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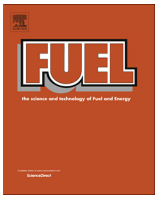

A new cubic equation of state for sweet and sour natural gases even when composition is unknown

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HIGHLIGHTS

- First worldwide cubic EOS when the gas composition is unknown.
- New gas critical properties through specific gravity correlations.
- Correction terms for H_2O and H_2.

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ABSTRACT

In this paper, the Heidaryan and Jarrahian equation of state (Heidaryan and Jarrahian, 2013) has been adapted as a first worldwide cubic EOS to calculate the density of dry natural gases, wet natural gases, and single-phase gas condensates "sweet and sour mixtures" (up to 73.85, 97.63 and 38.37 mol percent of H_2S, CO_2, and N_2 respectively) even when the gas composition is unknown, through new gas specific gravity correlation equations. Correction terms of water content as high as 10 mol percent of H_2O and hythane (natural gas + hydrogen) as high as 74.9 mol percent of H_2 were obtained. The equation of state was validated with 8985 experimental compressibility factor data points from 308 different mixtures in a range of atmospheric pressures up to 1570 bar and temperatures from −94 to 210 °C.

1. Introduction

Natural gas is one of the most important primary energy sources, accounting for almost one-fourth of the world's primary energy consumption [1]. Even though natural gas is a fossil fuel, it is comparatively environmentally sound, and due to its longer estimated future availability compared to oil, it is gaining in importance.

Thermodynamics information is required to select, design and optimize the process of getting natural gases from hydrocarbon reservoirs to users. The cost of such information might be as high as $200,000 if the process requires the design and construction of a new, complicated apparatus and a qualified engineer or technician must spend one to two years of operating time before the first result is obtained [2]. However, with a good mathematical model information can be delivered within seconds.

The first model of the volumetric properties of light hydrocarbons was carried out by Benedict et al. [3], with eight constants known as the Benedict–Webb–Rubin Equation of State (BWR-EOS). Starling [4] expanded this EOS to have eleven constants for more reliability; the new equation is known as BWRS-EOS. Li and Guo [5] introduced 33 constants into the BWRS-EOS to predict properties of natural gases. Extended corresponded states [6], virial equation of state [7] and generalized virial equation of state [8] for natural gas systems were presented.

Starling and Savidge [9] and Kunz et al. [10] introduced standard EOSs of AGA8-DC92 and GERG 2004. In general, these EOSs are inconvenient for engineering proposes because of the large number of calculations involved, and have not drawn the attention of the industry, as they are more applicable when there is a high amount of methane and no plus fraction mixtures [11]. From an industrial point of view, cubic EOSs could be used to predict volumetric properties of pure hydrocarbons even though they have a poor ability to predict volumetric properties of mixtures without a binary interaction coefficient [12]. There are also quite a few empirical correlations based on statistical fitting methods [13–17] for natural gas *Z*-factors. Unfortunately, these correlations have a limited range of application and cannot be used to predict other volumetric properties. Predicting the volumetric properties

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of natural gas is vital enough to have spurred the development of artificial-intelligence approaches [18–24].

The purpose of this study is to adapt the Heidaryan and Jarrahian EOS [25] to calculate the volumetric properties of dry natural gases, wet natural gases, and single-phase gas condensates "sweet and sour mixtures" even when the gas composition is unknown through new gas specific gravity correlations.

2. Literature review

2.1. Unknown composition equation of state

During the 1930s and 1940s there was great interest in representing the volumetric properties of hydrocarbon gases through charts as a primitive graphical EOSs. Cope et al. [26] developed a general plot of the *Z*-factor against reduced pressure ($P_r = P/P_C$), on curves of constant reduced temperature ($T_r = T/T_C$); this plot was considered applicable to light paraffins. Brown et al. [27] found that the data on the PVT relations of light hydrocarbons indicated that at constant volume the pressure is substantially a linear function of the temperature for each compound. They concluded that if reduced pressures are plotted against reduced temperatures on lines of constant reduced isochors, the data for compounds of widely different critical temperatures can be brought together on a single plot so that the variations of the individual compounds may be examined conveniently. Thus, they developed a similar chart from the experimental data on saturated vapors and the PVT relations of methane and *n*-pentane, and from the interpolated isochors for propane in which the deviations of the individual hydrocarbons had been considered. However, the gases encountered in petroleum production, natural gasoline and the refining divisions vary widely in composition, and in other properties that could not be represented with these charts.

Standing and Katz [28] measured the density of 16 saturated gases that were in equilibrium with crude oils in the range of 35–250 °F and 1000–8220 psi. Finally, by using Kay's [29] mixing rule they developed relationships to compute the *Z*-factor of gases to high pressure in the form of charts; these charts are reliable for gas condensate mixtures [30], and under the name of the Standing & Katz Z-Chart [31–38] are widely accepted in the petroleum and natural-gas industry. The Standing & Katz Z-Chart has been digitalized as tabulated numbers [39].

