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Prediction of CO_2 freezing points for the mixtures of CO_2-CH_4 at cryogenic conditions of NGL extraction plants

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Abstract−The carbon dioxide freezing phenomenon is investigated at the cryogenic operating conditions of the turbo-expansion-based NGL plants. The Peng-Robinson equation of state is used for predicting the CO_2 freezing points for liquid and vapor mixtures of CO_2-CH_4. A new quadratic temperature dependent k_{ij} correlation is also presented for proper description of binary interactions at low temperatures. The overall average absolute relative deviation between experimental and predicted CO_2 freezing temperatures is 0.26%.

Key words: CO_2-CH_4, Freezing, Peng-Robinson, Interaction Coefficient, NGL, Cryogenic

INTRODUCTION

The turboexpansion process is widely used in NGL plants to provide the required cryogenic condition for efficient separation of C_2^+ components from natural gas. In this type of process, the cooled expanded gas is directed to a demethanizer where the temperatures lower than the triple point of carbon dioxide are usually necessary to achieve the desired level of C_2^+ recovery. Since carbon dioxide has a limited solubility in both the liquid and vapor hydrocarbon phases, the possibility of CO_2 freezup should be checked at the outlet of the turboexpander, in the top section of the demethanizer column and other key locations within a given processing scheme. These types of checkings are usually carried out by using empirical correlations, and a minimum temperature safety margin is then employed to ensure that CO_2 freezing conditions are avoided.

White et al. [1973] have presented a correlation for predicting the conditions under which CO_2 freezup can occur. Bergman and Yarborough [1978] performed a series of CO_2 freeze out experiments on light hydrocarbon systems. This work resulted in correlations similar to the one given by White et al. [1973]. The liquid freezup curves from these two correlations are essentially identical except at the high temp end (200 K). Experience has shown that these empirical correlations are not trustworthy enough to be used for industrial applications.

Methane is a key component which its level of separation from C_2^+ dictates the required level of temperature at the coldest section of a turboexpansion based NGL plant. Therefore, the CO_2 freezing conditions for CO_2-CH_4 system are examined in this study.

In this work the standard form of the Peng-Robinson equation of state [Peng and Robinson, 1976] is used for prediction of CO_2 freezing conditions in the CO_2-CH_4 system. The predicted CO_2 freezing points for the vapor phase are compared with the experimental data reported in GPSA Engineering data book [1998], and the predicted freezing points for liquid phase are compared with the presented data in Kurata [1974]. These sources present the most reliable CO_2 freezing temperatures for the CO_2-CH_4 system at different operating conditions [ZareNezhad, 2005].

MODELLING OF THE SOLID CO_2 FORMATION

The equation of state approach has the advantage of providing a consistent theoretical framework that is more easily extended to new situations. We chose a standard form of PR EOS [Peng and Robinson, 1976] for phase equilibrium calculations since it is widely used to model natural gas processing systems. This equation can be written as:

$$P=\frac{RT}{v-b_m}-\frac{a_m}{v(v+b_m)+b_m(v-b_m)} \tag{1}$$

To apply such an EOS to mixtures, mixing rules are used to calculate the values of a_m and b_m of the mixtures. Classical mixing rules are used in this study:

$$a_m=\sum_{i=1}^{N}\sum_{j=1}^{N}z_iz_j(a_ia_j)^{0.5}(1-k_{ij}) \tag{2a}$$

$$b_m=\sum_{i=1}^{N}z_ib_i \tag{2b}$$

where

$$a_i=0.45724\frac{R^2T_{ci}^2}{P_{ci}}\left[1+m_i\left(1-\left(\frac{T}{T_{ci}}\right)^{0.5}\right)\right]^2 \tag{3a}$$

$$b_i=0.0778\frac{RT_{ci}}{P_{ci}} \tag{3b}$$

$$m_i=0.37464+1.54226\omega_i-0.26992\omega_i^2 \tag{3c}$$

and z_i represents the mole fraction of component i in a mixture, and N the number of components in the mixture. In Eqs. (2a) and (2b), the summations are over all chemical species. k_{ij} is the binary interaction parameter characterizing molecular interactions between molecules i and j.

