

Calculation of natural gas isentropic exponent

Ivan Marić^{a,*}, Antun Galović^b, Tomislav Šmuc^a

^aRuder Bošković Institute, Division of Electronics, Laboratory for Information Systems, Bijenička 54, 10002 Zagreb, Croatia

^bFaculty of Mechanical Engineering and Naval Architecture, Department of Thermodynamics, Thermal and Processing Technology, Ivana Lučića 5, 10000 Zagreb, Croatia

Received 21 June 2004; received in revised form 21 September 2004; accepted 11 November 2004

Abstract

A detailed numerical procedure for the calculation of the isentropic exponent of a natural gas is derived. The procedure follows the Redlich–Kwong solution using the AGA8/1992 extended virial-type characterization equation (AGA8-92DC equation) for the determination of the compression factor. The AIChE generic ideal heat capacity equations are used to derive the molar heat capacities of the natural gas mixture. The compression factor and its derivatives are calculated on the basis of ISO-12213-2. Two calculation examples are given and the results are graphically illustrated. The calculation procedure is implemented in a digital computer using an object-oriented programming approach. The effect of the isentropic exponent on the accuracy of orifice-based flow-rate measurements is demonstrated and discussed.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Isentropic exponent; Molar heat capacity; Fugacity; Natural gas; Compression factor

1. Introduction

When using differential pressure devices to measure gas flow-rate, an ‘adiabatic correction factor’ has to be applied to the flow-rate equation to compensate for various imperfections of the ideal, one-dimensional flow equation and frictional effects within the device. The isentropic exponent has a limited effect on the adiabatic correction factor but should nevertheless be accurately calculated to reduce uncertainties in high pressure applications. When forced to flow through the reduced area of a differential pressure measurement device the gas expands to a lower pressure. Supposing both a short expansion length and a small pressure difference, one might assume an ideal one-dimensional isentropic expansion. Upon these assumptions the relations between pressures and volumes are defined

as follows

$$\frac{p_1}{p_2} = \left(\frac{V_2}{V_1} \right)^\kappa = \left(\frac{\rho_1}{\rho_2} \right)^\kappa, \quad (1)$$

where (p_1, V_1, ρ_1) and (p_2, V_2, ρ_2) are the upstream and downstream pressures, volumes and densities of the gas, respectively, and the exponent κ is the isentropic exponent. The calculation of the isentropic exponent depends on whether the gas is assumed to be ideal ($\kappa = c_p/c_v$) or real. In cases of extreme pressures and temperatures, however, the real gas isentropic exponent should be calculated since it can deviate markedly from c_p/c_v . Sullivan [1] proposed several isentropic flow models that predict the isentropic exponent from the equations of state. It was pointed out that in applications where precision is of utmost importance such as flow metering, non-ideal or “real gas” effects should be considered. The Redlich–Kwong solution is based on the derivation of the gas fugacity from a two-parameter compression factor equation and its first and second derivatives [2,3]. Paper [4] describes the procedure for the calculation of the natural gas isentropic exponent based on the Redlich–Kwong approach and the AGA8/1985 equation of state.

* Corresponding address: Ruder Bošković Institute, Division of Electronics, Laboratory for Information Systems, Bijenička c. 54, P.O.B. 180, 10002 Zagreb, Croatia. Tel.: +385 1 4561191; fax: +385 1 4680114.

E-mail address: ivan.maric@irb.hr (I. Marić).

2. Method

The following procedure is based on the Redlich–Kwong approach. It uses the high accuracy AGA8/1992 [5] extended virial type characterization equation adopted by the International standard ISO12213-2 [6] instead of the low accuracy Redlich–Kwong two-parameter equation of state. The AGA8/1992 equation of state is combined with the AIChE 1986 [7] generic ideal heat capacity equations to derive the expressions necessary to calculate the isentropic exponent. The isentropic exponent κ of a real gas is defined by

$$\kappa = -\frac{c_p}{c_v} \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{v}{p} \right), \quad (2)$$

where c_p and c_v are the corresponding molar heat capacities of the gas at constant pressure and constant volume, while p and v are the pressure and specific volume. The molar heat capacity c_p is defined by

$$c_p = c_{pI} - RT(T\Phi'' + 2\Phi'), \quad (3)$$

where Φ' and Φ'' are the first and the second derivatives of the gas fugacity coefficient, R is the molar gas constant and c_{pI} is the ideal molar heat capacity of a gas mixture at flowing temperature T , respectively. The molar heat capacity c_v is

$$c_v = c_p - Mpv\alpha\beta T \quad (4)$$

where M denotes the molar mass of a gas mixture while α and β are

$$\alpha = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_v \quad (5)$$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p. \quad (6)$$

