from:

$$-\frac{dA}{dt} P_{pr} - \frac{dB}{dt} y^2 + \frac{dC}{dt} y^D + \frac{dD}{dt} Cy^D \ln y$$
$$+ \left[\frac{1 + 4y + 4y^2 - 4y^3 + y^4}{(1-y)^4} - 2By + CDy^{D-1} \right] \frac{\partial y}{\partial t} = 0 \tag{25}$$

$$\frac{dA}{dt} = 0.06125 e^{-1.2(1-t)^2} + 0.147 t(1-t) e^{-1.2(1-t)^2}$$

$$\frac{dB}{dt} = 14.76 - 19.52t + 13.74t^2,$$

$$\frac{dC}{dt} = 90.7 - 484.4t + 127.2t^2, \quad \frac{dD}{dt} = 2.82$$

3. Using the values of y and $\partial y / \partial t$ from Eqs. (24) and (25), $\partial^2 y / \partial t^2$ is computed from:

$$-\frac{d^2 A}{dt^2} P_{pr} - \frac{d^2 B}{dt^2} y^2 + \frac{d^2 C}{dt^2} y^D + \frac{d^2 D}{dt^2} Cy^D \ln y + 2\frac{dC}{dt}\frac{dD}{dt} y^D \ln y$$
$$+ \left(\frac{dD}{dt} \ln y \right)^2 Cy^D + 2\left[-2\frac{dB}{dt} y + \frac{dC}{dt} Dy^{D-1} \right.$$
$$+ \left. \frac{dD}{dt} Cy^{D-1}(D \ln y + 1) \right] \frac{\partial y}{\partial t} + \left[\frac{8 + 20y - 4y^2}{(1-y)^5} \right.$$
$$- 2B + CD(D-1)y^{D-2} \left] \left(\frac{\partial y}{\partial t} \right)^2 \right.$$
$$+ \left[\frac{1 + 4y + 4y^2 - 4y^3 + y^4}{(1-y)^4} - 2By + CDy^{D-1} \right] \frac{\partial^2 y}{\partial t^2} = 0 \tag{26}$$

$$\frac{d^2 A}{dt^2} = 0.294(1-t)e^{-1.2(1-t)^2} - 0.147t(1-t)e^{-1.2(1-t)^2}$$
$$+ 0.3528t(1-t)^2 e^{-1.2(1-t)^2}$$

$$\frac{dB}{dt} = -19.52 + 27.48t, \quad \frac{dC}{dt} = -484.4 + 254.4t, \quad \frac{dD}{dt} = 0$$

The logarithmic plot of the dimensionless residual specific heat capacity is plotted with the logarithmic reduced pressure as shown in Fig. 10.

An explicit correlation derived to predict the dimensionless residual specific heat capacity is given as follows:

$$C_{p,\,\text{residual}} = R \left[\frac{\left(1 + \left(a_1 e^{a_2(1-t)^2} P_{pr} t \right)^2 \right)}{\left(a_7 + a_6(P_{pr}t) + a_5(P_{pr}t)^2 + a_4(P_{pr}t)^3 \right)} \right.$$
$$- \left. \frac{\left(a_1 e^{a_2(1-t)^2} P_{pr} t \right)^2 \left(a_3(P_{pr}t)^6 \right)}{\left(a_7 + a_6(P_{pr}t) + a_5(P_{pr}t)^2 + a_4(P_{pr}t)^3 \right)^3} \right];$$
$$1.2 \leq T_{pr} \leq 3 \text{ and } 0.01 \leq P_{pr} \leq 15 \tag{27}$$

where

Table 5
Result of statistical analyses.