Eq. (1) can also be written in cubic form:

$$z^3-(1-B)z^2+(A-3B^2-2B)z-(AB-B^2-B^3)=0 \tag{4a}$$

where

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$$A=\frac{a_m P}{R^2T^2} \tag{4b}$$

$$B=\frac{b_m P}{RT} \tag{4c}$$

Solving Eq. (4a) analytically can produce meaningless results since it is sensitive to round off errors in low temperature region [Zhi and Lee, 2002]. Therefore, the numerical methods are preferred. However, it is important to initialize the root finding calculation for Eq. (4a) with a reasonably good guess. This equation may only have one real root and if the initial guess is far off target, the resulting compressibility might correspond to that of a vapor rather than a liquid phase, such that the root finding calculation will converge to a meaningless answer.

Using the PR equation of state, the fugacity coefficient of a component in the mixture can be evaluated by the following equation:

$$\phi_i=\exp\left(\frac{b_i}{b_m}(z-1)-\ln(z-B)\right.$$
$$\left.-\frac{A}{2\sqrt{2}B}\left(\frac{2\psi_i}{a_m}-\frac{b_i}{b_m}\right)\ln\left(\frac{z+2(1+\sqrt{2})B}{z+2(1-\sqrt{2})B}\right)\right) \tag{5a}$$

where

$$\psi_i=\sum_j z_j(a_ia_j)^{0.5}(1-k_{ij}) \tag{5b}$$

The CO_2 freezing phenomena in the vapor phase can be described by the the following equilibrium relationship.

$$F_1(T)=y_{CO_2}\phi^V_{CO_2}P-P^{Sat}_{CO_2Solid}\phi^{Sat}_{CO_2}\exp\left[\frac{v_{CO_2Solid}}{RT}(P-P^{Sat}_{CO_2Solid})\right]=0 \tag{6}$$

where y_{CO_2} is the mole fraction of CO_2 in vapor phase, $\phi^V_{CO_2}$ the vapor phase partial fugacity coefficient for CO_2, P the system pressure in kPa, $P^{Sat}_{CO_2Solid}$ the vapor pressure of solid CO_2 at system pressure in kPa, $\phi^{Sat}_{CO_2}$ the fugacity of pure CO_2 vapor at $P^{Sat}_{CO_2Solid}$, v_{CO_2Solid} the molar volume of solid CO_2 and T the temperature.

Although Eq. (6) derived from equating partial fugacities describes the necessary condition for solid CO_2 formation, it is not sufficient to show the stability of the produced solids. Thus the following criterion should also be checked:

$$T\le T^{TP} \tag{7}$$

where T^{TP} is the triple point temperature for CO_2, 216.55 K [Gerhartz, 2001]. There are several cases where solids formation are thermodynamically predicted, but the temperature is too high for a stable solid.

The linear regression analysis of experimental solid CO_2 vapor pressure data [Perry and Green, 1997] in the form of $\ln P^{sat}$ versus 1/T with the overall average absolute deviation (AAD) of 0.1% gives:

$$P^{Sat}_{CO_2Solid}=\exp\left[-3108.2\left(\frac{1}{T}\right)+20.6654\right] \tag{8}$$

RESULTS AND DISCUSSION

It is accepted that the binary interaction parameter k_{ij} depends on temperature. This temperature dependence has been described by a few authors [Valderrama et al., 1988; Kordas et al., 1994]. In the present work, the temperature dependency of the k_{ij} is found by minimization of the difference between experimental and calculated freezing temperatures. For a given vapor phase CO_2 composition, y_{CO_2} and pressure, P, a k_{ij} is assumed in Eq. (5) and the freezing temperature, T_{calc} is determined by Newton-Raphson method. The solution reaches when $F_1(T)\le 10^{-5}$. The calculated freezing temperature (T_{calc}) is then compared with the experimental data (T_{exp}) at the same y_{CO_2} and the following error function:

