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Computing Thermal Properties of Natural Gas by Utilizing AGA8 Equation of State

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Abstract— **In current study, an attempt has been made to develop a numerical method and a computer program to calculate the thermal properties of natural gas mixture such as enthalpy and internal energy in addition of the compressibility factor using AGA8 state equation. The method has been applied to a typical Iranian natural gas mixture to calculate the thermal properties of the gas. Finally, the developed program has been utilized to model single reservoir fast filling process of a typical natural gas vehicle on-board cylinder. The computed results have been compared with simulation results of same process (fast filling) in which the pure methane was acted as working fluid. The results show the similar trends and good agreements.**

Index Terms—**Natural Gas, AGA8 equation of state, Thermal properties, numerical method**

I. INTRODUCTION

Given the current surge in the petrochemical and natural gas businesses, trustworthy estimates of thermodynamic properties are necessary to design engineering processes. Accurate prediction of thermodynamics properties for hydrocarbon fluids is an essential requirement in optimum design and operation of most process equipment involved in petrochemical production, transportation, and processing. Accurate value of natural gas compressibility factors is crucial in custody transfer operations. Other thermodynamic properties, e.g., enthalpy and internal energy of the gas, are used in the design of processes and storage facilities; Joule–Thomson coefficients are used in throttling processes and dew points are used in pipeline design.

An Equation of State (EoS) can describe the thermodynamic state of a fluid or fluid mixture and also its vapor-liquid phase equilibrium behavior. An ideal EoS should predict thermodynamic properties of any fluid accurately over a wide range of temperature, pressure and composition for vapor and liquid phases. The AGA8-DC92 EoS **[1]** and ISO-12213-2 **[2]** is currently the industry standard to predict the density or compressibility factor of natural gas with an acceptable accuracy. There are other correlations/equations of state (EoS) for calculating natural gas properties **[3]-[4]**.

Peng and Robinson (PR) EoS are often used in the gas industry for predicting natural gas equilibrium properties. Farzaneh et al. **[5]** have obtained a PR style expression for a typical Iranian natural gas based on mixture components of PR EoS.

Mc Carty **[6]** reported an accurate extended corresponding states (ECS) model for LNG systems, Using ECS models. Estela-Uribe and Trusler **[3]** and Estela- Uribe et al. **[4]** predicted the compressibility factors, densities, speeds of sound and bubble point pressures of natural gas mixtures quite accurately.

Maric [7] 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. Maric et al. **[8]** derived a numerical procedure for the calculation of the isentropic exponent of natural gas on the basis of the extended virial type characterization equation specified in AGA8/1992**[9]**. Maric **[9]** has also used the similar method to calculate Joule-Thompson coefficient of natural gas.

Nasrifar and Boland **[10]** used 10 equations of state to predict the thermo-physical properties of natural gas mixtures. They proposed two-constant cubic EoS. This EoS is obtained by matching the critical fugacity coefficient of the EoS to the critical fugacity coefficient of methane. Special attention is given to the supercritical behavior of methane as it is the major component of natural gas mixtures and almost always supercritical at reservoir and surface conditions. As a result, the proposed EoS accurately predicts the supercritical fugacity of methane for wide ranges of temperature and pressure. Using the van der Waals mixing rules with zero binary interaction parameters, the proposed EoS predicts the compressibility factors and speeds of sound data of natural gas mixtures with best accuracy among the other EoSes. The average absolute error was found to be 0.47% for predicting the compressibility factors and 0.70% for the speeds of sound data.

Although, the AGA8 EoS has been used to calculate some properties of the natural gas, no attempted yet has been made to calculate thermal properties of natural gas such as internal energy and enthalpy. In this study, a computer program has been developed to calculate the thermal properties of natural gas mixture in addition of the compressibility factor based on the AGA8 EoS. The method has been applied to a typical Iranian natural gas mixture to calculate the properties of the natural gas. Finally, the developed program has been utilized to model single reservoir fast filling process of natural gas vehicle natural gas cylinder.