Statistical parameter	Value
Correlation of regression	0.999882
Maximum relative error	0.017384
Root mean square of relative error	0.004176

$$P_{pr} = \frac{P}{P_{pc}}, \quad \text{and } t = \frac{T_{pc}}{T}$$

As a function of specific gravity (Air = 1.0), Sutton (1985) provides:

$$P_{pc} = 756.8 - 131.07\gamma_g - 3.6\gamma_g^2$$

$$T_{pc} = 169.2 + 349.5\gamma_g - 74.0\gamma_g^2$$

The values for the constants in Eq. (27) are contained in Table 6. The excellent performance of Eq. (27) is reflected in the comparison of its result to that of Sterling Carnahan as indicated by 99.9% correlation of regression coefficient (Table 7).

The specific heat capacity of natural gas can thus be written as:

$$C_{p,\,real} = C_{p,\,ideal} + C_{p,\,residual}$$

In SI units,

$$R = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$$

In field units,

$$R = 1.9830 \text{ BTU R}^{-1} \text{ lbmol}^{-1}$$

The cross plot in Fig. 11 shows the comparison between Eq. (27) and the Cp residual obtained from Sterling Carnahan equation of state.

6. Examples

In order to demonstrate how the model can be applied, the following examples are provided. Please note that the solutions to Example 1 are provided after each problem, while the solution to Example 2 is provided in subsection 6.2.1.

6.1. Example 1

To calculate the specific heat capacity of a 0.6 gravity natural gas at 5000 psi and 400 °F

1. Determine the pseudo-critical condition

$$P_{pc} = 756.8 - 131.07\gamma_g - 3.6\gamma_g^2 = 676.862$$
$$T_{pc} = 169.2 + 349.5\gamma_g - 74.0\gamma_g^2 = 352.26$$

2. Determine the pseudo-reduced condition

$$T_{pr} = \frac{T}{T_{pc}} = \frac{400 + 460}{352.26} = 2.4414$$

$$t = \frac{1}{T_{pr}} = 0.4096, \quad P_{pr} = \frac{P}{P_{pc}} = \frac{5000}{676.862} = 7.3870$$

3. Determine the ideal isobaric specific heat capacity

$$\begin{aligned}
C_{p,\,ideal} &= \left(8.0211\gamma_g + 3.3359\right) + \left(2.0744 \times 10^{-2}\gamma_g\right. \\
&\quad \left. - 4.2441 \times 10^{-3}\right)T + \left(-8.1528 \times 10^{-6}\gamma_g\right. \\
&\quad \left. + 4.8536 \times 10^{-6}\right)T^2 + \left(1.2887 \times 10^{-9}\gamma_g\right. \\
&\quad \left. - 1.1626 \times 10^{-9}\right)T^3 = 11.3985 \text{ BTU R}^{-1} \text{ lbmol}^{-1}
\end{aligned}$$

4. Determine the residual isobaric specific heat capacity

$$C_{p,\,residual} = 1.986 \times 0.81115 = 1.6109 \text{ BTU R}^{-1} \text{ lbmol}^{-1}$$
$$C_{p,\,real} = 13.0094 \text{ BTU R}^{-1} \text{ lbmol}^{-1}$$

6.2. Example 2

To calculate the amount of heat to be extracted from a 0.6 gravity natural gas at 5000 psi in order to bring its temperature down from 600 °F to 200 °F.

6.2.1. Solution

Because of the complexities of the functions involved, the computation cannot be performed analytically, therefore, the numerical approach was used. The use of Simpson's numerical integration scheme (Canale and Chapra, 2010) can be justified from the fact that the plot of specific heat capacity with temperature (Fig. 12) is nearly quadratic.

1. Take evenly spaced temperatures between 200 °F and 600 °F inclusive and calculate the real gas isobaric specific heat capacities at these points (Table 8);
2. Perform Simpson's integration scheme over the temperature range, thus:

$$\begin{aligned}
\Delta H = \int_{T_1}^{T_2} C_{p,\,real}\,dT &= \frac{50}{3}\left[10.6121 + 4\sum_{i=2}^{4} C_{p,\,real}(2i)\right. \\
&\quad \left. + 2\sum_{i=1}^{3} C_{p,\,real}(2i+1) + 18.0886\right] \\
&= 5343.367 \text{BTU/lbmol}
\end{aligned}$$

Using the Brown's chat (George and Brown, 1944) to evaluate the enthalpy change, therefore:

$$\Delta H = 5500 - 250 = 5250 \text{BTU/lbmol}$$

The result from the new method is within 1.7% of result from Mollier diagram.