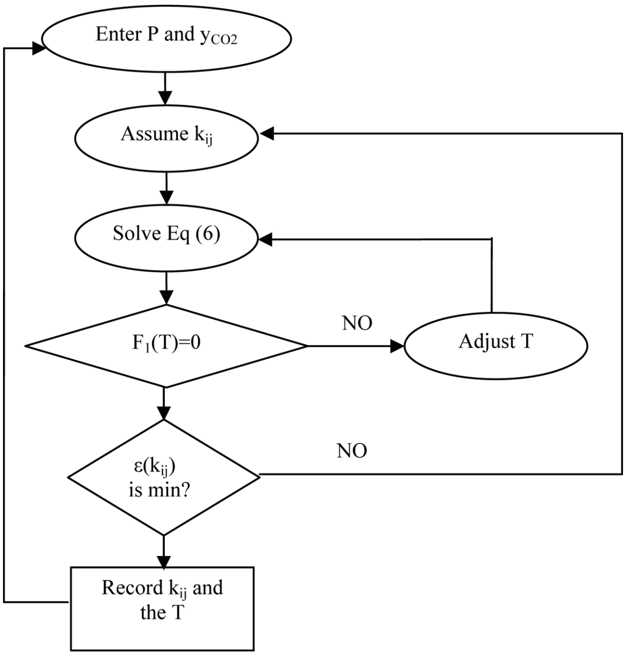

Fig. 1. The proposed algorithm for k_{ij} calculation.

$$\varepsilon(k_{ij})=|T_{exp}-T_{calc}| \tag{9}$$

is determined. This procedure is repeated for different k_{ij}s until the minimum value of $\varepsilon(k_{ij})$ for a given y_{CO_2} is obtained. This optimum value of k_{ij} at the given vapor phase CO_2 composition and pressure corresponds to a definite CO_2 freezing temperature. The set of (k_{ij}, T) values can be determined at different equilibrium pressure and fluid phase compositions according to the proposed algorithm as shown in Fig. 1.

Since a constant k_{ij} is not adequate to describe the CO_2-CH_4 solid-vapor and solid-liquid equilibrium at low temperatures, a temperature dependent k_{ij} correlation is required for equilibrium calculations.

Fisher and Leland [1970] derived the following quadratic mixing rule for description of molecular interactions:

$$a_m=\sum_i\sum_j z_iz_ja_{ij}\left(1+\varepsilon_{ij}\frac{f}{T}\right) \tag{10}$$

where $a_{ij}=(a_ia_j)^{0.5}(1-k^o_{ij})$, ε_{ij} is the interaction energy, f is an empirical constant and k^o_{ij} is the asymptotic interaction coefficient at infinite temperature. Rowlinson and Sutton [1955] showed using the theory of noncentral forces between nonspherical molecules, that:

$$\varepsilon_{ij}=\varepsilon^o_{ij}\left(1+\frac{\eta_{ij}}{kT}\right) \tag{11}$$

where ε^o_{ij} is the value of ε_{ij} at infinite temperature and η_{ij} is the noncentral-energy parameter.

Substituting Eq. (11) in Eq. (10) and comparing with Eq. (2a), an expression showing a quadratic dependency of the binary interaction parameter k_{ij} with the inverse temperature results:

$$k_{ij}=\frac{\alpha}{T^2}+\frac{\beta}{T}+k_{ij}^{o} \tag{12}$$

Thus, a linear regression analysis of k_{ij} versus 1/T with R^2 of 0.99 was carried out and the following correlation was obtained:

$$k_{ij}=-36.134\frac{1}{T^2}+5.4835\frac{1}{T}+0.09980 \tag{13}$$

It is interesting to note that at high temperatures, the predicted k_{ij} according to Eq. (13) approaches to 0.0998, which is very close to the value of 0.1 suggested by Kordas et al. [1994] for temperatures greater than 300 K.

Experimental [GPSA, 1998] and predicted CO_2 freezing temperatures for CO_2-CH_4 vapor mixtures at different pressure and CO_2 compositions are compared in Table 1 with the average AAD of 0.23%. Fig. 2 represents the comparison between the predicted and experimental freezing points of CO_2 at different pressure and vapor compositions. As shown, the measured freezing temperatures are well predicted by the proposed algorithm especially at CO_2 concentrations higher than 2%.

In order to check the validity of Eq. (13), the freezing points of CO_2 in the liquid mixtures of CO_2-CH_4 are also predicted by the PR equation of state using the proposed temperature dependent k_{ij} equation (Eq. (13)). In this case the fugacities of CO_2 in solid and liquid phases must be equated. The following equation holds at equilibrium:

$$F_2(T)=x_{CO_2}\phi_{CO_2}^{L}P-P_{CO_2Solid}^{Sat}\phi_{CO_2}^{Sat}\exp\left[\frac{v_{CO_2Solid}}{RT}(P-P_{CO_2Solid}^{Sat})\right]=0 \tag{14}$$

