Prediction of hydrogen solubility in PYGAS with equations of state

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Abstract. The objective of this contribution was to explore the effect of thermodynamic model selection on predicting the solubility of hydrogen in Pyrolysis Gasoline (PYGAS). In order to do this, different combinations of cubic equations of state (EOS), cohesion functions and mixing rules were compared, using both own algorithms and those implemented in the PRO/II 8.0 process simulation software. The models were selected following the recommendations made by some authors for H\textsubscript{2} + hydrocarbons systems similar to the studied here. The cubic EOS of Redlich-Kwong (RK) and Peng-Robinson (PR) were considered using: five different cohesion functions, and the classical quadratic mixing rule (CQMR) with five single correlations to estimate the binary interaction parameters (BIP). Additionally, the system was simulated with PRO/II employing the Panagiotopoulos-Reid Modified (PA-RE-Mod) and the modified PA-RE mixing rule implemented by SimSci. The results were validated with experimental data reported in the literature for four temperatures 298 K, 313 K, 323 K, 343 K and pressures up to 6 MPa. The model composed by the RK EOS, Soave (1993) cohesion function, the CQMR with the BIP calculated with the Gray et al. correlation is the recommended selection to predict the solubility of H\textsubscript{2} in PYGAS, under the considered conditions, with a 3.1% AARD (average absolute relative deviation).

Keywords: PYGAS, hydrogen, solubility, equation of state, Redlich-Kwong, Peng-Robinson

1. Introduction

The Pyrolysis Gasoline (PYGAS) is obtained as a byproduct in the preparation of ethane and/or propene by means of high-temperature pyrolysis (i.e. cracking in the presence of steam) of gaseous or liquid hydrocarbons, such naphtha or gas oil. PYGAS is extremely unstable due, on one hand, to the presence of a relative high proportion of highly olefinic unsaturated hydrocarbons (HC), known as gum-forming compounds, and, on the other hand, to the content of aromatic compounds and alkenes having a high octane number which are particularly valuable and useful as stable motor gasoline components [1].

In order to obtain a stable gasoline with high octane number and/or prevent gum formation during downstream processing or storage, the PYGAS product is further stabilized by a selective hydrogenation process. The advantage of this process is that it can efficiently remove most of the unstable compounds and convert them to desirable olefins and aromatics, thus increasing overall yield [2].

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The knowledge of the hydrogen concentration in the liquid phase is very important for the understanding of the kinetics in hydrogenation processes, and therefore for the design of such processes. However, there are only a few studies related to the solubility of hydrogen in petroleum systems, and even less for its solubility in PYGAS. Rodríguez [3] evaluated the vapor-liquid equilibrium (VLE) of mixtures containing H$_2$-HC focused on the selective hydrogenation of 1,3-butadiene, recommending the use of the Peng-Robinson (PR) [4] equation of state (EOS) and the Stryjek-Vera (SV) [5] cohesion function, with the classical quadratic mixing rule (CQMR) and any correlation for binary interaction parameters (BIP). This combination provides the best reproduction of the experimental data among the alternatives considered by Rodríguez, with less than 8% of average absolute relative deviation (AARD) on H$_2$ solubilities. Zhou et al. [6] measured the solubility of hydrogen in PYGAS under experimental conditions similar to those found in the first-stage reactor (temperature range between 298 and 343 K and pressures up to 6.0 MPa), furthermore, they used the Soave-RK [7] EOS to describe the vapor-liquid equilibrium (VLE) in the H$_2$-PYGAS system, using the CQMR and the Gray et al. correlation [8] to describe the mixture behavior and calculate the binary interaction parameter between hydrogen and HC. They showed that, in these conditions, the RK-Soave-CQMR-Gray equation can predict Henry’s constant very well and the solubility of hydrogen increases with the rise of temperature and pressure.

An alternative approach for the representation of VLE of hydrogen-hydrocarbon systems are the family of equations of state based on the statistical associating fluid theory (SAFT) of Chapman et al. [9]. This family is considered as one of the more mature molecular EOS, and due to their theoretical basis are more suitable to extrapolate the results beyond the fitting domain [10]. Among others, Thi et al. [11], and Tran et al. [12] have obtained good results using a group contribution method which can be applied to any hydrocarbon [10]. In both cases the authors report results for mixtures containing hydrogen that compared well with those obtained from the classical Grayson-Streed model [13], particularly for long-chain HC. The deviations obtained by these authors between calculated bubble point pressures and experimental data of binary systems composed of hydrogen and n-alkenes [11,12], and aromatics and cycle-alkenes [11], where close to 5%, which are comparable to those expected when more simpler cubic EOS are employed [10,11]. The major disadvantages of the SAFT EOS family are the lack of estimations methods for the parameters of petroleum pseudo-components [10] and their algebraic complexity.

The purpose of the present study is to extend the study of Zhou et al. [6] and determine the performance of different thermodynamic models in the prediction of the solubility of hydrogen in PYGAS reported in their work. The thermodynamics models under consideration where selected following the recommendations made by some authors for H$_2$ + hydrocarbons systems similar to the studied here and taking into account the ease of use and the expected accuracy reported in the literature. These models comprise the combinations of the RK and PR cubic EOS with five cohesion functions, three mixing rules, and six correlations for binary interaction parameters.