II. THE NUMERICAL METHOD

The common equation of state for a real gas can be given

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as follow:

$$P = \frac{ZRT}{v} \tag{1}$$

In which compressibility factor can be calculated using various equation of states. According to AGA8/1992 and ISO-12213-2/1997,the equation for the compressibility factor of natural gas is: **[1]**,**[2]**

$$Z = 1 + \frac{DB}{K^3} - D\sum_{n=13}^{18} C_n^* T^{-u_n} + \sum_{n=13}^{58} C_n^* T^{-u_n}(b_n - c_n K_n D^{k_n}) D^{b_n} \exp(-c_n D^{k_n}) \tag{2}$$

Where D is reduced density, B is second virial coefficient, K is mixture size 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 d and reduced density D are defined as

$$D = K^3 d \tag{3}$$

$$d = \frac{P}{ZRT} \tag{4}$$

The second virial coefficient and the mixture size coefficient are calculated using the following equations:

$$K^5 = \left[\sum_{i=1}^{N} X_i K_i^{5/2}\right]^2 + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} X_i X_j (K_{ij}^5 - 1)(K_i K_j)^{5/2} \tag{5}$$

$$B = \sum_{n=1}^{18} a_n T^{-u_n} \sum_{i=1}^{N}\sum_{j=1}^{N} X_i X_j E_{ij}^{u_n} (K_i K_j)^{3/2} B_{nij}^* \tag{6}$$

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

$$B_{nij}^* = (G_{ij} + 1 - g_n)^{gn} . (Q_i Q_j + 1 - q_n)^{q_n} (F_i^{1/2} F_j^{1/2} + 1 - f_n)^{f_n} . (S_i S_j + 1 - s_n)^{s_n} . (W_i W_j + 1 - w_n)^{w_n} \tag{7}$$

$$E_{ij} = E_{ij}^* . (E_i E_j)^{1/2} \tag{8}$$

$$G_{ij} = \frac{G_{iJ}^* (G_i + G_j)}{2} \tag{9}$$

Where T is temperature, N is the total number of gas mixture components, X_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 $\{C_n^*, n = 1, \cdots, 58\}$ are defined by the following relation:

$$C_n^* = a_n (G + 1 - g_n)^{g_n} (Q^2 + 1 - q_n)^{q_n} (F + 1 - f_n)^{f_n} U^{u_n} \tag{10}$$

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

$$U^5 = \left[\sum_{i=1}^{N} X_i E_i^{5/2}\right]^2 + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} X_i X_j (U_{ij}^5 - 1)(E_i E_j)^{5/2} \tag{11}$$

$$G = \sum_{i=1}^{N} X_i G_i + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} X_i X_j (G_{ij}^* - 1)(G_i + G_j) \tag{12}$$

$$Q = \sum_{i=1}^{N} X_i Q_i \tag{13}$$

$$F = \sum_{i=1}^{N} X_i^2 F_i \tag{14}$$

Where $\{U_{ij}\}$ is the binary interaction parameter for mixture energy

The above equations have been discussed more in AGA8/1992 and ISO-12213-2/1997 and can be utilized to calculate the natural gas compressibility factor **[1]**,**[2]**. In this study, the aim was to calculate the thermodynamics properties of natural gas mixture such as internal energy and enthalpy. To calculate the internal energy of the gas mixture, the fundamental thermodynamics relation has been the starting point as follow:

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{15}$$

According to Maxwell relations the equation (15) can also be expressed as below:

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \tag{16}$$

The equation (16) can be integrated to evaluate the internal energy of natural gas at any position if a reference value is given as follow:

$$u - u_{ref} = \int_{Tref}^{T_2} c_v dT + \int_{vref}^{v_2} \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \tag{17}$$

To be able to evaluate the above integral, the value of $\left(\frac{\partial P}{\partial T}\right)_v$ has to be known. Here, the value was derived using general state equation (1) as below:

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{Z.R}{v} + \left(\frac{\partial Z}{\partial T}\right)_v \times \frac{R.T}{v} \tag{18}$$

Finally, by replacing equation (1) and (18) into equation (17), the following equation could be obtained:

$$u - u_{ref} = \int_{Tref}^{T_2} c_v dT + \int_{vref}^{v_2} \left[\frac{R.T^2}{v} \times \left(\frac{\partial Z}{\partial T}\right)_v\right] dv \tag{19}$$

In which, the first derivative of the compressibility factor with respect to temperature ($\left(\frac{\partial Z}{\partial T}\right)_v$) is:

$$\left(\frac{\partial Z}{\partial T}\right)_v = \frac{D}{k^3} . \left(\sum_{n=1}^{18} - u_n a_n T^{(-u_n - 1)} \sum_{i=1}^{N}\sum_{j=1}^{N} X_i X_j E_{ij}^{u_n} (k_i k_j)^{\frac{3}{2}} B_{n_{ij}}^*\right) + \left(D \sum_{n=13}^{18} u_n C_n^* T^{(-u_n - 1)}\right) - \left(\sum_{n=13}^{58} u_n C_n^* T^{(-u_n - 1)} (b_n - c_n k_n D^{k_n}) D^{b_n}\right) \times \exp(-c_n D^{k_n}) \tag{20}$$

