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Thermodynamic Behavior of Hydrogen/Natural Gas Mixtures

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ABSTRACT

The process gas of ethylene plants and methyl tertiary butyl ether plants is normally a hydrogen/methane mixture. The molecular weight of the gas in such processes ranges from 3.5 to 14. Thermodynamic behavior of hydrogen/methane mixture has been and is being researched extensively. The gas dynamic design of turboexpanders which are extensively utilized in such plants depends on the equations of state of the process gas. Optimum performance of the turboexpander and associated equipment demands accurate thermodynamic properties for a wide range of process gas conditions.

The existing equations of state, i.e. Benedict-Webb-Rubin (BWR), Soave-Redlich-Kwang and Peng-Robinson have some practical limitations. The equations of state developed by the University of Illinois also have only a limited range of applications. By using the various equations of state, especially in the vapor-liquid equilibrium region, this paper shows that predictions by the various models are not the same and that they also differ from actual field results. The field data collected for hydrogen/methane mixtures are in the range of 100°F to -200°F containing some polar components i.e. H₂S and CO₂.

In this paper, the authors compare performance of several equations of state with the field performance of many expander units.

region. An accurate vapor-liquid equilibrium condition for the hydrogen rich mixture is an essential prerequisite in the design of these process plants handling such mixtures.

In this paper, the authors evaluate the available mathematical models for the equations of state of hydrogen mixtures. Evaluation is carried out using field performance data from several plants.

APPLICATIONS

There are several applications which require accurate thermodynamic data for hydrogen rich hydrocarbons. Some of these applications are as follows:

Methyl Tertiary Butyl Ether (MTBE)

The need for high octane unleaded gasoline and clean air is increasing the demand for oxygen containing additives to gasoline, such as MTBE. This product reduces the carbon monoxide in the exhaust gas while enhancing the octane number of the gasoline. The process requires refrigeration in which peak cold is generated by expansion of a hydrogen rich hydrocarbon gas. In the process design where refrigeration is achieved by expander train(s), the turboexpander feed contains hydrogen mixed with light hydrocarbons up to and including butane.

Ethylene Plants

High ethylene recovery from the tail gas that is normally used as a fuel is possible by using a turboexpander.¹ All ethylene process plants using turboexpander(s) have process gas in two phase operation. Through a cryogenic process, most of the ethylene and almost all of the heavier hydrocarbon components are liquified in one process. In another process, ethylene is separated from the liquid. Turboexpander feed gas contains hydrogen and light hydrocarbons such as methane, ethane, ethylene and trace acetylene.

Propylene Plants

Many refineries are also using a similar process to fractionate propylene from the liquid feed.

INTRODUCTION

Thermodynamic properties of hydrogen in hydrocarbon mixtures have been studied in the past by utilizing correlation techniques. Most of these mathematical models are for single phase gas mixtures with high pressures and warmer than cryogenic temperatures. Process plants such as ethylene plants, Methyl Tertiary Butyl Ether (MTBE) plants, and hydrogen purification plants operate at medium pressures, with cryogenic temperature, and in the two phase

Hydrogen Purification

Traces of impurities such as nitrogen, carbon monoxide and methane may be separated after liquification at deep cryogenic temperatures. The preferred process design uses turboexpanders to produce the deep cryogenic temperatures.

All the above applications requires accurate thermodynamic data of the hydrogen rich hydrocarbons.