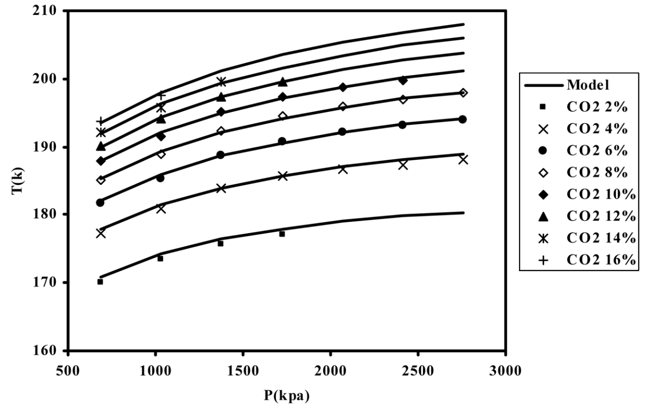

Fig. 2. Comparison between model predictions and experimental CO_2 freezing points for CO_2-CH_4 vapor mixtures.

whereis x_{CO_2} the mole fraction of CO_2 in liquid phase, $\phi_{CO_2}^{L}$ the liquid phase partial fugacity coefficient for CO_2, and the other parameters are the same as those explained for vapor-solid equilibrium.

The predicted CO_2 freezing temperatures at 5 MPa and different liquid phase compositions are compared with experimental data [Kurata, 1974] in Table 2 with the average AAD of 0.38%. This comparison is shown more clearly in Fig. 3. The measured values are well represented by the PR EOS using Eq. (13).

CONCLUSIONS

The Peng-Robinson equation of state is used for predicting the CO_2 freezing points for vapor and liquid mixtures of CO_2-CH_4. A semi-empirical quadratic temperature dependent k_{ij} correlation is derived (Eq. (13)) to express the CO_2-CH_4 interactions at cryogenic

Table 1. Comparison of the predicted and experimental CO_2 freezing points for CO_2-CH_4 vapor mixtures

Pressure (kPa)	T at CO_2=2%		T at CO_2=4%		T at CO_2=6%		T at CO_2=8%	
	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.
689.2857	170.9183	170.0944	177.8298	177.3167	182.1381	181.7611	185.3284	185.0944
1033.929	174.1902	173.4278	181.4545	180.8722	185.9895	185.3722	189.3476	188.9833
1378.571	176.3905	175.7611	183.934	183.9833	188.6470	188.7056	192.1392	192.3167
1723.214	177.9603	177.0389	185.7461	185.6510	190.6111	190.6501	194.2171	194.5389
2067.857	179.0920	177.5944	187.1054	186.7611	192.1086	192.0389	195.8164	195.9278
2412.510	179.8789	177.0389	188.1226	187.3167	193.2585	193.1510	197.0618	197.0389
2757.143	180.3509	178.0317	188.8556	188.1504	194.1275	193.9833	198.0247	197.8722

Pressure (kPa)	T at CO_2=10%		T at CO_2=12%		T at CO_2=14%		T at CO_2=16%	
	Model	Exp.	Model	Exp.	Model	Exp.	Model	Exp.
689.2857	187.8758	187.8722	190.0141	190.0944	191.8616	192.0389	193.4925	193.7056
1033.929	192.0384	191.4833	194.2959	194.0944	196.248	195.7611	197.9726	197.5944
1378.571	194.9392	195.0944	197.2897	197.3167	199.3234	199.5389	201.1211	
1723.214	197.1093	197.3167	199.5380	199.5389	201.6401		203.4991	
2067.857	198.7902	198.7056	201.2879		203.4501		205.3626	
2412.510	200.1112	199.8167	202.6719		204.8886		206.8494	
2757.143	201.1467		203.7670		206.0347		208.0401	

$$AAD\%=\frac{1}{n}\sum_{i=1}^{n}|(T_{calc.}-T_{exp.})/T_{exp.}|\times 100=0.23\%$$

Table 2. Comparison of the predicted and experimental CO_2 freezing points for CO_2-CH_4 liquid mixtures at 5 MPa