2. Thermodynamics models

The thermodynamic state of a substance is known for a pure substance when two of three independent properties are fixed. These three properties for a pure substance can be related by means of an EOS, e.g. the relationship between temperature, pressure and volume take the form $(P, V, T) = 0$. The traditional cubic (in volume) EOS are the simplest equations capable of representing both the liquid and vapor states and have found considerable application in VLE computations. They represent a compromise between simplicity of and sufficient flexibility to describe wide ranging phase behavior. Hundreds of cubic EOS have been proposed to the date in the literature, modifying the EOS itself as well as their parameters functionality and their mixing rules for the case of multi-component systems [14].
2.1. Cubic EOS

The RK [15] and PR [4] EOS are part of what is known as the van der Waals cubic EOS family. These cubic EOS are commonly represented in the general form proposed by Martin [16]:

\[
P = \frac{RT}{(V - b)} - \frac{a(T)}{(V + \mu_1 b)(V + \mu_2 b)}
\]  

(1)

Where the coefficients \(\mu_1\) and \(\mu_2\) take the values of: 0 and 1 for RK; and \(1 + \sqrt{2}\) and \(1 - \sqrt{2}\) for PR, respectively. Defining the compressibility factor: \(Z = PV/RT\), Eq. (1) takes a cubic polynomial form in terms of \(Z\) as:

\[
Z^3 - E_2 Z^2 + E_1 Z - E_0 = 0
\]  

(2)

where:

\[
E_2 = \left[ 1 - (\mu_1 + \mu_2)B + B \right]
\]

(3)

\[
E_1 = \left[ \mu_1 \mu_2 - (\mu_1 + \mu_2)B^2 - (\mu_1 + \mu_2)B + A \right]
\]

(4)

\[
E_0 = \mu_1 \mu_2 B^2 (B + 1) + AB
\]

(5)

For VLE computation, the values of the fugacity coefficients are required. In the case of the RK and PR cubic EOS and the classical quadratic mixing rule (CQMR) the fugacity coefficient for the \(i^{th}\) compound in the mixture can be obtained from:

\[
\ln \phi_i = -\ln(Z - B) + \frac{B_i}{B} (Z - 1) + \frac{1}{(\mu_1 - \mu_2) B} \left( \frac{2}{A} \sum_{j=1}^{NC} y_j \sqrt{A_i A_j (1 - k_{ij}) - B_i} \right)
\]

\[
\ln \left( \frac{Z + \mu_2 B}{Z + \mu_1 B} \right)
\]

(6)

Where: \(A_i = \Omega_A P_{r,i} \alpha_i / T_{r,i}^2\) and \(B_i = \Omega_B P_{r,i} / T_{r,i}\). \(\Omega_A\) and \(\Omega_B\) are constants: \(1/9 (2^{1/3} - 1)\) and \((2^{1/3} - 1) / 3\), for RK; and 0.45724 and 0.07780, for PR. \(\alpha_i\) is the cohesion \(\alpha\) function for the \(i^{th}\) compound and it is in general an expression dependent on the temperature and in some cases of characteristic physical properties such as the acentric factor, \(\omega\), or the critical compressibility factor, \(Z_c\), (see Section 2.2). \(\alpha\) and \(\beta\) are obtained through a specific mixing rule (Section 2.3). The BIP, \(k_{ij}\) in Eq. (4) is calculated either from fitting experimental binary VLE data or through a correlation previously determined for each binary pair (Section 2.4).

2.2. Cohesion functions

One of the requirements to achieve accurate predictions of VLE on multicomponent systems is the accuracy of the EOS in the prediction of pure-component vapor pressures. This requirement can be attained through the introduction of an appropriate cohesion function [7]. This concept was first presented by Wilson [17] in the form of a temperature dependence of the parameter \(a(T)\) in Eq. (1) as \(a(T) = \alpha(T)a_c\) where \(a_c\) is the value of \(a\) at the critical point, \(\alpha(T)\) is the cohesion function which by definition at the critical temperature: \(\alpha(T_c) = 1\). Wilson [18] expressed \(\alpha(T)\) as a function of the reduced temperature and the acentric factor but this first attempt was not as successful as the further ones in the reproduction of vapor pressures, therefore the Wilson’s function never becomes popular in EOS applications [19].
2.2.1. Soave (S72)

Soave [7] modified the original term \( a(T) \) of the RK equation, proposing a new improved version of Wilson’s idea, redefining the \( \alpha(T) \) function as:

\[
\alpha_i = \left[ 1 + m_i \left( 1 - \sqrt{T_{r,i}} \right) \right]^2
\]  

(7)

where \( m_i \) is a fluid dependent parameter obtained by Soave from vapor pressure data points at \( T_r = 0.7 \) generated from the definition of the acentric factor in the range of \( 0 \leq \omega \leq 0.5 \). Whereupon \( m_i \) was correlated in terms of \( \omega_i \):

\[
m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2
\]  

(8)