The ideal molar heat capacity c_{pI} is calculated by

$$c_{pI} = \sum_{j=1}^N y_j c_{pi}^j \quad (7)$$

where y_j is the component j molar fraction of the gas mixture and c_{pi}^j is the molar heat capacity of the same component at flowing temperature. The molar heat capacities of the ideal gas mixture components can be approximated by polynomials, or using the equations of AIChE 1986 [7], i.e.

$$c_{pi}^j = a_j + b_j \exp\left(-\frac{c_j}{T_K^{d_j}}\right), \quad (8)$$

where c_{pi}^j is the molar heat capacity of the component j of the ideal gas mixture, a_j , b_j , c_j and d_j are the corresponding constants, and T_K is the flowing temperature. The constants a , b , c and d for some gases are shown in Table 1.

The fugacity coefficient of a real gas is defined by

$$\Phi = \int_0^p (Z - 1) \frac{dp}{p}, \quad (9)$$

Table 1
The AIChE gas heat capacity constants

Gas	AIChE constants			
	a	b	c	d
Methane—CH ₄	3.3106×10^4	9.9975×10^4	2.3380×10^3	1.1347
Ethane—C ₂ H ₆	3.8380×10^4	1.7500×10^5	8.4350×10^2	1.0204
Propane—C ₃ H ₈	4.7497×10^4	2.4670×10^5	6.9858×10^2	1.0074

where Z , p and p_f are the gas compression factor, pressure variable and flowing or operating pressure, respectively.

To compute the isentropic exponent Eqs. (2)–(9) should be solved. The following equations, derived by means of the AGA8/1992 extended virial type characterization equation, enable the solution to the problem.

According to AGA8/1992 [5] and ISO-12213-2/1997 [6], the equation of state for the compression factor of natural gas is

$$Z = 1 + B\rho_m - \rho_r \sum_{n=13}^{18} C_n^* + \sum_{n=13}^{58} C_n^* D_n^*, \quad (10)$$

where

$$D_n^* = (b_n - c_n k_n \rho_r^{k_n}) \rho_r^{b_n} e^{-c_n \rho_r^{k_n}}, \quad (11)$$

and ρ_m is the gas mixture molar density, ρ_r is the reduced density, B is the second virial coefficient and $\{C_n^*\}$ are the temperature dependent coefficients, while $\{b_n\}$, $\{c_n\}$ and $\{k_n\}$ are the equation of state parameters given in ISO-12213-2/1997. The gas molar density ρ_m and reduced density ρ_r are defined by

$$\rho_m = \frac{p}{RTZ}, \quad (12)$$

and

$$\rho_r = K^3 \rho_m, \quad (13)$$

where p , T and R are pressure, temperature and molar gas constant R , respectively. The mixture size parameter K is calculated using the following equation:

$$K^5 = \left(\sum_{i=1}^N y_i K_i^{5/2} \right)^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N y_i y_j (K_{ij}^5 - 1) (K_i K_j)^{5/2}, \quad (14)$$

where y_i denotes the molar fraction of the component i , while $\{K_i\}$ and $\{K_{ij}\}$ are the corresponding size parameters and the binary interaction parameters given in ISO-12213-2/1997. The second virial coefficient is calculated using the following equation:

$$B = \sum_{n=1}^{18} a_n T^{-u_n} \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{nij}^* E_{ij}^{u_n} (K_i K_j)^{3/2} \quad (15)$$

and the coefficients $\{B_{nij}^*\}$, $\{E_{ij}\}$ and $\{G_{ij}\}$ are defined by the following equations

$$B_{nij}^* = (G_{ij} + 1 - g_n)^{g_n} (Q_i Q_j + 1 - q_n)^{q_n} \times (F_i^{1/2} F_j^{1/2} + 1 - f_n)^{f_n} \cdot (S_i S_j + 1 - s_n)^{s_n} \times (W_i W_j + 1 - w_n)^{w_n}, \quad (16)$$

$$E_{ij} = E_{ij}^* (E_i E_j)^{1/2}, \quad (17)$$

and

$$G_{ij} = G_{ij}^* (G_i + G_j)/2, \quad (18)$$

where T is temperature, N is the total number of gas mixture components, y_i is the molar fraction of the component i , $\{a_n\}$, $\{f_n\}$, $\{g_n\}$, $\{q_n\}$, $\{s_n\}$, $\{u_n\}$ and $\{w_n\}$ are the equation of state parameters, $\{E_i\}$, $\{F_i\}$, $\{G_i\}$, $\{K_i\}$, $\{Q_i\}$, $\{S_i\}$ and $\{W_i\}$ are the corresponding characterization parameters while $\{E_{ij}^*\}$ and $\{G_{ij}^*\}$ are the corresponding binary interaction parameters. The temperature dependent coefficients $\{C_n^*; n = 1, \dots, 58\}$ are defined by the following relation:

