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Application of Peng–Rabinson equation of state for CO_2 freezing prediction of hydrocarbon mixtures at cryogenic conditions of gas plants

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Abstract

Carbon dioxide freezing problem is studied at cryogenic condition of NGL production gas plants. The Peng–Rabinson equation of state is used for predicting the CO_2 freezing points of hydrocarbon liquid and vapor mixtures. A quadratic temperature dependent correlation is presented for the proper description of a binary interaction parameter of methane and carbon dioxide at low temperatures. The overall average absolute relative deviation between the experimental and predicted CO_2 freezing temperatures for this binary system is 0.26%. The proposed model is then used for equilibrium calculations of a gas plant demethanizer column, and the CO_2 freezing points of the vapor and liquid hydrocarbon mixtures at the cold top trays of the demethanizer are predicted.

Keywords: Freezing; Peng–Rabinson; Interaction parameter; NGL; Cryogenic; Demethanizer

1. Introduction

Cryogenic processes are used in natural gas plants, petroleum refineries, ethylene plants and elsewhere in the process industries to recover and purify products that would normally be gaseous at ambient temperature and pressure. Carbon dioxide can freeze at the low temperature encountered in cryogenic plants, leading to plugged equipment and other operating problems. Accurate and reliable predictions of CO_2 freeze points are needed for the design of cryogenic to ensure that freeze conditions are avoided. CO_2 freeze-out prevention may dictate the type of cryogenic recovery process utilized, the maximum achievable recovery of products, or the amount of CO_2 recovered from the feed gas.

A typical process flow diagram for a turboexpansion-based NGL production plant is shown in Fig. 1. Carbon dioxide and its potential for freezing can be a limiting factor in gas plant design and operation. Feed CO_2 levels can dramatically affect project economics and risk as it may dictate the type of recovery process utilized, the maximum achievable NGL recovery, and/or the amount of amine treating required. The revamp of an existing NGL plant to recover additional ethane needs an accurate method for CO_2 freezing prediction.

A semi-empirical liquid freezup correlation based on the Mraw et al. [7] data has been suggested for CH_4–CO_2 binary system. Bergman and Yarborough [1] have 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. [12]. The liquid freezup curves from these two correlations are essentially identical except at the high temperature end (200 K). The experience has shown that these empirical correlations are not trustable enough to be used for industrial applications.

In the present paper, the standard form of Peng–Rabinson equation of state [8] with a modified interaction

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Nomenclature

AAD	average absolute deviation percent$=\sum_{i=1}^{n}\|(T_{\text{calc.}}-T_{\text{exp.}})/T_{\text{exp.}}\|/n\times 100$
a_i	pure component parameter used in equation of state
a_{m}	equation of state parameter used in Eq. (3)
b_{m}	equation of state parameter used in Eq. (4)
b_i	pure component parameter used in equation of state
f	empirical constant in Eq. (9)
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]
$P^{\text{Sat}}_{\text{CO}_2\text{Solid}}$	saturated vapor pressure of solid CO_2 at system temperature [kPa]
R	universal gas constant ($=8.314$) [J mol^{-1} K^{-1}]
R^2	regression coefficient
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. (4)
N	number of components
n	number of data points
P_{ci}	critical pressure [kPa]
v	molar volume of the mixture [m^3 mol^{-1}]
$v_{\text{CO}_2\text{Solid}}$	molar volume of solid CO_2 and T the temperature [m^3 mol^{-1}]
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)
$\Delta f^{\text{V-S}}_{\text{CO}_2}$	difference between fugacity of CO_2 in vapor and solid phases
$\Delta f^{\text{L-S}}_{\text{CO}_2}$	difference between fugacity of CO_2 in liquid and solid phases
$\phi^{\text{V}}_{\text{CO}_2}$	vapor phase partial fugacity coefficient for CO_2
$\phi^{\text{Sat}}_{\text{CO}_2}$	fugacity coefficient of pure CO_2 at system temperature
ϕ_i	fugacity coefficient of component i in the mixture
$\phi^{\text{L}}_{\text{CO}_2}$	liquid phase fugacity coefficient for CO_2
ε_{ij}	interaction energy
ε^0_{ij}	temperature independent interaction energy
η_{ij}	parameter of non-central energy
$\varepsilon(k_{ij})$	error function $=\|T_{\text{exp}}-T_{\text{calc}}\|$
ω_i	acentric factor for component i

parameter is used for the prediction of CO_2 freezing conditions. First a simple but very important case of freezing point prediction for the CH_4–CO_2 binary system is investigated. The predicted CO_2 freezing points for the vapor

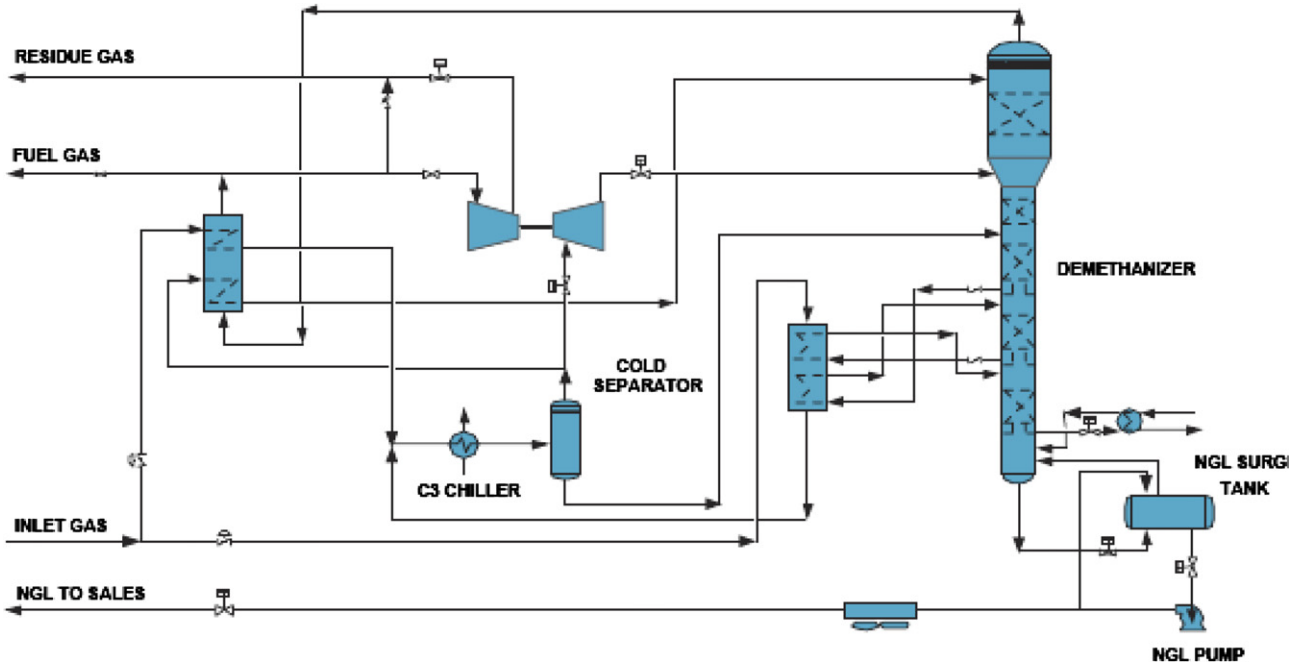

Fig. 1. Process flow diagram for a turboexpansion-based NGL production plant.