After Soave’s proposal, many modifications were presented in the literature with the goal of improving vapor pressures predictions or extending the range of applicability to more fluids (in general cubic EOS are more suitable to light hydrocarbons and non-polar or slightly polar systems). One of the most extended used is the modification proposed by Peng and Robinson [4]. After introducing a modification on the volume dependence of the attractive term in Eq. (1), they maintained the functional form proposed by Soave [7] but readjusted the \( m_i \) in terms of available vapor pressure data for fluids with acentric factors between 0 and 0.5. The expression for \( m_i \) in this case is:

\[
m_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2
\]  

(9)

2.2.2. Soave (S93)

Soave [20] proposed a new cohesion function that can be applied to polar and non-polar compounds. This new function provides better vapor pressures predictions for heavy hydrocarbons below their normal boiling points than the expression of 1972, known for their poor performance at low reduced temperature. The proposed expression incorporated a second adjustable parameter, \( n_i \):

\[
\alpha_i = 1 + m_i(1 - T_{r,i}) + n_i(1 - \sqrt{T_{r,i}})^2
\]  

(10)

The parameters \( m_i \) and \( n_i \) were obtained by correlating vapor-pressure values generated by the Lee-Kesler EOS:

\[
m_i = 0.484 + 1.515\omega_i - 0.44\omega_i^2
\]  

(11)

\[
n_i = 2.756m_i - 0.700
\]  

(12)

The parameters in Eqs (11–12) are valid for fluids in the range of \( 0 \leq \omega \leq 1 \).

2.2.3. Graboski and Daubert (GD)

Graboski and Daubert [21] presented an extension of the Soave equation to systems containing hydrogen. Due to the extremely supercritical state of hydrogen for most of the practical applications the basic Soave procedure does not reproduce VLE accurately. Graboski and Daubert developed a new temperature dependency for the hydrogen cohesion function for the RK EOS, Eq. (13), which eliminates the need for binary interaction coefficients \( k_{ij} = 0 \). The proposed function for hydrogen was adjusted from experimental VLE binary data of hydrogen and several hydrocarbons, including n-alkanes, cycloalkanes, and aromatics.

\[
\alpha_{H_2} = 1.202 \exp(-0.30288T_{r,H_2})
\]  

(13)

For the rest of the fluids the S72 function is maintained but with a new adjustment for the \( m_i \) parameter in terms of \( \omega_i \):

\[
m_i = 0.48508 + 1.5517\omega_i - 0.15613\omega_i^2
\]  

(14)
2.2.4. Gibbons and Laughton (GL) and Stryjek and Vera (SV)

Gibbons and Laughton [22] modified the S72 function for the RK EOS with the objective of extending the range of applicability of this EOS to polar and heavy compounds, which typically are at low reduced temperatures for practical applications. They proposed the two parameter function shown in Eq. (15), with parameters adjusted to experimental vapor pressure data.

\[
\alpha_i = 1 + m_i (T_{r,i} - 1) + n_i \left( \sqrt{T_{r,i}} - 1 \right)
\]  

(15)

Stryjek and Vera [5] were also concerned with the poor performance of the traditional S72 \( \alpha \) formulation at low reduced temperatures, where the deviations between predicted and experimental vapor pressures tend to increase dramatically. The authors proposed a two parameter cohesion function for the PR EOS, which reduces to the original formulation proposed by Peng and Robinson at \( T_{r,i} = 0.7 \).

\[
\alpha_i = \left\{ 1 + \left[ m_i + n_i \left( 1 - \sqrt{T_{r,i}} \right) (0.7 - T_{r,i}) \right] \left( 1 - \sqrt{T_{r,i}} \right) \right\}^2
\]  

(16)

The parameter \( m_i \) was adjusted by a procedure similar to the used by Peng and Robinson [4], obtaining:

\[
m_i = 0.378893 + 1.4897153 \omega_i - 0.1713184 \omega_i^2 + 0.0196554 \omega_i^3
\]  

(17)

On the other hand, \( n_i \) is an adjustable parameter characteristic of each pure compound. The authors reported values of \( n_i \) for over ninety compounds, and recommended its use from the low reduced temperature up to 0.7 and \( n_i = 0 \) for reduced temperatures above 0.7.

Figueira et al. [23] determined optimized parameters of the GL and SV cohesion functions for their use with the classical van der Waals, RK and PR EOS. They fitted the parameters from over eight hundred fluids using vapor pressure data generated with the correlations contained in the DIPPR database [2] from the triple point to the critical point. They also proposed a generalized correlation to determine these parameters for fluids not present in the database or for ill-defined compounds. Figueira et al. optimized parameters for the GL and SV functions were used in the present paper.

2.2.5. Twu-Bluck-Cunningham-Coon (TBCC)

Twu et al. [25] derived a new cohesion function, Eq. (18) for RK EOS, increasing the flexibility of an initial equation proposed in a previous work. This new function satisfies all the requirements proposed by then, e.g. it cannot become negative at high temperatures, and is claimed to reproduce more accurately the vapor pressure than the S72 function and gives a correct extrapolation into supercritical temperatures. The developers of the PRO/II 8.0 software [26] recommended the TBCC function when its use is possible. Actually, PRO/II uses the TBCC equation by default, mixing this equation with the original S72 function Eq. (7) in the cases when the \( N_i, M_i \) and \( L_i \) parameters are unknown.