$$C_n^* = a_n (G + 1 - g_n)^{g_n} (Q^2 + 1 - q_n)^{q_n} \times (F + 1 - f_n)^{f_n} U^{u_n} T^{-u_n}, \quad (19)$$

and the mixture parameters U , G , Q and F are calculated using the following equations:

$$U^5 = \left(\sum_{i=1}^N y_i E_i^{5/2} \right)^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N y_i y_j (U_{ij}^5 - 1) (E_i E_j)^{5/2}, \quad (20)$$

$$G = \sum_{i=1}^N y_i G_i + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N y_i y_j (G_{ij}^* - 1) (G_i + G_j), \quad (21)$$

$$Q = \sum_{i=1}^N y_i Q_i, \quad (22)$$

and

$$F = \sum_{i=1}^N y_i^2 F_i, \quad (23)$$

where U_{ij} is the binary interaction parameter for mixture energy.

The derived equations for the first and the second derivatives of the Eqs. (12), (13), (15), (19) and (11) with respect to temperature are

$$\rho_m' = -\frac{p}{R} \cdot \frac{Z + TZ'}{(TZ)^2} \quad (24)$$

$$\rho_m'' = \frac{p}{R} \cdot \frac{2(Z + TZ')^2 - TZ(2Z' + TZ'')}{(TZ)^3} \quad (25)$$

$$\rho_r' = K^3 \rho_m' \quad (26)$$

$$\rho_r'' = K^3 \rho_m'' \quad (27)$$

$$B' = -\sum_{n=1}^{18} a_n u_n T^{-u_n-1} \times \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{nij}^* E_{ij}^{u_n} (K_i K_j)^{3/2} \quad (28)$$

$$B'' = \sum_{n=1}^{18} a_n u_n (u_n + 1) T^{-u_n-2} \times \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{nij}^* E_{ij}^{u_n} (K_i K_j)^{3/2} \quad (29)$$

$$C_n^{*'} = -a_n u_n (G + 1 - g_n)^{g_n} (Q^2 + 1 - q_n)^{q_n} \times (F + 1 - f_n)^{f_n} U^{u_n} T^{-u_n-1} = -\frac{u_n}{T} C_n^* \quad (30)$$

$$C_n^{*''} = a_n u_n (u_n - 1) (G + 1 - g_n)^{g_n} (Q^2 + 1 - q_n)^{q_n} \times (F + 1 - f_n)^{f_n} U^{u_n} T^{-u_n-2} = \frac{u_n(u_n + 1)}{T^2} C_n^* = -\frac{u_n + 1}{T} C_n^{*'} \quad (31)$$

$$D_n^{*'} = D_{1n} \rho_m' \quad (32)$$

$$D_n^{*''} = D_{1n} \rho_m'' + D_{2n} \rho_m'^2 \quad (33)$$

where

$$D_{1n} = K^3 [b_n^2 - c_n k_n (2b_n + k_n - c_n k_n \rho_r^{k_n}) \rho_r^{k_n}] \times \rho_r^{b_n-1} e^{-c_n \rho_r^{k_n}} \quad (34)$$

and

$$D_{2n} = K^3 \left\{ D_{1n} [(b_n - 1) \rho_r^{-1} + k_n \rho_r^{-1} (1 - c_n \rho_r^{k_n})] + K^3 k_n (c_n^2 k_n^2 \rho_r^{2k_n} - b_n^2) \rho_r^{b_n-2} e^{-c_n \rho_r^{k_n}} \right\}. \quad (35)$$

After substituting Eq. (13) in (10), the first derivative of the compression factor with respect to temperature is

$$Z' = \rho_m' \left(B - K^3 \sum_{n=13}^{18} C_n^* + \sum_{n=13}^{58} C_n^* D_{1n} \right) + \rho_m \left(B' - K^3 \sum_{n=13}^{18} C_n^{*'} \right) + \sum_{n=13}^{58} C_n^{*'} D_n^*. \quad (36)$$

