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PVTx Modeling of CO₂ Pipeline at Depressurization Conditions Using SPUNG Equation of State (EoS) with a Comparison to SRK

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Abstract

The proper modeling of CO₂ depressurization is very important for the design for safety of a pipeline. One key element of the modeling process is the thermodynamics and transport properties modeling. In this work, an analysis of the error in thermodynamics for modeling CO₂ at depressurization conditions was conducted. For the study presented here, the sophisticated equation of state (EoS) SPUNG was used. The results were compared to an EoS of a different level of complexity and, consequently, accuracy. This EoS is the cubic equation Soave–Redlich–Kwong (SRK) with van der Waal's mixing rules. The results show the significance of the thermodynamics modeling at a set of pressures, temperatures and compositions PVTx over time steps complying with two sets of experimental data.

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1. Introduction

The CO₂ production and its effects on the climate change are among the current era challenges. Therefore, the Carbon Capture and Storage (CCS) research and industry are developing very fast to cope with the challenge. Transport of CO₂ in pipelines is one of the important links in the chain. During shutdown or by a fracture, the CO₂ is depressurized from very high pressures. This can result in large drop in temperatures. Very fast, non-controlled depressurization can cause dry ice formation and the steel of the pipelines to become very brittle. This can reduce

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integrity of the pipe significantly. The dissipation of CO₂ during depressurization can form clouds, which raise safety concerns. Therefore, the proper modeling and simulation of the depressurization process is very important for the safety and for efficiency of a design. The process modeling consists of many components from fluid dynamics to thermodynamics of the multi-phase multicomponent phenomena.

Nomenclature

a, b	Gas parameters in SRK [$\text{J m}^3 \text{mol}^{-2}$], [$\text{m}^3 \text{mol}^{-1}$]
C	Arbitrary variable [-]
f	Function of [-]
k	Binary interaction parameter
N	Total number of points
n	Amount of substance [mol]
NC	Number of components in a mixture
P	Pressure [Pa]
R	Universal gas constant [$\text{J K}^{-1} \text{mol}^{-1}$]
T	Temperature [K]
V	Volume [m^3]
x	Mole fraction [-]
Z	Compressibility factor [-]
θ	Shape factor [-]
φ	Shape factor [-]
ω	Acentric factor [-]

Subscripts/Superscripts

c	Critical state
i, j	Component i, j
M	Mixture
R	Reduced variable
Ref	Reference fluid
s	Simulation

A number of publications have studied the sensitivity of modeling transient pipeline flows to multiphase, friction, heat transfer and shock models. Other studied the effect of stream impurities on the overall results. Here, we studied the effect of impurities on the predictions from the thermodynamics point of view. This was done by comparing results of the same equation of state (EoS) when modeling pure CO₂ and mixtures with different compositions. Moreover, we studied the sensitivity of predictions to the quality of the EoS. This was done by comparing the results of two EoS of different classes of sophistication and, subsequently, of accuracy. There are a number of EoS classes available in literature. Among the most known and widely used in industry are the cubic EoSs like Soave-Redlich-Kwong (SRK) [1], SRK with Huron-Vidal mixing rules (SRK-HV) [2] and Peng-Robinson (PR) [3]. They are mainly used for their reasonable accuracy and low computation time. Among the highest in computation time are the full extended corresponding states (ECS) equations like the models implemented in the REFPROP library of the National Institute of Standards and Technology (NIST) [4], which are mainly used for transport properties. A modern approach that is less computationally expensive than ECS and offers generally good accuracy is the multi parameters approach. Nevertheless, it is at least one order of magnitude higher than Cubic EoS in computation time. Span-Wagner [5] for pure CO₂ and GERG (Groupe Européen de Recherches Gazières) [6] for mixtures belong to this category. The Cubic-Plus-Association (CPA) [7] and the Statistical Associating Fluid Theory (SAFT) [8] EoSs are state-of-the-art approaches. Results of the CPA and Perturbed Chain SAFT (PC-SAFT) for modeling CO₂-water were presented in [9] and [10], respectively. The two articles also provided a literature survey on CPA and SAFT type developments and recent achievements. Here, we used the Extended Corresponding States (ECS) EoS SPUNG for the prediction of

thermodynamic properties over a PVTx of two sets of CO₂ depressurization experimental data [11], [12]. The results were compared to the cubic EoS SRK, which was chosen because of its popularity in industry and low computational cost. The SPUNG EoS was chosen as it was shown to be more accurate than SRK for CO₂ non-polar mixtures [13] and polar mixtures [14, 15, and 16]. Furthermore, the relatively higher accuracy of SPUNG EoS comes on relatively low cost compared to other sophisticated concepts. This is because SPUNG EoS is only about five times more expensive than SRK. The concept captures the phase equilibrium very accurately and maintain the other properties accuracy very high, unlike cubic equations. The use of the standard ECS for long-pipeline Computational Fluid Dynamics (CFD) simulations was infeasible, and cubic EoS, or even simpler forms, are mainly used by industry due to the computational cost. However, SPUNG EoS is a class of ECS that with the usage of SRK for computing shape factors, computational cost of the ECS approach was significantly reduced, while the accuracy remained generally high. This might make the coupling to a flow solver and running a multi-component and multi-phase simulations feasible. In this study only thermodynamics was regarded, and the sets of PT pairs over which the predictions were conducted, were taken at different time steps from real experimental depressurization conditions [11], [12].