The ideal molar heat capacity C_v is also needed in equation (19) for evaluating internal energy. By knowing the ideal heat capacity and mole fraction of each component, the ideal molar heat capacity of natural gas (mixture) may be calculated as below:

$$Cv = \sum_{i=1}^{21} X_i Cv_i \tag{21}$$

Once the internal energy of the natural gas is calculated by numerical integration of equation 19, the enthalpy of the gas could be calculated by using the following equation:

$$h - h_{ref} = (u - u_{ref}) + (pv - p_{ref} v_{ref}) \tag{22}$$

III. CHEMICAL COMPOSITION OF NATURAL GAS

Natural gas composition (mixture) varies with location, climate and other factors and may contain up to 21 components. The primary component is Methane (CH_4) with about 90% in the mixture. It also contains heavier hydrocarbons such as Ethane (C_2H_6), Propane (C_3H_8) and Butane (C_4H_{10}). Table 1 shows an experimental analysis of natural gas composition of Shanol gas field in which is based for the analysis in this research work **[11]**.

Table 1-Experimental analysis of natural gas composition of Shanol gas field in summer

Component	Chemical formula	Experimental Analysis (mole Fraction %)
water	H_2O	0.05
Carbon dioxide	CO_2	0.52
Nitrogen	N_2	3.88
Methane	CH_4	90.86
Ethane	C_2H_6	2.89
Propane	C_3H_8	0.81
Iso butane	C_4H_{10}	0.23
n-Butane	C_4H_{10}	0.29
Iso-Pentane	C_5H_{12}	0.15
$PseudoC_6$	$PseudoC_6$	0.12
$PseudoC_7$	$PseudoC_7$	0.11
$PseudoC_8$	$PseudoC_8$	0.04
$PseudoC_9$	$PseudoC_9$	0.03
$PseudoC_{10}$	$PseudoC_{10}$	0.01
$PseudoC_{11}$	$PseudoC_{11}$	0.01

IV. RESULTS AND DISCUSSIONS

In this study based on numerical method discussed in section 2, a computer program has been developed to predict the natural gas internal energy and enthalpy in addition of compressibility factor.

Figure 1 and figure 2 show effects of pressure and temperature on natural gas compressibility factor for Shanol gas filed natural gas. As expected, the compressibility factor decreases as pressure increases and increases as temperature increases. The value of compressibility factor approaches 1 as pressure decreases for all temperatures.

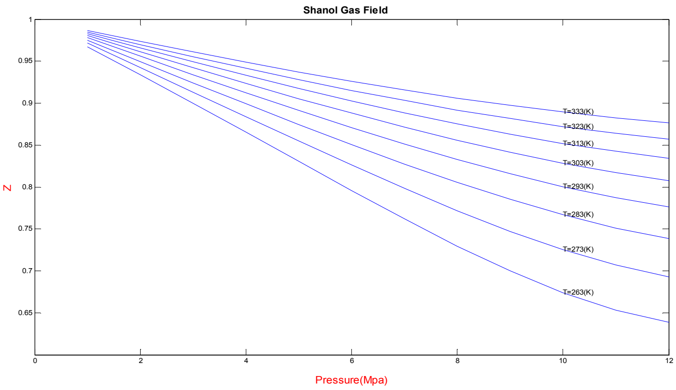

Figure 1-Effects of pressure on compressibility

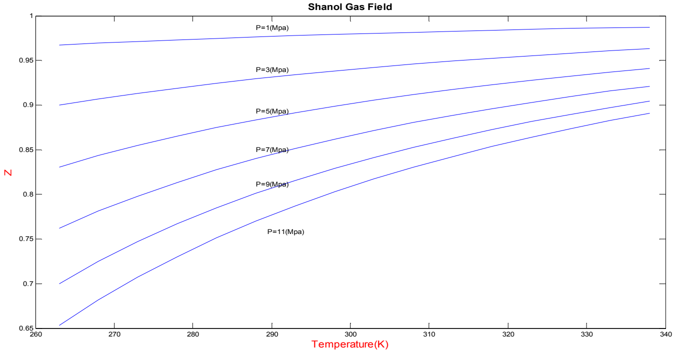

Figure 2-Effects temperature on compressibility factor

Figure 3 shows the effects of pressure and temperature on natural gas specific internal energy for Shanol gas filed. It can be seen that temperature and pressure growth causes the internal energy to increase. It can be also seen that the variation of internal energy at constant pressure follow a line. This is the case for various pressures. Figure 4 shows the effects of pressure and temperature on natural gas specific enthalpy. The same behavior as internal energy can be seen in this figure too.