If the computation was performed using only the ideal gas specific heat capacity, the result would have been:

$$\Delta H = \int_{T_1}^{T_2} C_{p,\,ideal}\,dT = 4556.691 \text{BTU/lbmol}$$
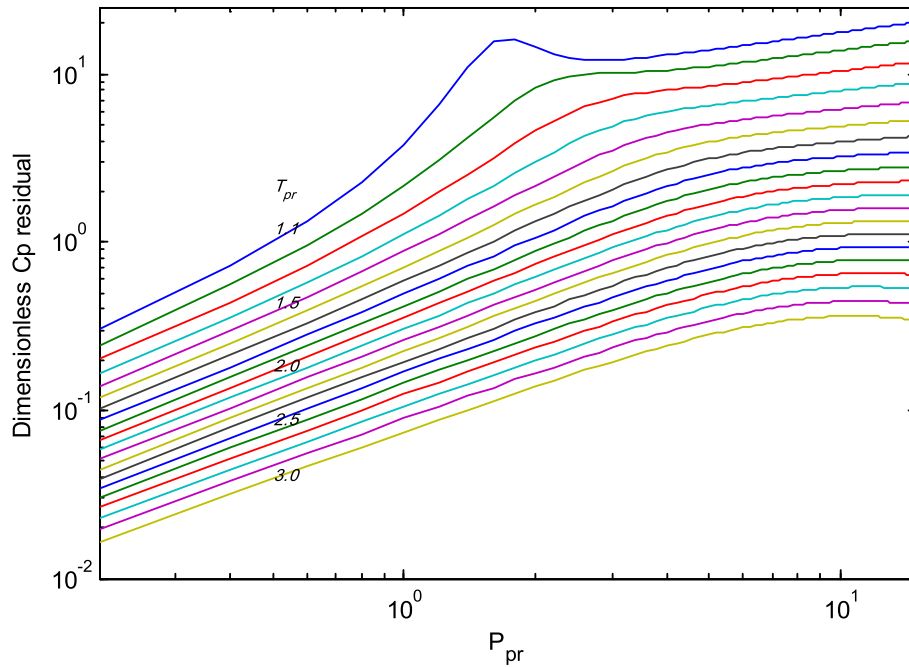
This would be 15% less than the Mollier chart value.

Fig. 10. Logarithm plot C_P residual versus logarithm of P_{pr}.

Table 6
Statistical parameters of the constants of correlation of the residual isobaric specific heat capacity.

	Estimate	Standard error	95% Confidence interval	t–Statistic	P–Value	R^2
a_1	4.80828	0.262652	{4.29305, 5.3235}	18.3066	1.8696×10^{-67}	0.996558
a_2	−4.01563	0.0128387	{−4.04081, −3.99045}	−312.775	5.7659×10^{-1324}	
a_3	−0.0700681	0.030703	{−0.130296, −0.00984063}	−2.28213	2.2628×10^{-2}	
a_4	0.0567	0.0148763	{0.0275183, 0.0858817}	3.81142	1.4401×10^{-4}	
a_5	2.36642	0.246228	{1.88341, 2.84942}	9.61067	3.0867×10^{-21}	
a_6	−3.82421	0.611042	{−5.02284, −2.62558}	−6.2585	5.1196×10^{-10}	
a_7	7.71784	0.674223	{6.39528, 9.04041}	11.447	4.2524×10^{-29}	

