Peng-Robinson equation of state: 40 years through cubics

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ABSTRACT

Since its publication in 1976, the Peng & Robinson equation of state (PR EoS) has become one of the most useful and successfully applied models for thermodynamic and volumetric calculations in both industrial and academic fields. For this reason, we have reviewed this cubic EoS, in order to explore the development around it and some general applications where it has been applied, including its most known modifications. So, a complete time-line of the PR EoS is presented, as a compilation of more than 200 modifications for pure compound applications and about 100 modifications for mixtures.

These modifications to the PR EoS have been grouped in four main categories according to the nature of the modification: (a) by changing the dependence structure of α with temperature or the expressions for parameter *a* and *b*, (b) by introducing deviation functions (like volume translation), (c) by incorporating new parameters or terms in the equation of state, and finally (d) by modifying the mixing rules for mixture applications. Although great efforts have been made to improve accuracy and performance of the PR EoS, as demonstrated by the wide range of modifications, the necessity for further development of a universal, simple and accurate model is a rich source for research and discussion, considering the success of most of modifications is restricted to the studied properties and compounds, and therefore, they are limited to be just applied to the studied field. However, after 40 years, PR is still an invaluable and prominent tool, which will be under continuous development and research for next decades.

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1. Introduction

In 1976, the Chemical Engineers Donald B. Robinson, from Canada, [1,2] (1922−1998) and Ding-Yu Peng (1943 − today), from China, presented a new cubic equation of state (CEoS) [3]. Peng & Robinson worked together in a Project for the Natural Gas Processors Association since 1974 to 1975 at the University of Alberta (Canada), they developed the equation of state (EoS) during this period. It is interesting to remember this new expression is the result of a trial to improve the predictive capability of the 1972 Soave modified Redlich-Kwong (SRK) CEoS [4,5]. In 1985, Peng & Robinson [5] pointed out, as they indicated, that their model was born as the result of seeking a modification in the Redlich-Kwong

model, which would preserve the attractive simplicity of the cubic form and yet increase the reliability of its performance in the critical region and along the saturated liquid curve.

Peng et al. [6] showed the high capability of SRK to predict the phase equilibrium in natural gas systems. However, this study also showed that SRK was inaccurate for liquid density calculations and for predicting other properties near the critical point. This notable shortcoming in SRK was common for heavy hydrocarbons, where the deviation increases near the vicinity of the critical point [7]. For this reason, Peng & Robinson began to work in a modified expression for SRK, finding a totally new expression. The Peng-Robinson (PR) EoS acquired its own nature, despite it was built on the same structure of Soave's dependence of α on temperature, as well as the dependence of the limiting volume and attraction factors *a* and *b* on T_c and P_c [8], even with the simplicity and predictive capability needed to get better results in the calculation of the studied properties.

Before their EoS was officially published, it was used to estimate the retrograde condensation in natural gas pipelines. When it was

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used by Bergman et al. [9], the equation gave good prediction results of dew points and liquid yield at pipeline conditions, being these better than those obtained by SRK. Later, it was demonstrated that PR could predict retrograde behavior even of near-critical gas-condensate fluids with the same potential [10].

Since its publication, the PR EoS has been widely used and studied in the academic and industrial fields, having a considerable development similar to its predecessor SRK. It has been considered as one of the best two constants third degree equations of state applicable to vapor-liquid equilibria (VLE), and volumetric and thermodynamic properties calculations for pure substances and mixtures [11—16]. Today, there are more than 220 modifications to the PR EoS for pure compounds and uncountable works related with parameter adjustment and extension to mixtures.

In this way, it is necessary to come back to this meaningful EoS and review its progress after 40 years. Many researchers have made comprehensive reviews and studies about this topic although in a general way [14,17—40]. Some of them discuss the PR EoS in depth [12,13,16,41—46], especially Zabaloy & Vera [15], who studied PR and compared it with other equations of state. They found, in 1998, that PR was clearly superior to the other forms considered in their study.