2.3. Mixing rules

Mixing rules are required to extend the use of EOS to multicomponent systems. The accuracy of the representation of VLE data using a cubic EOS relays on the selection of an appropriate mixing rule, which would be dependent on the type of system under study.
2.3.1. Classical quadratic mixing rule (CQMR)

For mixtures composed of non-polar and/or hydrocarbon fluids the classic quadratic mixing rule (CQMR), also known as the van der Waals mixing rule, have been proven to be sufficiently accurate and it is the common choice. The CQMR is given by:

\begin{align}
A &= \sum_{i=1}^{NC} \sum_{j=1}^{NC} y_i y_j \sqrt{A_i A_j} (1 - k_{ij}) \\
B &= \sum_{i=1}^{NC} y_i B_i
\end{align}

(19)

(20)

Where, \( k_{ij} \), are the binary interaction parameters (PIB), which take into account the differences in the interactions between every pair of components in the mixture. For the CQMR the PIB are symmetrical, \( k_{ij} = k_{ji} \), and by definition \( k_{ii} = k_{jj} = 0 \). The PIB are often used to improve the accuracy of the model, however even when they are used the CQMR fails to provide precise results for complex systems as highly polar mixtures, associated mixtures and other very complex systems [27].

2.3.2. Panagiotopoulos-Reid modified (PA-RE-Mod)

Panagiotopoulos and Reid [28] developed an asymmetric mixing rule for van der Waals-type cubic EOS making the normally used single binary interaction parameter \( k_{ij} \) a linear function of composition, where the definition \( k_{ij} = k_{ji} \) in Eq. (19) is not a mandatory condition. However, according to Sim-Sci [26], PA-RE is inconsistent for multicomponent systems in two (related) flaws: First, the dilution of the mixture with additional components (reducing all the mole fractions \( y_i \)) nullifies the effect of the second binary parameter \( k_{ij} \); second, the mixing rule is not invariant to dividing a component into a number of identical pseudo-components. Then, SimSci modified the original equation of PA-RE to eliminate the flaws mentioned above, proposing:

\begin{align}
A &= \sum_{i=1}^{NC} \sum_{j=1}^{NC} y_i y_j \sqrt{A_i A_j} \left[ (1 - k_{ij}) + (k_{ij} - k_{ji}) \left( \frac{y_i}{y_i + y_j} \right) C_{ij} \right] \\
B &= \sum_{i=1}^{NC} y_i B_i
\end{align}

(21)

where, there are four adjustable BIP \( k_{ij} \), \( k_{ji} \), \( C_{ij} \) and \( C_{ji} \).

2.3.3. SimSci

SimSci [26], in an effort to eliminate the flaws in PA-RE equation and improve the results obtained with Eq. (21), introduced in their software the modified mixing rule proposed by Twu et al. [25]:

\begin{align}
A &= \sum_{i=1}^{NC} \sum_{j=1}^{NC} y_i y_j \sqrt{A_i A_j} \left( 1 - \frac{k_{ij}}{T} \right) + \sum_{i=1}^{NC} y_i \left\{ \left[ \sum_{j=1}^{NC} \frac{H_{ij}^{1/3} G_{ij}^{1/3} (A_i A_j)^{1/6}}{y_j} \right]^3 / \sum_{j=1}^{NC} G_{ij} y_j \right\}
\end{align}

(22)

where: \( H_{ij} = k_{ij} - k_{ji}; G_{ij} = \exp(-\beta_{ij} H_{ij}); \) and \( \beta_{ij} \) is a new parameter.

As noted above the expression for the fugacity coefficients are dependent of the mixing rules considered for the system. All the computations with the mixing rules presented in Eqs (21) and (22) were performed directly in PRO/II 8.0, the corresponding expressions of the fugacity coefficients for these mixing rules can be found in references [25,28].
2.4. Binary interaction parameter correlations

The main function of the BIP in mixing rules is to improve the accuracy of EOS for multicomponent systems. These parameters are empirical by nature and are usually obtained from the regression of binary VLE data, although some simplifications are commonly used for certain systems. In general, the $k_{ij}$ are considered null for similar compounds; e.g., in the case of the interactions HC-HC $k_{ij} = 0$, and only taken into account for very dissimilar fluids, e.g., the parameters for H$_2$-HC are often required. For the later, a number of correlations have been proposed in the literature. A brief summary is presented here.

2.4.1. Moysan et al. (1983) (MO83)

Moysan et al. [29] proposed a generalized correlation of $k_{H_2,HC}$ for systems containing hydrogen and the RK-S72 and PR EOS. They restricted the study to pressures up to 10 MPa for “light solvents” ($T_c \leq 470$ K) and pressures up to 30 MPa for “heavy solvents” ($T_c > 470$ K). At these conditions they found that the BIP are strongly dependent on temperature and independent of the solvent. They expressed the BIP in terms of the cohesion function and the reduced temperature of the hydrogen:

$$k_{H_2,HC} = 1 + \left\{ \left[ u(T_{r,H_2} - 1) - 1 \right] / \sqrt{\alpha_{H_2}} \right\}$$

(23)

In Eq. (23) $u$ is a numerical coefficient that depends on the selected EOS: 0.0600 for RK-S72 and 0.0417 for PR.