Hankinson et al. [40] tried to develop an EOS for natural gases by fitting the tabulated data of the Standing & Katz Z-Chart [28] over the BWR-EOS [3] in the pseudo reduced temperatures above of 1.1. The accuracy of the data representation was improved considerably by breaking the data into two regions: one for pseudo-reduced pressure less than 5.0 (based on 252 data points), and one for pseudo-reduced pressure between 5.0 and 15.0 (based on 328 data points). Fatoorehchi et al. [41] propose an explicit series expansion equivalent to the Hankinson et al. [40] EOS by the aid of a powerful mathematical technique known as the Adomian decomposition method. Hall and Yarborough [42] presented an EOS based on 289 data points from the digitalized Standing & Katz Z-Chart [28] by applying the repulsive pressure term of Carnahan–Starling's hard-sphere theory [43–44]. Dranchuk et al. [45], in their work on pure components, observed that *Z*-factors were difficult to express algebraically when considered as a function of reduced pressure and temperature; that is, the rather complicated shape of the isotherms posed a difficult fitting problem. On the other hand, it was observed that *Z*-factors expressed as a function of reduced density and temperature resulted in isotherms that were both simpler in shape and easier to fit. It was reasoned that the Standing & Katz Z-Chart [28] could be treated in a similar fashion. Consequently, 1500 tabulated data points representing the chart were used to calculate pseudo-reduced densities at regular intervals. They assumed a value of 0.27 for critical compressibility (Z_C), which is considered to be an appropriate value for mixtures comprised chiefly of methane. Dranchuk and Abou-Kassem [46] reiterated Dranchuk et al.'s [45] procedure and fit 1500 data point over the BWRS-EOS [4]. Londono et al. [47] chose Nishiumi and Saito's EOS [48], considering 5960 data points and introducing 15 constants. Hall and Iglesias-Silva [49] modified Hall and Yarborough's EOS [42] based on 890 data points, with additional terms to represent data in the range of $1.05 < T_{pr} < 1.12$.

2.2. Critical properties for natural gases

As the level of impurities was limited [28], this was effectively a relationship of pseudocritical properties through Kay's mixing rules [29]. Gases containing over 2–3% of impurities or high concentrations of intermediate components, and those containing heptanes deviate from Kay's mixing rules [29]; nor are they particularly suited to EOSs based on the Standing & Katz Z-Chart [47]. Hydrocarbon gas specific gravity (γ_{gMix}) is the simple standard measure for natural gases [51–53] Standing and Katz introduced graphical correlations to estimate pseudocriticals from γ_{gMix} [28].

Studies on ternary mixtures of light hydrocarbons containing impurities [54–56] showed that these components cause different behavior than sweet mixtures. The concentrations of carbon dioxide (CO_2), hydrogen sulfide (H_2S), and water vapor (H_2O) are easily measurable through field methods like length-of-stain detector tubes [57–59]; thus the mixture of pseudocriticals should be considered for measuring the amount of non-hydrocarbons.

Standing [60] determined the hydrocarbon-gas gravity for gases containing non-hydrocarbons, and defined quadratic-form equations that were representative over the entire range of natural gas gravity. Wichert and Aziz's [61] method adjusted for CO_2 and H_2S content. Sutton [62] optimized Standing's [60] quadratic equations for the Dranchuk and Abou-Kassem EOS [46] with regard to gas condensates. Piper et al. [63] combined Standing's [60] equations with Stewart et al.'s [64] mixing rule for the Dranchuk and Abou-Kassem EOS [46] regarding gas condensates. Elsharkawy et al. [65] optimized Standing's [60] equations for the Dranchuk and Abou-Kassem EOS [46] concerning gas condensates, but only for sour mixtures. Elsharkawy and Elkamel [66] used the Dranchuk and Abou-Kassem EOS [46] to predict pseudocriticals, and proposed a set of equations concerning gas specific gravity and both hydrocarbon and non-hydrocarbon gas specific gravity. Londono et al. [47] optimized Standing's [60] equations for their EOS. Sutton [50] revised Standing's [60] equations as well as Wichert and Aziz's [61] pseudocritical-temperature adjustment parameter based on Dranchuk and Abou-Kassem EOS [46].

2.3. Natural-gas density literature data

There is great interest in the literature in the measurement of natural-gas density. It is measureable using PVT cell tests [67–68] or by direct densitometry [69–78].

Fortunately compositional data is convertible to γ_{gMix} through average molecular weight, using Eq. (1):

$$\gamma_{gMix} = Mw_{air}^{-1} \sum y_i Mw_i \tag{1}$$

A mixture with at least five components has been accepted in this study. Hydrocarbon gases have different definitions depending on whether composition is known or unknown, as listed in Table 1. Table 2 summarizes the collected data for this study [5,42,79–131]. Statistical distributions of the collected data are summarized in Table 3.

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