An interesting turn in these path of reviews is the recent work by Wilczek-Vera & Vera [11], who studied the basis for the success of the PR EoS, compared to those of van der Waals (vdW) [47] and Redlich-Kwong (RK). Their work focused on pure substances, included a discussion on the a and b parameter determination based on the van der Waals [47] and Martin & Hou [48] frameworks, besides the replacement of the actual critical volume for a hypothetical critical volume, the root nature, and the critical isotherm behavior. They also explored the Soave [4] and Stryjek & Vera [49,50] approaches on the temperature dependence of α. This last point has been extended by the recent work made by Young et al. [51], who evaluated the performance for P^{sat} prediction of 20 different α functions in PR (including some not originally proposed and applied to PR) for 56 substances, including the estimation of the needed parameters.

However, all these studies focus on the main developments around the EoS, which do not cover a complete time-line of PR, as it is the aim of the present work. Despite there are numerous studies on PR, this review is presented as an useful EoS data bank for future applications and recognition of all possible uses of the PR EoS. Therefore, the authors try to comprehensively cover the development of the PR EoS and its modifications, as much as possible, like a compendium (including those well-known studies and revisiting those scattered studies with, unfortunately, low dissemination), but without being our scope to do any properties evaluation in order to establish which modification is the best.

Because of its high reputation in the industry, especially petrochemical industry, the PR EoS has been extensively studied and modified in order to improve its predictive capability. Studies have been performed intensively since 1980, even increasing in the last 10 years (see Fig. 1), modifying the original expression at least in four different main ways (as it will be shown later), allowing it to be applied and extended to many substances, fields and applications. Thus, we will focus on those modifications for pure compounds, and we will present some of those that can be applied to mixtures.

2. The PR trip

Liquid volume predicted by the SRK EoS is usually higher than the experimental one [52,53], where deviation increases for compounds with a considerable value of ω. This behavior may be explained by the high-fixed value of the critical compressibility factor (Z_c) equal to 1/3, which is imposed by the RK EoS (due to the restrictions at the critical point) [24,54].

In considering this, Donald Robinson & Ding-Yu Peng proposed a new equation of state [5]. This equation was based on the improvements of the RK equation of state [55] performed by Giorgio Soave in 1972 [4]. However, the model was different to that of Soave's, having, based on the author's criteria, *significant advantages over other two-parameter models, because … it was built on rigorous criteria rather than circumstantial respect to RK* [12,56]. In this way, Peng & Robinson kept the dependence of α on temperature, but modified the van der Waals attractive term structure of EoS:
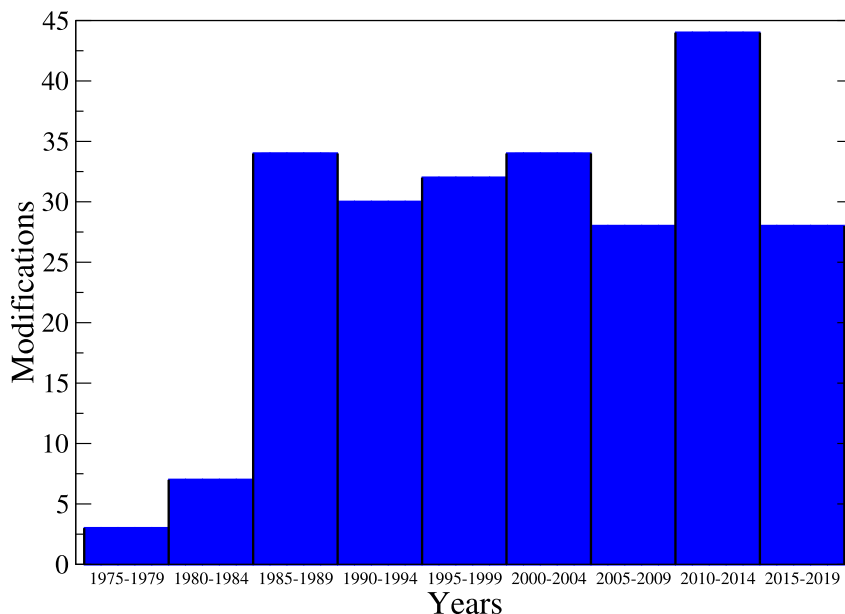

Fig. 1. Published modifications of the PR EoS since 1976 until 2017 (shown by 5 years periods) for pure compounds.