Substituting Eqs. (12) and (24) in (36) results in

$$Z' = \frac{R(TZ)^2 \sum_{n=13}^{58} C_n^{*'} D_n^* + pZ(TZ'_0 - Z_1)}{R(TZ)^2 + pTZ_1}, \quad (37)$$

where Z_0 , Z'_0 and Z_1 are

$$Z_0 = B - K^3 \sum_{n=13}^{18} C_n^* \quad (38)$$

$$Z'_0 = B' - K^3 \sum_{n=13}^{18} C_n^{*'} \quad (39)$$

$$Z_1 = Z_0 + \sum_{n=13}^{58} C_n^* D_{1n}. \quad (40)$$

The second derivative of the compression factor with respect to temperature is

$$\begin{aligned} Z'' = & \rho_m'' \left(B - K^3 \sum_{n=13}^{18} C_n^* + \sum_{n=13}^{58} C_n^* D_{1n} \right) \\ & + 2\rho_m' \left(B' - K^3 \sum_{n=13}^{18} C_n^{*'} + \sum_{n=13}^{58} C_n^{*'} D_{1n} \right) \\ & + \rho_m'^2 \sum_{n=13}^{58} C_n^* D_{2n} + \rho_m \left(B'' - K^3 \sum_{n=13}^{18} C_n^{*''} \right) \\ & + \sum_{n=13}^{58} \left(C_n^{*''} D_n^* \right). \end{aligned} \quad (41)$$

Substituting Eqs. (12), (24) and (25) in (41), we obtain

$$\begin{aligned} Z'' = & \frac{1}{R(TZ)^3 + PT^2ZZ_1} \left\{ 2pZ_1[(Z + TZ')^2 - TZZ'] \right. \\ & - 2pTZ \left(Z'_0 + \sum_{n=13}^{58} C_n^{*'} D_{1n} \right) (Z + TZ') \\ & + \frac{[p(Z + TZ')]^2}{RTZ} \sum_{n=13}^{58} C_n^* D_{2n} + p(TZ)^2 Z''_0 \\ & \left. + R(TZ)^3 \sum_{n=13}^{58} C_n^{*''} D_n^* \right\} \end{aligned} \quad (42)$$

where Z''_0 is

$$Z''_0 = B'' - K^3 \sum_{n=13}^{18} C_n^{*''}. \quad (43)$$

Eqs. (5) and (6) become

$$\begin{aligned} \alpha = & \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_v = \frac{1}{p} \left(\frac{\partial(RTZ\rho_m)}{\partial T} \right)_v \\ = & \frac{R\rho_m}{p} \left[Z + T \left(Z'_0\rho_m + \sum_{n=13}^{58} C_n^{*'} D_n^* \right) \right] \end{aligned} \quad (44)$$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{Mp v} (Z + Z'T). \quad (45)$$

The partial derivative of pressure with respect to specific volume can be written as

$$\begin{aligned} \left(\frac{\partial p}{\partial v} \right)_T = & \left(\frac{\partial p}{\partial \rho_m} \right)_T \left(\frac{\partial \rho_m}{\partial v} \right)_T = -MRT\rho_m^2 \\ & \times \left[Z + \rho_m \left(B - K^3 \sum_{n=13}^{18} C_n^* + \sum_{n=13}^{58} C_n^* D_{1n} \right) \right], \end{aligned} \quad (46)$$

where M denotes the molar mass of a gas mixture and D_{1n} is defined by (34). The molar mass is calculated by

$$M = \sum_{i=1}^N y_i M_i, \quad (47)$$

where y_i and M_i are the molar fraction and the molar mass of the component i in the gas mixture, respectively. The

specific volume v and the gas mixture molar density ρ_m are related by

$$v = \frac{1}{M\rho_m}. \quad (48)$$

The fugacity coefficient, defined by (9), and its derivatives with respect to T are

$$\begin{aligned} \Phi = & \int_0^p (Z - 1) \frac{dp}{p} = Z - 1 - \ln Z + Z_0\rho_m \\ & + \sum_{n=13}^{58} C_n^* \rho_r^{b_n} e^{-c_n \rho_r^{k_n}} \end{aligned} \quad (49)$$

$$\begin{aligned} \Phi' = & \left(\frac{\partial \Phi}{\partial T} \right) = Z' \left(1 - \frac{1}{Z} \right) + \rho_m Z'_0 + Z_0 \rho_m' \\ & + \sum_{n=13}^{58} C_n^{*'} \rho_r^{b_n} e^{-c_n \rho_r^{k_n}} + \frac{\rho_r'}{\rho_r} \sum_{n=13}^{58} C_n^* D_n^* \end{aligned} \quad (50)$$