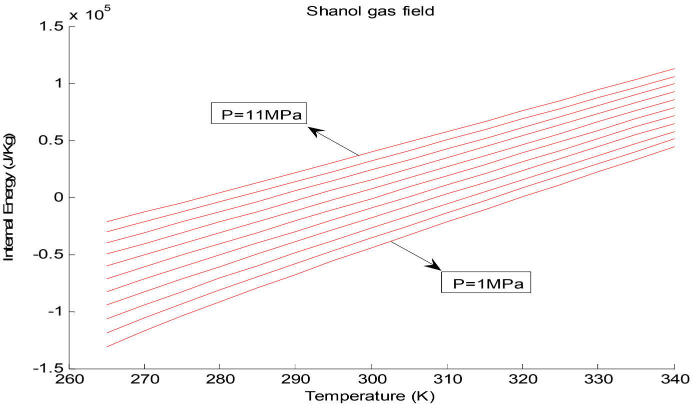

Figure 3-Effects of temperature and pressure on specific internal energy

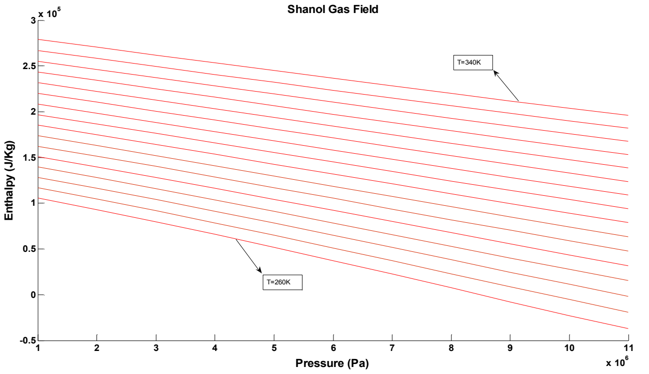

Figure 4-Effects of temperature and pressure on specific enthalpy

In addition to calculate the thermodynamics properties of natural gas as shown above, the developed program has been used to simulate the filling process of an onboard natural vehicle cylinder (NGV). A schematic diagram of the thermodynamic model has been shown in figure 5. The same system has been simulated and modeled in Farzaneh **[12]** when working fluid assumed to be pure methane . For the thermodynamic system as shown in figure 5, the governing equations are conservation of mass and first law of thermodynamic as:

$$\frac{dm_e}{dt} = \dot{m}_i \tag{23}$$

$$u_e \dot{m}_i + m_e \frac{du_e}{dt} = \dot{m}_i h_0 \tag{24}$$

Where u_e is specific internal energy of NGV cylinder, h_0 is specific enthalpy of reservoir thank and $\dot{m}_i$ is inlet mass flow rate. In the filling simulation, equations (23) and (24) have been solved numerically to find specific volume and internal energy. Then the developed program was used to find temperature and pressure of the gas. Farzaneh [12] utilized methane thermodynamics table to find temperature and pressure. For more information about the fast filling process and the thermodynamics model which utilized here see Farzaneh **[12]**.

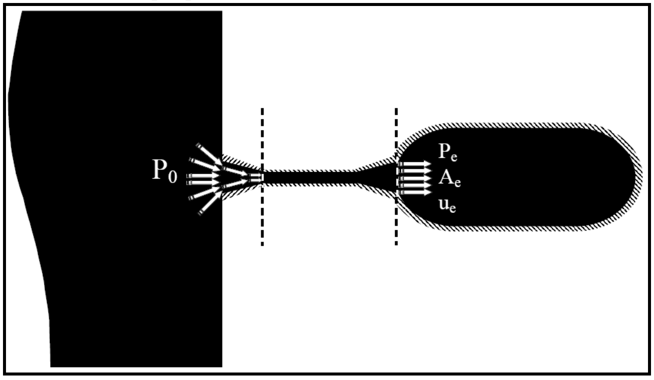

Figure 5- A schematic diagram of the thermodynamic model

Here to validate the numerical method of calculating thermodynamics properties of the natural gas, a comparison has been made between pure methane and natural gas dynamic properties for filling process of a NGV cylinder.