EQUATIONS OF STATE

There are several prediction methods for properties of mixtures from low molecular weight systems to complex heavy hydrocarbon mixtures. The most common equations are Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), and Benedict-Webb-Rubin-Starling (BWRS).^{2,3,4} Newton was the first to suggest that hydrogen could be evaluated with other gases by replacing their true critical constants with the effective critical constants.⁵ His correlation showed an improvement in PVT data at room temperature but demonstrated somewhat poorer results at lower temperature conditions. Newton's correlation has been modified over the years by using effective critical constants instead of true critical constants. For hydrogen rich hydrocarbons there are additional equations of state such as: Chao-Seader, Grayson-Streed, and Zudkevitch-Joffe, since hydrogen is used in the development of their respective models.^{6,7,8} The PR and SRK equations of state uses binary interaction parameters. The ZJ equation is a modified model of RK for the better prediction of the systems containing hydrogen. The CS and GS methods are semi-empirical with GS correlation being an extension of CS equations with specific emphasis on hydrogen. Mohsen-Nia et al. developed a simple and accurate cubic equations of state for the prediction of thermodynamic properties and phase behavior of sour natural gas and liquid mixtures containing hydrogen.⁹ The latter equations of state is designed specifically to predict thermodynamic properties and phase equilibria of liquid and vapors which consist of hydrogen, methane and light hydrocarbons.

Because of quantum effects, hydrogen and helium do not follow the simple law of corresponding states and therefore, do not fit the generalized correlations such as standard equations of state.

A new simple two-constant cubic equations of state for hydrocarbons, hydrocarbon mixtures, and other non-associating fluids has been introduced by Mohsen-Nia et al.⁹ This equation of state model is based on the statistical mechanical information available for the repulsive thermodynamic functions and the phenomenological knowledge of the attractive potential tail contributions to the thermodynamic properties. This new two-constant parameter cubic equation is as follows:

$$Z = (v + 1.3191b) / (v-b) - a / [RT^{3/2}(v + b)] \quad (1)$$

Equation (1) is cubic in terms of volume and contains only two adjustable parameters. By applying the critical point constraints on the above equation, parameters a and b are determined to be:

$$a = 0.486989R^2T_c^{5/2}/P_c \quad b = 0.064662RT_c/P_c \quad (2)$$

The critical compressibility factor based on these equations of state is calculated to be,

$$Z_c = 1/3 \quad (3)$$

The latter calculation is the same as the Redlich-Kwong (RK) equations of state. It has been shown, however, that these equations of state is more accurate than the Redlich-Kwong equation, which had been considered to be the best two-constant-parameter cubic equation of state for quite some time.⁹ For multi-component mixtures this equation of state takes the following form:

$$Z_m = (v + 1.3191b_{Rm}) / (v - b_{Am}) - a_m / [RT^{3/2}(v + b_{Am})] \quad (4)$$

where we use the following mixing rule for am, bAm and bRm

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$b_{Rm} = (3/4) \sum_i \sum_j x_i x_j b_{ij} + (1/4) \sum_i x_i b_{ii} \quad (6)$$

$$b_{Am} = \sum_i x_i b_{ii} \quad (7)$$

Subscript R in bRm stands for the repulsive mixing rule and subscript A in bAm stands for the attractive mixing rule of b. For reasons mentioned elsewhere (reference 9), the mixing rule for parameter b when it appears in the repulsive (positive) term of the equation of state (b_{Rm}) will be different from that of the attractive (negative) term (b_{Am}). For unlike-interaction parameters a_{ij} and b_{ij}, the following combining rules are used.

$$b_{ij} = (b_{ii}^{1/3} + b_{jj}^{1/3})^3 / 8 \quad (8)$$

$$a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} \quad (9)$$

Parameter k_{ij} is defined as the coupling parameter which can be determined using some mixture data. The theoretical foundations for the choice of the above mixing and combining rules are also discussed elsewhere. The above cubic equations of state has been used for calculating the thermodynamic properties of hydrocarbons and other non-associating fluids and fluid mixtures, and it has been shown that this two-constant cubic equation of state and its mixture version are far superior to the RK equation of state which is also a two-constant cubic equation, (reference 9). However, the better accuracies achieved by this simple cubic equations of state is still not sufficient to allow it to be used for engineering design calculations of turboexpanders.