2.4.2. Moysan et al. (1986) (MO86)

Moysan et al. [30] extended their initial correlation, MO83, for hydrocarbon systems containing gases such as H$_2$, CH$_4$, N$_2$, CO$_2$, CO, H$_2$S. In the development of this new correlation only data below 30 MPa for H$_2$, CH$_4$ and N$_2$, and below 130 MPa for CO$_2$, CO, H$_2$S were considered. For systems with H$_2$, CH$_4$, N$_2$ and CO the authors found a strong dependency of the BIP with temperature and a negligible effect of solvent, i.e., the BIP correlation is function only of the properties of these gases and the temperature. In the case of hydrogen, the BIP for the RK-S72 EOS and the CQMR are defined as:

$$k_{H_2,HC} = 1 - \frac{1 - 0.060(T_{r,H_2} - 1) + G_{H_2,HC}}{1 + 0.1252(1 - \sqrt{T_{r,H_2}})}$$

(24)

where $G_{H_2,HC}$, or $G_{ij}$ are, in general, corrective constants that take into account the high sensitivity of low temperature systems to the value of the BIP. For the fluids considered in this work those correctives parameters are null.

Moysan et al. [30] performed a number of calculations for the PR-EOS obtaining BIP values very similar to the found for the RK-S72, except for the H$_2$. For systems containing hydrogen they recommended the use of the correlation derived in [29] for the PR-EOS, i.e., Eq. (23).

2.4.3. Valderrama and Reyes (VA-RE)

Valderrama and Reyes [31] performed an exhaustive study on the application of the PR EOS to multicomponent systems containing hydrogen. After a meticulous selection of binary VLE data they obtained through a least-square fitting the BIP for 228 isotherms corresponding to 33 binary systems. The results showed a clear dependency of the BIP on temperature, this dependency was correlated in the simple two parameters form presented in Eq. (25).

$$k_{H_2,HC} = \mu_{HC} - \varepsilon_{HC}/T_{r,HC}$$

(25)
The parameters in Eq. (25) were generalized in terms of the acentric factor of the solvent, i.e. the HC. In the development of this generalization a few components were excluded due an appreciable deviation from the general tendency, most of them with \( \omega_{HC} \geq 0.5 \). The parameter correlations for the remaining systems are:

\[
\begin{align*}
\mu_{HC} & = 0.1805 + 3.2100\omega_{HC} + 2.4370\omega_{HC}^2 \\
\varepsilon_j & = 0.1323 + 0.5507\omega_j + 3.5994\omega_j^2
\end{align*}
\] (26)

2.4.4. Valderrama et al. (VAL)

Valderrama et al. [32] developed new correlations for the BIP for \( \text{H}_2\)-n-alkanes mixtures for the PR, RK-S72 and Valderrama and Cisternas (VC) EOS [33]. Instead of using the traditional bubble pressure minimization approach for fitting the BIP, they used the method proposed by Paunovic et al. [34] based on the isofugacity criteria. As previous works, the authors found that the BIP are strongly dependent on temperature but, unlike Moysan et al. [27,28], they concluded that the effect of the solvent is not negligible. The correlation and its generalization in terms of the acentric factor of the solvent are presented in Eqs (28) to (30). The parameters \( \mu_j \) and \( \varepsilon_j \) have the following values for the EOS considered in the present work: RK, \( \mu_0 = 0.2759, \mu_1 = 0.8422, \mu_2 = 6.2969, \varepsilon_0 = 0.1674, \varepsilon_1 = -0.5609, \varepsilon_2 = 5.1627 \); and PR, \( \mu_0 = 0.3063, \mu_1 = 0.7787, \mu_2 = 7.3040, \varepsilon_0 = 0.1815, \varepsilon_1 = -0.7770, \varepsilon_2 = 5.9287 \).

\[
\begin{align*}
k_{H_2,HC} & = \mu_{HC} - \varepsilon_{HC}/T_{r,HC} \\
\mu_{HC} & = \mu_0 + \mu_1\omega_{HC} + \mu_2\omega_{HC}^2 \\
\varepsilon_{HC} & = \varepsilon_0 + \varepsilon_1\omega_{HC} + \varepsilon_2\omega_{HC}^2
\end{align*}
\] (28)

2.4.5. Gray et al.

Gray et al. [8] studied the VLE predictions of multicomponent systems containing \( \text{H}_2 \) with cubic EOS. They fit the RK-S72 and PR EOS using data ranging from cryogenic to high temperatures conditions. The BIP correlation proposed by them is dependent on the critical temperature of the HC (in Kelvin) as follows:

\[
k_{H_2,HC} = A + B \left[ \frac{(T_{c,HC} - 50)}{(1000 - T_{c,HC})} \right]^3 \left/ \left[ 1 + \left[ \frac{(T_{c,HC} - 50)}{(1000 - T_{c,HC})} \right]^3 \right] \right. \] (31)

Where the constants \( A \) and \( B \) take the values of 0.0067 and 0.63375 for RK-S72 EOS, and 0.0736 and 0.58984 for PR EOS. The correlation is applicable to HC with critical temperatures between 50 and 525 K. The deviations on predicted BIP for fluids with \( T_{c,HC} > 550 \) K are about 14.5% while for fluids with \( T_{c,HC} < 550 \) K are just 3.8%. The authors neither recommend the use of Eq. (31) for cryogenic systems if it is required a high degree of accuracy.