Figure 6 shows dynamic temperature profiles in NGV cylinder during filling process for pure methane and natural gas. As shown in Figure 6, in early filling time, the cylinder gas temperature dips significantly, before rising to a final value. The reason for the dip in temperature profile, in the early part of the filling of a nearly empty cylinder is result of the Joule-Thompson cooling effect, which the gas undergoes in the isenthalpic expansion through the orifice, from the 205 bar supply pressure to the initially low 1 bar cylinder pressure. This cold gas mixes with and compresses the gas originally in the tank, with the result that the combined mixed gas temperature initially reduces. It can be seen that the dip for natural gas profile is higher than for pure methane case. This shows that the Joule-Thompson effects are higher in natural gas than pure methane. This behavior is expected for a mixture with heavier hydrocarbons (natural gas) comparing with pure methane. Note from the figure, the trends for both profiles are similar.

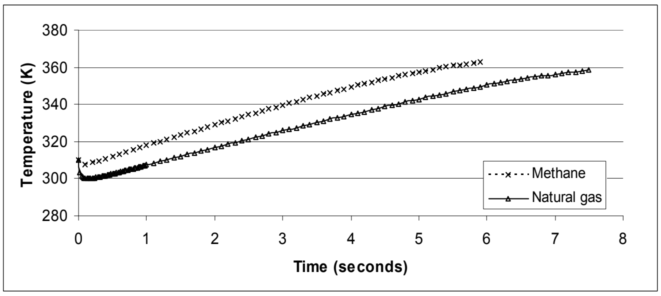

Figure 6- Variation of NGV cylinder temperature during filling process

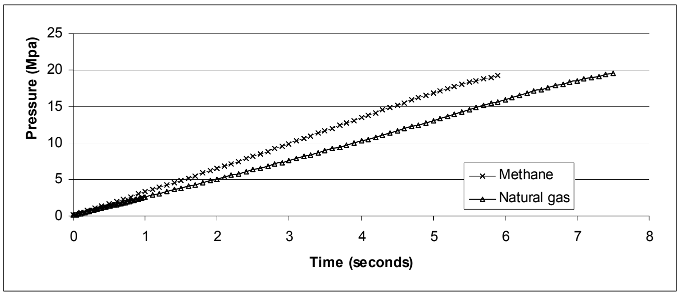

Figure 7- Variation of NGV cylinder pressure during filling process

Figure 7 shows dynamic pressure profiles in NGV cylinder during filling process for pure methane and natural gas. It can be seen that both profile have similar trends and are in good agreement. It is worth mentioning that the differences between the two profiles are expected as the thermodynamic properties of two working fluids are not the same.

V. CONCLUSION

Given the current surge in the petrochemical and natural gas businesses, trustworthy estimates of thermodynamic properties are necessary to design engineering processes. Accurate prediction of thermodynamics properties for hydrocarbon fluids is an essential requirement in optimum design and operation of most process equipment involved in petrochemical production, transportation, and processing.

In current study, a computer program has been developed to calculate the thermal properties of natural gas mixture such as enthalpy and internal energy in addition of the compressibility factor. The method has been applied to a typical Iranian natural gas mixture to calculate the properties of the natural gas. To validate the method, the developed program has been utilized to model fast filling process of natural gas vehicle natural gas cylinder. The computed results have been compared with simulation results of same process in which the pure methane was acted as working fluid. The results show the similar trends and good agreements.

VI. ACKNOWLEDGMENTS

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VII. NOMENCLATURE

Symbol	Description	units

B	Second virial coefficient	-
$B^*_{n_{ij}}$	Mixture interaction coefficient	-
C^*_n	Temperature and composition dependent coefficient	-
c_p	Molar heat capacity at constant pressure	J/(kmol K)
A	Coefficient	K^{-1}
B	Coefficient	K^{-1}
+ $C_{6...11}$	All hydrocarbon compounds with more than 5 carbon in their chemical formula	-
c_v	Molar heat capacity at constant volume	J/(kmol K)
D	Reduced density	-
d	Molar density	kmol/m^3
E^*_{ij}	Binary energy interaction parameter for second virial coefficient	-
E_i	Characterization 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	-
G^*_{ij}	Binary interaction parameter for orientation	-
G_i	orientation parameter for i-th component	-
G_{ij}	Binary orientation parameter	-
h	Specific enthalpy	kj/kg
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)
$\dot{m}$	Mass flow rate	kg/s
N	the total number of gas mixture components	-
P	pressure	Mpa or kpa
Q	Quadrupole parameter	-
Q_i	Quadrupole parameter for i-th component	-
R	Universal molar gas constant	J/(kmol K)
S_i	Dipole parameter for i-th component	-
T	Temperature	K
U	Mixture energy parameter	K
u	Specific internal energy	kj/kg
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	-
X_i	Molar fraction of i-th component in gas mixture	-
Z	Compressibility factor	-
ρ	Density	kg/m^3

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