In order to improve the accuracy of the present equation of state to the level that it could be used for engineering design calculations, it is necessary to make parameters a and b temperature-dependent similar to the many modifications of the van der Waals and RK equations of

state. For this purpose we replace parameters "a" and "b" with the following temperature-dependent expressions.

$$a = a_c \alpha (T_r) \quad b = b_c \beta (T_r) \quad (10)$$

Where

$$a_c = 0.486989R^2T_c^{5/2}/P_c, \quad b_c = 0.064662RT_c/P_c \quad (11)$$

The dimensionless temperature-dependent parameters $\alpha(T_r)$ and $\beta(T_r)$, while different from each other, reduce to unity at the critical point:

$$\alpha (T_r = 1) = \beta (T_r = 1) = 1 \quad (12)$$

There have been a variety of empirical functional forms for α and β reported in the literature. However, in line with the variational and perturbation molecular theories of fluids Equation (10), the following polynomial expression for $\beta(T_r)$ may be used:

$$\beta (T_r)^{1/3} = [1 + \beta_1/T_r + \beta_2/T_r^2 + \dots] / [1 + \beta_1 + \beta_2 + \dots] \quad (13)$$

Then for simplicity, and as a first approximation, the following form for $\beta(T_r)$ is used.

$$\beta (T_r) = (1 + \beta_1/T_r)^3 / (1 + \beta_1)^3 \quad (14)$$

where β_1 is a constant. Equation (14) satisfies the basic theoretical conditions for $\beta(T_r)$ at the critical point, i.e.: $\beta(T_r) \rightarrow 1$ at $T_r \rightarrow 1$. This functional form will remain finite and positive for all possible temperature ranges. For symmetry and simplicity the same functional form for parameter $\alpha(T_r)$, maybe used i.e.

$$\alpha (T_r) = (1 + \alpha_1/T_r)^3 / (1 + \alpha_1)^3 \quad (15)$$

Where α_1 is a constant. Equation (15) also satisfies the basic theoretical conditions for $\alpha(T_r)$ at the critical point, i.e.: $\alpha(T_r) \rightarrow 1$ at $T_r \rightarrow 1$. It can also be inferred from the form of these equations of state that as temperature tends to infinity, the attractive term $-a/[RT^3/2(v+b)]$, must also approach zero. The form of $\alpha(T_r)$ considered in this work is conducive to this requirement.

The constants α_1 and β_1 have been determined for the components of hydrogen and sour natural gas mixtures and of hydrogen gas-condensate mixtures and are reported in Table I. These constants were found by minimization of the vapor pressures and saturation liquid densities.

For ease of calculations, parameters α_1 and β_1 are correlated for the major components of natural gas (see Table I) to their eccentric factor in the following forms:

$$\alpha_1 = 0.036139 + 0.14167\omega; \quad \beta_1 = 0.0634 - 0.18769\omega \text{ for } -0.22 \leq \omega \leq 0.18 \quad (16)$$

These correlations are for ω in the range of $-0.22 \leq \omega \leq 0.18$ and they do not hold very well for parameters of components of natural gas which are in minute quantities ($C_4 - C_7^+$). Because of very small concentrations of these components in natural gas streams, however, application of the above correlation Equation (15) for these components will not cause any appreciable error in the computation of thermodynamic properties for hydrogen and natural gas mixtures. Formulation of equations of state of hydrocarbon mixtures containing appreciable amounts of heavier hydrocarbons requires application of the continuous thermodynamics and C_7^+ fraction characterization techniques Equations (10), (11), and (12).