2.4.6. PRO/II 8.0 Databanks

The PRO/II 8.0 Databanks [26] already contain a large data base of adjustable binary parameters for several EOS obtained by fitting published experimental and/or plant data. In most cases, the software does not require additional input of binary interaction parameters from the user. When one or more of the \( k_{ij} \) are unknown, PRO/II uses a correlation to estimate them. The temperature-dependent correlation for the BIP is given by:

\[
k_{ij} = k_{ij,A} - k_{ij,B}/T_{r,j} + k_{ij,C}/T_{r,j}^2
\] (32)
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>( w_i )</th>
<th>( T_C ) (K)</th>
<th>( P_C ) (MPa)</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYGAS: ( \rho = 0.8535 \text{ g cm}^{-3} ) (at 293 K) and ( MW = 88.36 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.470</td>
<td>562.60</td>
<td>4.9244</td>
<td>0.2090</td>
</tr>
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<td>4.1087</td>
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<td>2.9455</td>
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<td>2.9200</td>
<td>0.1853</td>
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<td>Hydrogen: ( MW = 2.01588 )</td>
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<td></td>
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<td>–</td>
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<td>1.3130</td>
<td>–0.21599</td>
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</table>

3. Computation methodology

As mentioned above, Zhou et al. [6] studied the solubility of \( H_2 \) on PYGAS at conditions resembling those found in the first stage reactor in the high-temperature naphtha pyrolysis process. They reported 24 experimental points of the hydrogen solubility in terms of temperature (298, 313, 323 and 343 K) and pressure (ranging roughly from 0.6 to 6 MPa). These measures were realized using an isochoric method and the reported solubility have an uncertainty within 2%.

In order to evaluate the accuracy of the different thermodynamic models under study, the experimental data was modeled through adiabatic-isothermal flash separators operated at the same temperature-pressure conditions reported by Zhou et al. [6]. For every flash calculation a feed with a hydrogen-PYGAS volume ratio of 1:2 was used in order to ensure two-phase separation. The mass compositions reported by Zhou et al. and considered in this study for the PYGAS are reported in Table 1. As can be seen, the liquid mixture is composed of nine different HC and a residual component with less than 7% in mass.

In the case of the EOS with the CQMR (with the exception of the TBCC cohesion function) the flash calculations were performed using a program developed by us based on the Rachford-Rice method Eqs (33) to (35). Through this method are obtained the vapor fraction, \( \beta \), and the compositions at equilibrium, \( x_i \), and \( y_i \), at the given temperature, pressure and global composition, \( z_i \), of the feed.

\[
\sum_{i=1}^{NC} \left( \frac{z_i(K_i - 1)}{1 + \beta(K_i - 1)} \right) = 0 \tag{33}
\]

\[
x_i = \frac{z_i}{1 + \beta(K_i - 1)} \tag{34}
\]

\[
y_i = x_iK_i \tag{35}
\]

The \( \phi - \phi \) method was used to calculated the equilibrium constants, \( K_i = y_i/x_i \). The \( \phi - \phi \) approach applies to non-polar and slightly polar systems at low and high pressures, including regions near the critical point. This method is based on the isofugacity equilibrium criterion, which implies that the fugacity of every component in each phase is identical, i.e. \( f_i^V = f_i^L \). These fugacities can be obtained from the fugacity coefficients as: \( f_i^V = \phi_i^V y_iP \) and \( f_i^L = \phi_i^L x_iP \). Finally, the \( K_i \) constant can be obtained from the equation of state as: \( K_i = \phi_i^L / \phi_i^V \).
The Fig. 1 shows the block diagram for the flash calculations. The iterative algorithm, known as the successive substitution method, consists of three main steps: the initiation, the estimation of the vaporized fraction ($\beta$), and calculation of the fugacity coefficient of each component in both phases. This method has proven to converge rapidly to the solution in most cases. The method compares the value of the $K_i$ obtained in consecutive iterations, calculating the error between steps as, $error = |(K_{oi} - K_i)/K_{oi}|$ until the specified tolerance is achieved ($Tol = 10^{-5}$). If the tolerance is not attained, then the value of $K_{oi}$ is updated to $K_i$ and the procedure continues.

In order to estimate the initial value of the vaporization equilibrium ratio ($K_i = y_i/x_i$), the empiric Wilson correlation is employed, Eq. (36). This correlation is frequently used in the oil and natural gas industry.

$$K_{oi} = P_{ri}^{-1} \exp[5.37(1 + \omega_i)(1 + T_{ri}^{-1})]$$  (36)

In the case of the models that incorporated the Twu-Bluck-Cunningham-Coon (TBCC) cohesion functions the PRO/II 8.0 process simulator was used to simulate the flash separation. Once the values of the
solubility of hydrogen have been obtained for each experimental point, the AARD for each model were evaluated by:

$$AARD = \frac{1}{24} \sum_{N=1}^{24} \left| \frac{x_{\text{cal}}^{N} - x_{\text{exp}}^{N}}{x_{\text{exp}}^{N}} \right| \times 100$$

(37)

where $x_{\text{exp}}^{N}$ is the experimental hydrogen solubility reported by Zhou et al. for the $n^{th}$ data point and $x_{\text{cal}}^{N}$ is the calculated hydrogen solubility obtained by the flash procedure.