CH_4	CO_2	T (Exp)	T (Model)
0.9984	0.0016	129.6500	129.3387
0.9975	0.0025	135.2055	134.6121
0.9963	0.0037	139.4277	139.4500
0.9942	0.0058	144.5388	145.2616
0.9907	0.0093	150.3722	151.7002
0.9817	0.0183	162.0389	161.5848
0.9706	0.0294	169.8722	168.9983
0.9415	0.0585	182.1500	180.5035
0.8992	0.1008	189.2611	190.1682
0.8461	0.1539	196.9278	197.5099
0.7950	0.2050	201.2611	201.2047

$$AAD\% = \frac{1}{n}\sum_{i=1}^{n}|(T_{calc.} - T_{exp.})/T_{exp.}| \times 100 = 0.38\%$$

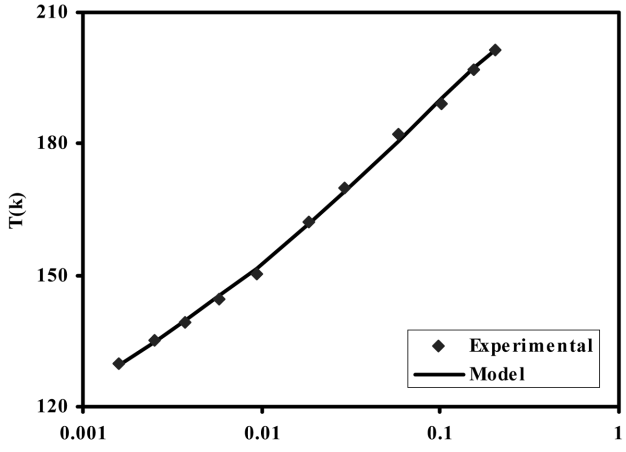

Fig. 3. Comparison between model predictions and experimental CO_2 freezing points for CO_2-CH_4 liquid mixtures at 5 MPa.

conditions of NGL Plants. The proposed thermodynamic model is capable of predicting the vapor-solid CO_2 freezing points of CO_2-CH_4 system with the AAD of 0.23% and the liquid-solid CO_2 freezing points are also predicted with the accuracy of 0.38%. The overall average absolute deviation between experimental and predicted CO_2 freezing temperatures is about 0.26%. The proposed model can be used for accurate prediction of CO_2 freezing temperatures of CO_2-CH_4 mixtures at cold sections of demethanization system of NGL extraction plants.

NOMENCLATURE

a_{ij} : binary interaction parameter used in Eq. (10)

a_i : pure component parameter used in equation of state

a_m : equation of state parameter used in Eq. (2a)

b_m : equation of state parameter used in Eq. (2b)

b_i : pure component parameter used in equation of state

F_1 : function defined in Eq. (6)

F_2 : function defined in Eq. (14)

f : empirical constant in Eq. (10)

i, j : components i and j

k_{ij} : binary interaction coefficient

k^o_{ij} : temperature independent binary interaction coefficient

k : Boltzmann constant

P : system pressure [kPa]

$P^{Sat}_{CO_2Solid}$: vapor pressure of solid CO_2 at system temperature [kPa]

R : universal gas constant (=8.314) [J $mol^{-1}K^{-1}$]

T^{TP} : CO_2 triple point temperature [K]

T_{exp} : experimental freezing point [K]

T_{calc} : calculated freezing point [K]

T : system temperature [K]

T_{ci} : critical temperature [K]

m_i : parameter defined in Eq. (3c)

N : number of components

n : number of data points

P_{ci} : critical pressure [kPa]

x_{CO_2} : mole fraction of CO_2 in liquid phase

y_{CO_2} : mole fraction of CO_2 in vapor phase

z_i : mole fraction of component i in the mixture

z : compressibility factor

Greek Letters

α and β : parameters in Eq. (12)

$\phi^V_{CO_2}$: vapor phase partial fugacity coefficient for CO_2

$\phi^{Sat}_{CO_2}$: fugacity coefficient of pure CO_2 vapor at $P^{Sat}_{CO_2Solid}$

ϕ_i : fugacity coefficient of component i in the mixture

$\phi^L_{CO_2}$: liquid phase fugacity coefficient for CO_2

ε_{ij} : interaction energy

ε^o_{ij} : temperature independent interaction energy

η_{ij} : parameter of non-central energy

v : molar volume of the mixture [m^3mol^{-1}]

v_{CO_2Solid} : molar volume of solid CO_2 and T the temperature [m^3mol^{-1}]

$\varepsilon(k_{ij})$: error function defined in Eq. (9)

ψ_i : parameter in Eq. (5b)

ω_i : acentric factor for component i

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