7. Conclusions

A robust correlation for isobaric specific heat capacity has been developed. This correlation is in two parts. The first is the ideal gas isobaric specific heat capacity given by Eqs. (19) and (20). The second part is the residual of the isobaric specific heat capacity given by Eq. (27). Eq. (19) has a correlation of regression of 0.9999 and a maximum relative error of 0.04. It is applicable to samples with specific gravity in the range of [0.55, 1.0] and temperature in the range of [100, 1500] K. Eq. (27) has a regression coefficient of 0.997 and maximum relative error of 0.05 compared to the Starling Carnahan equation of state. It is applicable when the pseudo reduced pressure and temperature fall within [0.01, 15] and [1.1, 3], respectively. An exhaustive regression analysis of the constants of the correlations developed was also conducted. The P-values (max = 0.022628) and 95% confidence interval show that the probability that these constants could have been derived by chance is negligible. This correlation gives results in excellent agreement with those obtained from natural gas enthalpy chat (George and Brown, 1944) and can be used in the design of gas transportation system or any other application where the isobaric specific heat capacity of natural gas is a requirement.
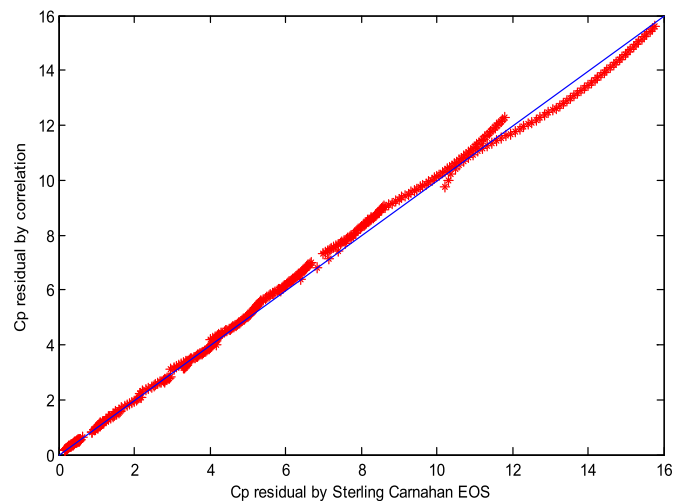
Table 7
Result of statistical analysis of least square fit for the residual specific heat capacity.

Statistical parameter	Value
Correlation of regression	0.9990
Maximum relative error	0.0499
Root mean square of relative error	0.0299

Fig. 11. Cross plot of the residual specific heat capacity by Eq. (27) versus Sterling Carnahan EOS.
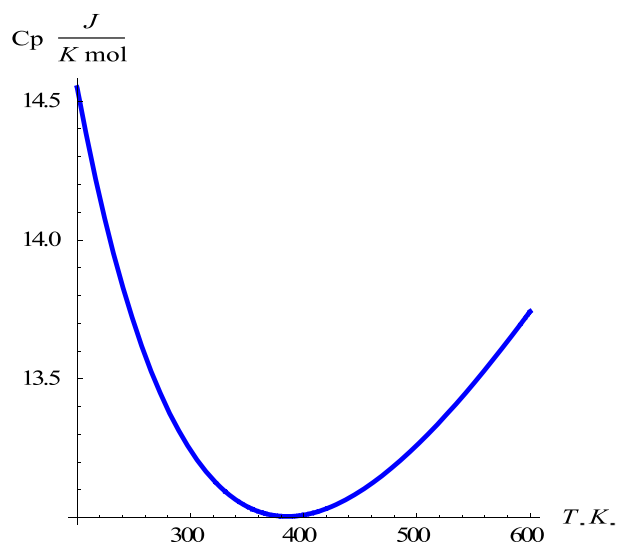
Fig. 12. Plot of real gas isobaric specific heat capacity with temperature.

Table 8
Specific heat capacity of a sample gas at different temperatures ($200 \leq T \leq 600$).

i	Temp °F	$C_{p,\,real}$ BTU R^{-1} lbmol^{-1}	i	Temp °F	$C_{p,\,real}$ BTU R^{-1} lbmol^{-1}
1	200	14.5496	6	450	13.0952
2	250	13.7025	7	500	13.2611
3	300	13.2430	8	550	13.4827
4	350	13.0402	9	600	13.7430
5	400	13.0094			

Acknowledgement

The authors wish to thank the two anonymous reviewers for their constructive criticism, suggestions and advice.