and

$$\begin{aligned} \Phi'' = & \left(\frac{\partial \Phi'}{\partial T} \right) \\ = & Z'' \left(1 - \frac{1}{Z} \right) + \frac{Z'^2}{Z^2} + 2Z'_0 \rho_m' + \rho_m Z''_0 + Z_0 \rho_m'' \\ & + \sum_{n=13}^{58} C_n^{*''} \rho_r^{b_n} e^{-c_n \rho_r^{k_n}} + 2\rho_r' \rho_r^{-1} \sum_{n=13}^{58} C_n^{*'} D_n^* \\ & + \rho_r^{-2} \left(\rho_r'' \rho_r - \rho_r'^2 \right) \sum_{n=13}^{58} C_n^* D_n^* \\ & + K^{-3} \rho_r'^2 \rho_r^{-1} \sum_{n=13}^{58} C_n^* D_{1n}. \end{aligned} \quad (51)$$

The following section summarizes the programming implementation of the calculation of natural gas isentropic exponent using Eqs. (2)–(51). It also describes the interface to the software object, which implements the procedure.

3. OOP implementation

Table 2 outlines the procedure for natural gas isentropic exponent solution. Prior to the calculation of the isentropic exponent, the compression factor of natural gas must be calculated, as described in AGA8/1992. The false position method has been used to find the roots of the equation of state. In the instances when the false position method did not converge, the successive bisection method has been employed. Object-oriented realization of the measurement standards and calculation procedures [8] enables their easy integration into the measurement system. Fig. 1 illustrates the interface to the software object S , which calculates the isentropic exponent, compression factor and other related parameters based on AGA8 [5] and ISO12213-2 [6]. The object function *Calculate* maps the input into the output parameters.

Table 2

The input/output parameters and the calculation sequence for the computation of the natural gas isentropic exponent

Input parameters—constant:

- molar gas constant ($R = 8314.51 \text{ J}/(\text{kmol K})$)
- natural gas equation of state parameters ($a_n, b_n, c_n, k_n, u_n, g_n, q_n, f_n, s_n, w_n; n = 1, 2, \dots, 58$), characterization parameters ($M_i, E_i, K_i, G_i, Q_i, F_i, S_i, W_i; i = 1, \dots, 21$) and binary interaction parameters ($E_{ij}^*, U_{ij}, K_{ij}, G_{ij}^*; i = 1, 2, \dots, 21, j = 1, 2, \dots, 21$) (see ISO 12213-2)
- AIChE gas heat capacity constants ($a_i, b_i, c_i, d_i; i = 1, 2, \dots, N$)

Input parameters—time varying:

- absolute pressure: p [MPa]
- absolute temperature: T [K]
- molar fractions of the natural gas mixture: $y_i; i = 1, 2, \dots, N$

Calculation sequence:

1. molar mass of a gas mixture M (Eq. (47))
2. mixture size parameter K (Eq. (14)), second virial coefficient B (Eqs. (15)–(18)) and temperature dependent coefficient C_n^* (Eqs. (19)–(23))
3. compression factor Z (Eq. (10)) (see ISO-12213-2 for details of calculation)
4. molar density ρ_m (Eq. (12)) and reduced density ρ_r (Eq. (13))
5. coefficients D_n^*, D_{1n} and D_{2n} (Eqs. (11), (34) and (35), respectively)
6. specific volume v (Eq. (48))
7. 1st and 2nd derivative of the second virial coefficient B : B' (Eq. (28)) and B'' (Eq. (29))
8. 1st and 2nd derivative of the coefficient C_n^* : $C_n^{*'} (Eq. (30))$ and $C_n^{*''} (Eq. (31))$
9. 1st and 2nd derivative of the comparison factor Z : Z' (Eq. (37)) and Z'' (Eq. (42))
10. 1st and 2nd derivative of the molar density ρ_m : ρ_m' (Eq. (24)) and ρ_m'' (Eq. (25))
11. 1st and 2nd derivative of the reduced density ρ_r : ρ_r' (Eq. (26)) and ρ_r'' (Eq. (27))
12. coefficients α (Eq. (44)) and β (Eq. (45)) and partial derivative $(\partial p/\partial v)_T$ (Eq. (46))
13. 1st and 2nd derivative of the fugacity Φ : Φ' and Φ'' (Eqs. (50) and (51))
14. ideal molar heat capacity of a gas mixture: c_{pI} (Eqs. (7) and (8))
15. molar heat capacity of a gas mixture at constant pressure: c_p (Eq. (3))
16. molar heat capacity of a gas mixture at constant volume: c_v (Eq. (4))
17. fugacity coefficient Φ (Eq. (49))
18. isentropic exponent κ (Eq. (2))

4. Results and discussion

The natural gas isentropic exponent calculation procedure, outlined in Table 2, has been embedded into the software object (COM object), which can be easily included into the new software developments either locally or as a remote component. The procedure is applicable to the natural gas mixtures satisfying the restrictions given in ISO12213/2 [6]. The main program accepts the natural gas composition and the values of the flowing pressure and temperature as the input variables, initiates the object function and retrieves the results. The composition of the gas can be given in any of the three forms including molar, volume or mass fractions. If the composition is given in volume or mass fractions they are converted into the corresponding molar fractions before they are written into the COM object.