For all the models considered in this work, the physical properties required for the cubic EOS were taken from DIPPR [24] and SimSci [26] databases.

4. Results and discussion

The Table 2 and Fig. 2 show the absolute average relative deviation (AARD) for each combination of EOS, cohesion function, mixing rule and BIP correlation studied in this work. This AARD were obtained using both the program developed in this work and the PRO/II simulation software. It can be observed in the table that the lowest AARD is attained with the RK EOS using the S93 cohesion function for the HC and the S72 for the H$_2$. The CQMR and the Gray et al. BIP correlation. For this model the AARD is 3.1%. The second best model is the RK EOS, TBCC-S72 cohesion function and the SimSci mixing rules with PRO/II databanks BIP, with an AARD of 3.4%. The variability of the AARD demonstrates the importance of the choice of the thermodynamic model for prediction of solubility of H$_2$ in HC for the system under study.

It should be noted that in some cases it is necessary to combine different cohesion functions in the same model, as suggested by Graboski and Daubert [21] and usually implemented in process simulators [26]. The reason is that certain cohesion functions, such as S93 and GL, produce negatives values of $\alpha$ at high
reduced temperatures. In the system studied this situation arises for the hydrogen due its extremely low critical temperature (with $T_r$ ranging from 9 to 10.3). In cases when the cohesion function is negative none of the mixing rules considered in this work are applicable due the $\sqrt{A_i A_j}$ term, which would be undetermined in the real number field. Therefore, in the models studied involving the functions S93 and GL, those were used only for the hydrocarbons and the function S72 for the hydrogen.

An additional difficulty encountered during calculations was the inadequacy of the Wilson correlation, Eq. (36), to produce reasonable initial guesses for the equilibrium constant of hydrogen. In this case the values were too low compared to the expected, e.g. using the $\phi - \phi$ method, causing some convergence issues in the flash calculations. This can be attributed to the supercritical condition of the $H_2$, and that the Wilson correlation has been deduced from vapor pressure data. To overcome this difficulty a multiplying factor of 4 is recommended.

Comparing the accuracy of the different models studied, one of the notorious results is the consistent superiority of the RK over the PR EOS when the S72 cohesion function, the CQMR and the MO83, VA-RE, VAL and Gray et al. correlations were considered. The unique exception is the PR-VAL with an 18.4% vs. 19.9% AARD for the RK-S72-VAL. The best results for the S72 cohesion function were obtained with the Gray et al. correlation, with a 4.5% AARD. A similar analysis can be performed for the GL-S72 and SV models, where once again the RK EOS produces lower deviations than the PR EOS when the CQRM is used. It should be noted the high contrast in performance of the Gray et al. BIP correlation between the RK and PR EOS. For the later the AARD were about the double than for the RK EOS when the S72 cohesion function were used. We have the suspicion that there is a typo in the original reference [8] where there is one order of magnitude of difference between constant $A$ in Eq. (31) for both EOS. A preliminary test with “a corrected” version of the correlation seems to point at that direction.

In the case of the models studied with the help of the PRO/II process simulator, the PR and RK EOS were compared only with the combination of cohesion function TBCC–S72, CQMR and BIP obtained from the PRO/II databanks. For this case the RK EOS exhibits a lower deviation, 8.9% AARD, than the
Fig. 3. Solubility of H$_2$ in PYGAS. Symbols for experimental data [6]: ♦ 298 K, ○ 313 K, ▲ 323 K, □ 343 K. Lines for predictions from: a) RK/S93-S72/Gray et al./CQMR, b) RK/TBCC-S72/PROII 8.0 Databanks/SimSci, c) RK/TBCC-S72/PROII 8.0 Databanks/PA-RE-Mod, and d) RK/S72/Gray et al./CQMR.

PR EOS, 9.5% AARD. Although these results do not represent an improvement over the produced by the simpler models discussed above, they confirm the superiority of the RK over the PR for the H$_2$-PYGAS system.

There are still some models involving the RK EOS to be considered in this discussion, which are those including the S93-S72 and GD cohesion functions with the CQMR and the PA-RE-Mod and SimSci mixing rules. Among those options, the best results are obtained with the model combining the S93-S72 functions and the CQMR with the Gray et al. correlation, which turns to be the global best, as mentioned before. Despite that the GD function is one of the most recommended to estimate the VLE in H$_2$-HC systems and possesses the additional advantage of not requiring and BIP; this model produced large deviations, 18.0 AARD, on the prediction of H$_2$ solubilities in PYGAS. Therefore, as an additional test, the GD function was combined with the Gray et al. BIP correlation. In this case an improved value of 5.0% AARD was achieved. This result highlights the importance of the BIP in the accuracy of the models studied in this work.