One of the requirements of equations of state for industrial applications is their analytic representation of thermodynamic functions. Such properties of fluids (like entropy, enthalpy, and fugacity) are of direct interest in energy balance and phase behavior calculations in industrial practice. The analytic expressions of these functions are as follows:

$$H_m - \frac{H_{m,ig}}{RT} = (Z_m - 1) - 2.3191Tb_{m,0}'/(v-b_{m,0}) - a_m' \ln[v/(v+b_{m,0})] Rb_{m,0}T^{1/2} + [b_{m,0} + a_m/[b_{m,0}(v+b_{m,0})] + 1.5a_m/b_{m,0}RT^{3/2}] \ln[v/(v+b_{m,0})] \quad (17)$$

$$\frac{S_m - S_{m,ig}}{R} = \ln Z_m + 2.3191 \ln[(v-b_{m,0})/v] - 2.3191 Tb_{m,0}'/(v-b_{m,0}) - [a_m/(b_{m,0}T^{1/2})] \ln[v/(v+b_{m,0})] - [a_m b_{m,0}'/T^{1/2}] (1/b_{m,0}) \ln[v/(v+b_{m,0})] + 1/(b_{m,0}v+b_{m,0}^2) + [a_m/(2b_{m,0}T^{3/2})] \ln[v/(v+b_{m,0})] \quad (18)$$

$$\ln f_1 = -2.31915 \ln(1-b_{m,0}/v) + 2.3191 [nb_{m,0}/dn_1] / (v-b_{m,0}) + [d(nb_{m,0})/dn_1] [a/(b_{m,0}v+b_{m,0}^2) + (a/b_{m,0}) \ln(1-b_{m,0}/v)] / (RT^{3/2}) - [d(n^2 a_{m,0})/dn_1] \ln[(1+b_{m,0}/v)] / RT^{3/2} nb_{m,0} - \ln Z_m \quad (19)$$

Table I
Equation of state constants

Substance	α_1	β_1
	Major components	of Natural gas
H ₂	-0.07099	0.12307
N ₂	-0.02474	0.06393
CO	-0.02281	0.06066
CO ₂	-0.00580	0.01456
H ₂ S	-0.02351	0.04207
CH ₄	-0.03662	0.05957
C ₂ H ₄	-0.02898	0.03865
C ₂ H ₆	-0.02133	0.04504
C ₃ H ₆	-0.00841	0.04624
C ₃ H ₈	-0.01457	0.03657
Components of natural gas in minute quantities		
n-C ₄ H ₁₀	-0.00663	0.03613
i-C ₄ H ₁₀	-0.01373	0.02852
n-C ₅ H ₁₂	-0.00878	0.02251
n-C ₆ H ₁₄	-0.00761	0.01258
n-C ₇ H ₁₆	0.00425	0.01342

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In the above equation $\frac{H_m - H_{m,ig}}{RT}$ and $\frac{S_m - S_{m,ig}}{R}$ are the mixture enthalpy departure function and mixture entropy departure function, respectively, and f_i is the fugacity of component i in a multi-component mixture, a_m , b_{Rm} and b_{Am} are defined by Equations (5), (6) and (7), parameters a' and b' refer to (da/dT) and (db/dT) , respectively. Expressions for the other thermodynamic functions can be readily derived from the above equations.

RESULTS

Table II depicts expander feed gas in a typical MTBE plant. Table III shows a typical expander feed in an ethylene plant. Table IV and V present the expected performance data using the various equations of state.

Table II
Turboexpander inlet condition for a typical MTBE plant

Inlet Gas Composition	
H ₂	86.96
C ₁	12.49
C ₂ H ₄ /C ₂	.12/.29
C ₂ H ₆ /C ₃	.07/.12
IC ₄ /NC ₄	0.01/.008
I-C ₄ =/NC ₄ =	0.01/.38
P ₁ (KPa)	717
P ₂ (KPa)	510
T ₁ (C)	-64
T ₂ (C)	-78
FLOW(KG/Hr)	12000
Wt. % Liq.	5.2

Table III
Turboexpander inlet condition for a typical ethylene plant

Inlet Gas Composition	
H ₂	35
C ₁	64.83
C ₂	0.15
C ₂ H ₄	.02
C ₂ H ₂	TRACE
P ₁ (KPa)	3100
P ₂ (KPa)	345
T ₁ (C)	-95.5
T ₂ (C)	-154
FLOW(KG/Hr)	17000
Wt. % Liq.	14.3