The isentropic exponents for both the pure methane and the hypothetical natural gas mixture have been calculated and the results are given in Figs. 2 and 3. Fig. 2 presents a graphical interpretation of the calculated isentropic exponents for methane in the range of pressure from 0 to 50 MPa in 1 MPa steps and for six discrete temperatures in the range from 245 to 345 K. Figs. 2 and 3 clearly show a minor effect of temperature on the isentropic exponent of methane for the pressures up to approximately 3.5 MPa.

In this particular interval the value of κ increases slightly with the decrease of temperature and is a little above the value 1.3, which corresponds to the value of the isentropic exponent of methane when considering it as an ideal gas. By following the curves one can also conclude that, for each particular pressure, the value of the isentropic exponent always increases when decreasing the temperature. That means that the value of the partial derivative $(\partial p/\partial v)_T$ in Eq. (2) strictly decreases when decreasing the temperature. This is physically comprehensible, because all the considered temperatures are higher than the critical temperature for methane ($T_{cr} = 191.1 \text{ K}$; $p_{cr} = 4.64 \text{ MPa}$). By positioning the analyzed temperatures into the available pressure–enthalpy (p, h) diagram one can conclude that the lowest temperature $T = 245 \text{ K}$ and the pressure $P = 50 \text{ MPa}$ correspond to the methane in liquid state (compressed liquid), while the highest temperature $T = 345 \text{ K}$ and pressure $P = 50 \text{ MPa}$ correspond to the gas phase. Therefore, the results obtained at higher temperatures and pressures, at which the state of the methane corresponds to the superheated vapor with the properties of real gas, are also expected. However, with sufficient pressure decrease, all the methane states in the selected temperature range correspond to the superheated vapor that could be considered as ideal gas with the isentropic exponent approximately the same

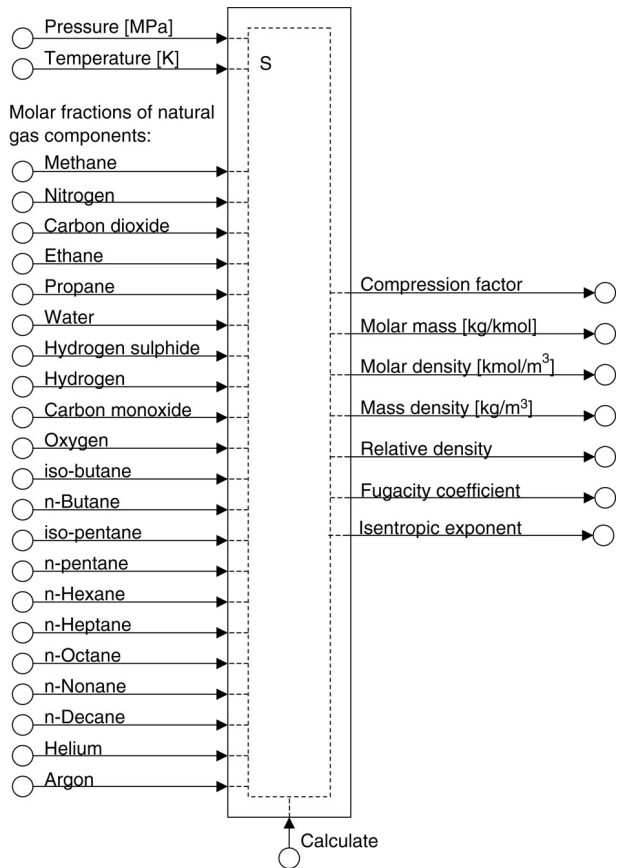


Fig. 1. Interface to the software object, which implements the calculation of the isentropic exponent and the natural gas properties in accordance with ISO12213-2.