Nomenclature

a	Constant of degree 3 fit for C_p (kJ/kmol K)
b	constant of degree 3 fit for C_p (kJ/Kmol^2 K)
c	constant of degree 3 fit for C_p (kJ/Kmol^3 K)
d	constant of degree 3 fit for C_p (kJ/Kmol^4 K)

C_p	ideal specific heat capacity (kJ/(kmol K) or BTU/(lbmol R))
MW	molecular weight (lb/lbmol or g/gmol)
P	Pressure (psi)
P_{pc}	Pseudo-critical pressure (psi)
P_{pr}	Pseudo-reduced pressure
T	Temperature (K or F)
T_{pc}	Pseudo-critical temperature (R)
T_{pr}	Pseudo-reduced temperature
t	Reciprocal of pseudo-reduced temperature
γ_g	specific gravity of gas (air = 1)

References

Abou-kassem, J.H., Dranchuk, P.M., 1975. Calculation of Z factors for natural gases using equations of state. J. Can. Pet. Technol 14 (3). http://dx.doi.org/10.2118/75-03-03.

Abou-Kassem, J.H., Dranchuk, P.M., 1982. Isobaric heat capacities of natural gases at elevated pressures and temperatures. Proc. SPE Annu. Tech. Conf. Exhib. http://dx.doi.org/10.2523/10980-MS.

Canale, R.P., Chapra, S.C., 2010. Numerical Methods for Engineers, sixth ed. McGraw Hill, New York.

Cengel, Y.A., Boles, M.A., 2002. Thermodynamics: an Engineering Approach, fourth ed. McGraw Hill.

Dranchuk, B.P.M., Quon, D., 1964. A General Solution of the Equations Describing Steady State Turbulent Compressible Flow in Circular Conduits, pp. 60–65.

Dranchuk, P.M., Purvis, R.A., Robinson, D.B., 1976. Computer calculation of natural gas compressibility factors using the standing and Katz correlation. Pet. Soc. CIM.

Farzaneh-Gord, M., Khamforoush, A., Hashemi, S., Namin, H.P., 2010. Computing thermal properties of natural gas by utilizing AGA8 equation of state. Int. J. Chem. Eng. Appl. 1, 20–24 http://dx.doi.org/10.7763/IJCEA. .V1.4.

George, B., Brown, G., 1944. A Series of Enthalpy-entropy Charts for Natural Gases.

Goodwin, R.D., 1961. Apparatus for Determination of Pressure-Density-Temperature Relations and Specific Heats of Hydrogen to 350 Atmospheres at Temperatures Above 14°K, p. 65.

Seifarthi, J.H., Joffe, J., 1952. Isobaric heat capacity of propane. J. Ind. Eng. Chem. 44, 2894–2897.

Sutton, R.P., 1985. Compressibility factor for high- molecular- weight reservoir gases. In: 60th Annual Technical Conference and Exhibition of Society of Petroleum Engineers.

Trube, A., 1957. Compressibility of natural gases. J. Pet. Technol 9. http://dx.doi.org/10.2118/697-G.

Weissl, A., Joffe, J., 1957. Generalized correlation for effect of pressure on isobaric heat capacity of gases. J. Ind. Eng. Chem. 49 (1), 120–124 http://dx.doi.org/10.1021/ie50565a039.

Wolberg, J., 2006. Data Analysis Using the Method of Least Squares: Extracting the Most Information from Experiments, second ed. Springer.

Yorizane, M., Yoshimura, S., Masuoka, H., Yoshida, H., 1983. Thermal Conductivity of Pure Gases at High Pressures by Use of a Coaxial Cylindrical Cell, pp. 454–458.