Table IV
MTBE plant

	SRK	BWR	PR	CS	GS	MMM
T ₂ (C)@85%	-75.3	-76.7	-79.8	-80.2	-80.8	-77.5
DH(KJ/KG)	138.2	128.4	134.6	135.2	135.1	130
kW	391.5	363.7	381	383	383	368
Wt% Liq.	2.0	4.9	3.20	2.1	1.2	5.2

Table V
Ethylene plant

	SRK	BWR	PR	CS	GS	MMM
T ₂ (C)@85%	-151.9	-152.2	-151.9	-154	-164.8	-154
DH(KJ/KG)	200.5	199.7	198.7	204.3	201.6	199.6
kW	805	801	797	820	809	801
Wt% Liq.	11.94	12.26	12.86	10.79	3.82	14.3

Table VI

Systems (1) + (2)	T Range (K)	No. of data points	P %Deviation			y ₁ % Deviation		
			SRK	PR	MMM	SRK	PR	MMM
(H2+CH4)	103-143	12	24.4	16.2	19.4	4.2	5	2
(H2+C2H4)	173-198	16	22.1	38	4.9	2.2	3	0.2
(H2+C2H6)	173-223	16	15.8	29.2	7.6	1.5	3.5	1.4
Overall % deviations			20.7	27.8	10.6	2.6	3.8	1.2

QUALIFICATION

The MMM equations of state has been tested based on some available thermo physical data, reference 9. Table VIII presents the vapor-liquid equilibrium calculation of different binary hydrogen containing gas mixtures. According to this table the MMM equations of state appear to be superior to the other equations for the mixtures that were studied in this paper. Based on these results MMM equations of state for hydrogen rich natural gas depicts less deviation and hence are recommended for similar applications. The percentage of deviation for pressure and vapor compositions between theoretical and experimental data for different binary mixtures by using the Pr and SRK equations of state all with $k_i^j=0$, are shown in Table VI.

FIELD EXPERIENCES

In order to verify accuracy of the above equations, several MTBE and ethylene plants that utilize turboexpander(s) in their process design were selected. Field performance data were obtained for plants with the inlet condition, as close to the design condition as practical. Deviation between theoretical and actual performance is tabulated in tables VII and VIII. As it is shown in the above tables, MMM equations of state has shown more dependable results.

**Table VII
MTBE Plant***

% DEVIATION	SRK	BWR	PR	CS	GS	MMM
DH	1.5	0.5	4.2	4.80	4.80	0.7
DT	18	10	13	16	20	4

*Average of 10 MTBE Plants

**Table VIII
Ethylene Plant***

% DEVIATION	SRK	BWR	PR	CS	GS	MMM
DH	1.5	0.5	4.2	4.8	4.8	0.7
DT	2.7	1.7	2.6	0.8	19.5	0.3

*Average of 15 Ethylene Plant

CONCLUSION

The importance and criticality of accurate gas mixture properties in turboexpander design is a well know fact. Several equations of state have been analyzed and evaluated using available field performance data. This study is limited to gas dynamic behavior of turboexpander using hydrogen rich natural gas as a process fluid. The MMM equation of state stands out to be more accurate and consistent as well as have more dependable results.

NOTATIONS

a	parameter in equation of state
b	parameter in the equations of state
f	fugacity
H	enthalpy
k_{ij}	coupling parameter
n	total number of moles
P	pressure
R	Universal gas constant
S	entropy
T	absolute temperature
T_r	$=T/T_c$
v	molar
Z	$=Pv/RT$, compressibility factor

GREEK LETTERS

α	parameter in equation of state
α_1	constant
β	parameter in equation of state
β_1	constant
ρ	density
π	3.1415927
ω	acentric factor

SUBSCRIPTS

A	attractive
c	critical
i,j	component indices
ij	property of i-j interaction
ig	ideal gas
m	mixture
r	reduced
R	repulsive

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