It is also noteworthy the marked differences observed between the BIP correlations considered. This behavior has been reported by Rodríguez [3], who observed a great dependency of the accuracy of a given correlation on the nature of the solvent for systems containing H$_2$. In the present work, the worst results were found with the VA-RE and VAL correlations, with AARD above 18%. Although these correlations have been recommended for systems like the considered in this work, here the results are disappointing. It seems a good recommendation to evaluate the accuracy of any general correlation or model against experimental data, when available, in order to select the more suitable model for the case to be studied.
The solubilities of hydrogen in PYGAS for the four best models are shown in Fig. 3. In the figure can be observed that predictions obtained from our program, Figs 3(a) and 3(d), have a good agreement with the experimental data reported by Zhou et al. In all cases, the solubility of hydrogen in PYGAS increases with the temperature and pressure as expected. In the figures can be observe how for each isotherm the deviations increase with the pressure. In the Fig. 3, it can be also observed that the largest deviations from the experimental values occur at the largest temperatures (323 K and 343 K). This can be attributed to the fact that the cohesion functions used in this work, particularly the S72 which was used to estimate the $\alpha$ for H$_2$ in the models referenced in the figure, are extrapolated well beyond from the temperature value where the function was fitted, $T_r = 0.7$.

It is interesting to note that for most the models studied the largest deviations were found at 298 K and 1.380 MPa. This can be considered contrary to what is expected for this type of models. However, this was particularly observed when the BIP correlations of Moysan et al., Valderrama and Reyes, and Valderrama et al. were considered, therefore this can be attributed to a deficiency of these correlations. In the case of the models including the Grey et al. BIP correlations a more uniform distributed deviations were observed among the points. This uniformity tend to reduce the deviations at larger temperatures and pressures, which explains the lower overall AARD attained with this correlations. In the case of the RK-S72 and PR EOS with BIP from the SimSci database, the typical behavior for the deviations were found, i.e. better approximation at the lower temperatures and pressures, and an increment of the deviations with temperature and pressure.

As a final remark, in this work has been confirmed that the use of more complex relations to estimate the VLE of a mixture involving H$_2$-HC systems, such as the hydrogenation of PYGAS, does not ensure that the best result will be obtained.

5. Conclusions

In this work, the effect of model or EOS selection on the prediction of the solubility of hydrogen in PYGAS has been studied. Twenty different combinations of EOS, cohesion functions, mixing rules and BIP correlations were considered. The lowest deviations were achieved using the model combining the RK EOS, the S93 and S72 cohesion function, the CQMR and the Gray et al. correlation, with an AARD of 3.1%; being this combination the recommended for predicting the solubility of H$_2$ in PYGAS in the temperature and pressure ranges worked here. The present work confirms the sensibility of model selection on VLE predictions. The use of more complex relations to estimate the VLE of a mixture involving H$_2$-HC systems, such as the hydrogenation of PYGAS, does not ensure that the best result will be obtained.

Nomenclature

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<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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</thead>
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<tr>
<td>$A$</td>
<td>Dimensionless cohesion parameter, BIP correlation Constant</td>
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<tr>
<td>$a$</td>
<td>Cohesion parameter</td>
<td>kPa m$^6$ kmol$^{-2}$ m$^6$</td>
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<tr>
<td>AARD</td>
<td>Average absolute relative deviation</td>
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<tr>
<td>$B$</td>
<td>Dimensionless covolume, BIP correlation Constant</td>
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</tr>
<tr>
<td>$b$</td>
<td>Covolume</td>
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<tr>
<td>BIP</td>
<td>Binary interaction parameters</td>
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### Mathematical Symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>CQMR</td>
<td>Classical quadratic mixing rule</td>
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<tr>
<td>$E_i$</td>
<td>Cubic EOS coefficient $i = 0, 1, 2$</td>
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<tr>
<td>EOS</td>
<td>Equation(s) of state</td>
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<tr>
<td>$f$</td>
<td>Fugacity [kPa]</td>
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<td>GD</td>
<td>Graboski and Daubert</td>
</tr>
<tr>
<td>$G_{ij}$</td>
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<td>GL</td>
<td>Gibbons and Laughton</td>
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<tr>
<td>HC</td>
<td>Hydrocarbons</td>
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<td>PA-RE</td>
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<tr>
<td>PA-RE-Mod</td>
<td>Panagiotopoulos-Reid modified</td>
</tr>
<tr>
<td>PR</td>
<td>Peng-Robinson</td>
</tr>
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<td>PYGAS</td>
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<tr>
<td>S93</td>
<td>Soave 1993</td>
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<td>SAFT</td>
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<td>SV</td>
<td>Stryjek and Vera</td>
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<td>Valderrama et al.</td>
</tr>
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<td>Valderrama and Reyes</td>
</tr>
<tr>
<td>VC</td>
<td>Valderrama and Cisternas</td>
</tr>
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<td>VLE</td>
<td>Vapor-Liquid Equilibrium</td>
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#### Greek Symbols

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<tr>
<td>$\mu$</td>
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<td>Acentric factor [-]</td>
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#### Subscripts

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<td>$c$</td>
<td>Critical property</td>
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<td>$i$</td>
<td>Component $i^{th}$</td>
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</table>
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\[
\begin{array}{cccc}
\text{Component } j^{th} & r & \text{Reduced property} \\
\text{Superscripts} & \text{cal} & \text{Calculated values (from model)} \\
\text{exp} & \text{experimental values (from Data)} \\
L & \text{Liquid} \\
V & \text{Vapor} \\
\end{array}
\]

References