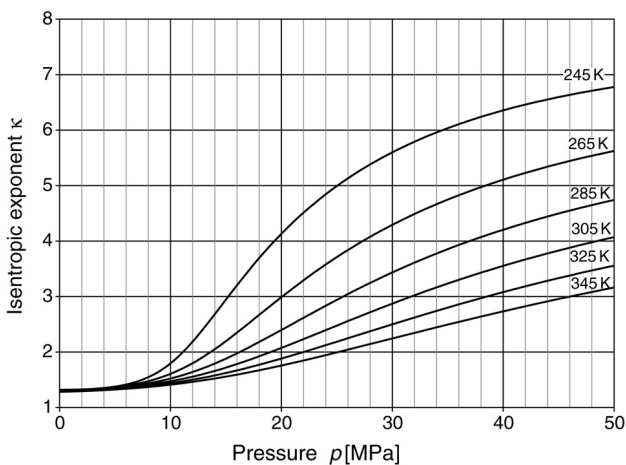


Fig. 2. Isentropic exponent κ for methane for pressures from 0 to 50 MPa and temperatures from 245 to 345 K.

for all temperatures. At these conditions Eq. (2) transforms into the well known equation for the isentropic exponent of the ideal gas $\kappa = c_p/c_v$. Thus, the applied mathematical model describes the behavior of the isentropic exponent from the liquid to superheated vapor states for supercritical temperatures.

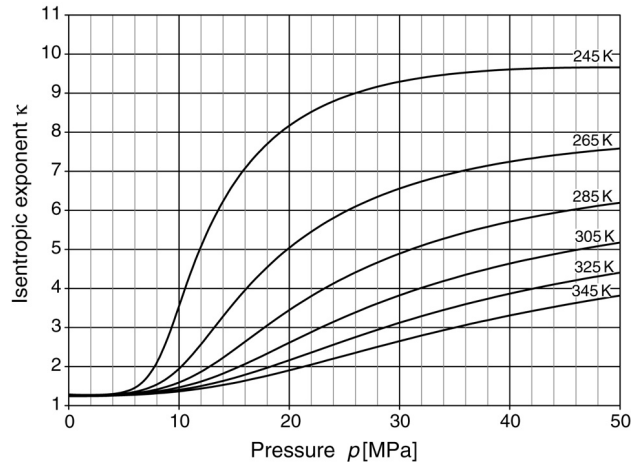


Fig. 3. Isentropic exponent κ for hypothetical natural gas mixture with the following molar fractions: 0.8—methane, 0.15—ethane and 0.05—propane and for pressures from 0 to 50 MPa and temperatures from 245 to 345 K.

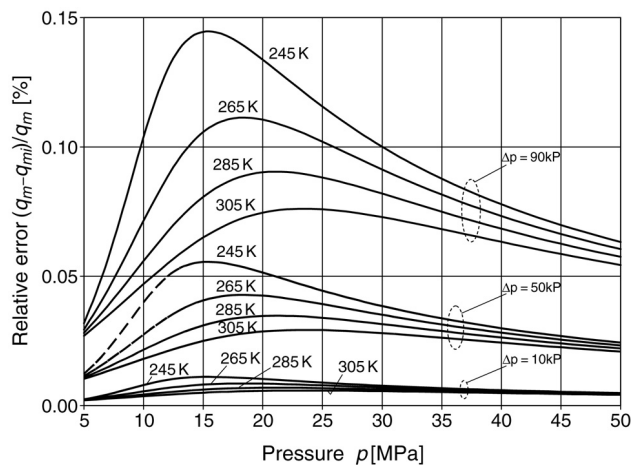


Fig. 4. Relative error in the flow-rate of methane $E = (q - q_i)/q$ measured by an orifice plate with corner tapplings when using the isentropic exponent of real gas (q) instead of ideal gas (q_i). The pressure p varies from 5 to 50 MPa in 1 MPa steps, temperature T from 245 to 305 K in 20 K steps and the differential pressure Δp from 10 to 90 kPa in 40 kPa steps.

Similarly, Fig. 3 presents calculations for the hypothetical natural gas mixture (molar percentages: 80% methane 15% ethane, and 5% propane) in the range of pressure from 0 to 50 MPa in 1 MPa steps and for six discrete temperatures in the range from 245 to 345 K. The obtained results are a considerable improvement on the results obtained in [4] or by using the Redlich–Kwong compression factor equation. This is primarily due to the high accuracy of the compression factor calculation when using the AGA8/1992 equation. The outlined procedure (Table 2) is computationally intensive but, nevertheless, is easily programmed on a digital computer. Since microprocessors have become a common part of the advanced measuring instruments, the implementation of such a computational procedure in the flow algorithm may be considered.

Fig. 4 demonstrates the effect of the isentropic exponent on the accuracy of flow-rate measured by an orifice plate

with corner taps [9]. The flow-rate through the orifice is proportional to the expansibility factor, which is a function of the isentropic exponent [9]. Fig. 4 shows a relative error in the mass flow-rate of methane $E = (q_m - q_{mi})/q_m$ obtained when using the isentropic exponent of ideal gas (q_{mi}) instead of real gas (q_m). The errors are calculated by varying the pressure p from 5 to 50 MPa in 1 MPa steps, temperature T from 245 to 305 K in 20 K steps and the differential pressure Δp from 10 to 90 kPa in 40 kPa steps. From Fig. 4 it can be seen that the relative error increases when decreasing temperature or when increasing differential pressure. At low differential pressures the isentropic exponent of ideal gas can be used with negligible effect on error but at higher differential pressures and lower temperatures the error increases significantly and the isentropic exponent of real gas must be calculated in order to reduce the error.

5. Conclusion

The numerical procedure for the calculation of the isentropic exponent of natural gas has been derived on the basis of the extended virial type characterization equation specified in AGA8/1992. The calculated isentropic exponents show much better agreement with the known data than the results obtained in [4] or by using the Redlich–Kwong compression factor equation [2]. We attribute this primarily to the higher accuracy of the AGA8/1992 equation. One possible real-time application of the procedure is in the measurements of flow-rate based on differential pressure devices.

Symbols and units

Symbol	Description	Units
B	Second virial coefficient	–
B_{ij}^*	Mixture interaction coefficient	–
C_n^*	Temperature and composition dependent coefficients	–
c_p	Molar heat capacity at constant pressure	J/(kmol K)
c_v	Molar heat capacity at constant volume	J/(kmol K)
E_{ij}^*	Binary energy interaction parameter for second virial coefficient	–
E_i	Characteristic energy parameter for i -th component	K
E_{ij}	Binary energy parameter for second virial coefficient	K
F	Mixture high-temperature parameter	–
F_i	High-temperature parameter for i -th component	–
G	Mixture orientation parameter	–

Symbol	Description	Units
G_{ij}^*	Binary interaction parameter for orientation	–
G_i	Orientation parameter for i -th component	–
G_{ij}	Binary orientation parameter	–
K	Size parameter	–
K_i	Size parameter for i -th component	–
K_{ij}	Binary interaction parameter for size	–
M	Mixture molar mass	kg/(kmol)
M_i	Molar mass of i -th component	kg/(kmol)
p	Pressure	MPa
Q	Quadrupole parameter	–
Q_i	Quadrupole parameter for i -th component	–
R	Molar gas constant 8314.51	J/(kmol K)
S_i	Dipole parameter for i -th component	–
T	Temperature	K
U	Mixture energy parameter	K
U_{ij}	Binary interaction parameter for mixture energy	–
v	Specific volume	m ³ /kg
V	Volume	m ³
W_i	Association parameter for i -th component	–
y_i	Molar fraction of i -th component in gas mixture	–
Z	Compression factor	–
α	Coefficient	K ⁻¹
β	Coefficient	K ⁻¹
Δp	Differential pressure	MPa
ρ	Density	kg/m ³
Φ	Fugacity coefficient	–
κ	Isentropic exponent	–
ρ_m	Molar density	kmol/m ³
ρ_r	Reduced density	–

References

- [1] D.A. Sullivan, Historical review of real-fluid isentropic flow models, Trans. ASME 103 (1981) 258–267.
- [2] O. Redlich, J.N.S. Kwong, On the thermodynamics of solutions. V An equation of state, fugacities of gaseous solutions, Chem. Rev. 44 (1949) 233–244.
- [3] R.W. Miller, Flow Measurement Engineering Handbook, McGraw-Hill, New York, 1996.
- [4] I. Marić, Derivation of natural gas isentropic exponent from AGA-8 equation of state, Strojarsstvo 39 (1997) 27–32.
- [5] AGA 8, Compressibility and supercompressibility for natural gas and other hydrocarbon gases, Transmission Measurement Committee Report No. 8, AGA Catalog No. XQ 1285, Arlington, VA, 1992.
- [6] ISO-12213-2, Natural gas—Calculation of compression factor—Part 2: Calculation using molar-composition analysis, ISO, Ref. No. ISO-12213-2:1997(E), (ISO 1997).

- [7] AIChE, Data Compilation Tables of Properties of Pure Compounds, Design Institute for Physical Property Data, AIChE, New York, 1986.
- [8] I. Marić, Software objects in distributed flow measurements, *ISA Trans.* 42 (2003) 497–504.
- [9] ISO-51671-2, Measurement of fluid flow by means of pressure differential devices inserted in circular-cross section conduits running full—Part 2: Orifice plates, ISO, Ref. No. ISO-51671-2:2003(E), (ISO 2003).