2. Theory

An EoS is a model that calculates for both the liquid and gas phase using the same expression, which enhances the continuity near the critical point. An EoS for an NC component mixture is an expression for pressure as a function of the mole fractions, the temperature and the volume. Given this expression, it can be manipulated to calculate the fugacity of each component. In the following subsection, a brief description of the EoS used in the work will be given together with further references.

2.1. The standard SRK

The classical SRK model with van der Waal's mixing rules [1] is a cubic EoS that is written for a mixture as

$$P = \frac{RTn}{V - bn} - \frac{an^2}{V^2 + bnV} \quad (1)$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}), \quad b = \sum_i x_i b_i \quad (2)$$

$$b_i = \frac{0.08664 RT_{c,i}}{P_{c,i}} \quad (3)$$

Here, $T_{c,i}$, $P_{c,i}$ are the critical temperature and pressure of component i .

2.2. The corresponding states principle

The principle of corresponding states assumes that all substances exhibit the same behavior at a reduced state. A corresponding states EoS typically has one or more reference components described very accurately by a reference EoS. Therefore, the compressibility of the investigated fluids or mixtures can be evaluated as

$$Z = f(V_{Ref}, T_{Ref}, \omega, \dots)_{Ref} \quad (4)$$

In the corresponding states approach the V_{Ref} and T_{Ref} of the reference fluid are the reduced volume and temperature V_R , and T_R of the fluid or the mixture investigated.

2.3. The extended corresponding states principle

In the extended corresponding states concept, the mapping between the investigated fluid or mixture T and V and the reference fluid V_{Ref} , T_{Ref} is done via the shape factors φ and θ . These shape factors take into account how the fluids or the mixture in consideration differs from the reference fluid.

$$T_{Ref} = \frac{T}{\theta} \quad (5)$$

$$V_{Ref} = \frac{V}{\varphi} \quad (6)$$

where the shape factors φ and θ are function of T_{Ref} and V_{Ref} . This implicit formulation make it very computationally expensive to calculate them using an accurate EoS. However, they can be computed analytically, or by using simpler forms of EoS.

2.4. The SPUNG EoS

The SPUNG EoS investigated here, is an extended corresponding state approach that uses the SRK cubic EoS to calculate the shape factors and propane as a reference fluid. The SPUNG EoS uses the accurate modified Benedict-Webb-Rubin (MBWR) [17] EoS for the reference fluid. The SPUNG EoS was introduced in the doctoral thesis of Jørstad in 1993 [18] for low temperature hydrocarbon mixtures, which was enlightened by the work of Mollerup (1980) [19]. Propane was chosen as the reference fluid to ensure that the reduced temperature of the considered mixtures would be above the reduced triple point of the reference fluid in order to avoid extrapolation of the reference equation.

3. Methodology

3.1. The numerical tools

The NTNU-SINTEF in-house thermodynamic library was used for the study presented. The library is a tool for predicting the thermodynamic properties using various approaches that ranges in level of sophistication and underlying theory. The library was used with a tolerance of 10^{-4} for both the multi-phase flash algorithm and the compressibility factor calculations.

3.2. Setup

The first setup investigated here was the depressurization of a 50 km long 24 inches CO₂ pipeline by Clausen et al. [11]. The article provided temperature and pressure profiles over time at the first end and second end of the pipeline during the process. Here, we computed the densities and speed of sound for the pairs of pressure and temperature obtained from the graphs of [11] at different time steps of the first end. We conducted the numerical simulations for three compositions using SPUNG and SRK. The first was a pure CO₂ case. The second was a mixture of 99.14 % of CO₂, 0.22% of N₂, 0.63% of CH₄ and 0.01% of water and is what we refer to as real. The third was a mixture of 98%CO₂ and 2% of water.

The second setup was of the conditions tested by de Koeijer et al. [12] for pure CO₂ at 139 m downstream.

3.3. Error definition

Since the cited literature did not provide experimental density data, but only measurements of temperature and pressure over time and at different locations, we used the SPUNG EoS as a reference when computing the deviation of SRK. We considered this as a valid strategy since SPUNG EoS had proven to be a way more accurate than SRK [13, 14, 15, 16]. The deviations of predictions was measured here by the Average of Absolute Deviation (AAD) defined for an arbitrary variable C as:

$$AAD(C, \%) = \frac{100}{N} \sum_{r=1}^N \frac{(C_{datum} - C)}{C_{datum}} \quad (7)$$

Where subscript datum denotes the dataset towards which the deviations is calculated (e.g. SPUNG EoS results).

4. Results and discussion

The results of the density predictions of the three tested compositions are plotted in Fig. 1. The Real mixture refers to the CO₂, N₂, CH₄ and water case described in the setup section. The results show that the CO₂-water mixture density predictions are higher than that of pure CO₂ until it turned to gas phase. This difference was due to the existence of only 2% of water. The realistic mixture went through the two phase region between 1.5 and 2.5 hours for SPUNG EoS and at 1.5 to 2.0 hours for SRK, which led to the less steep drop of density seen in Fig. 1. The AAD of the CO₂-water case from the pure one was 69.2% and 40.5% for SPUNG EoS and SRK, respectively. The AAD of the realistic mixture was 9.8% and 13.7% for SPUNG EoS and SRK, respectively.

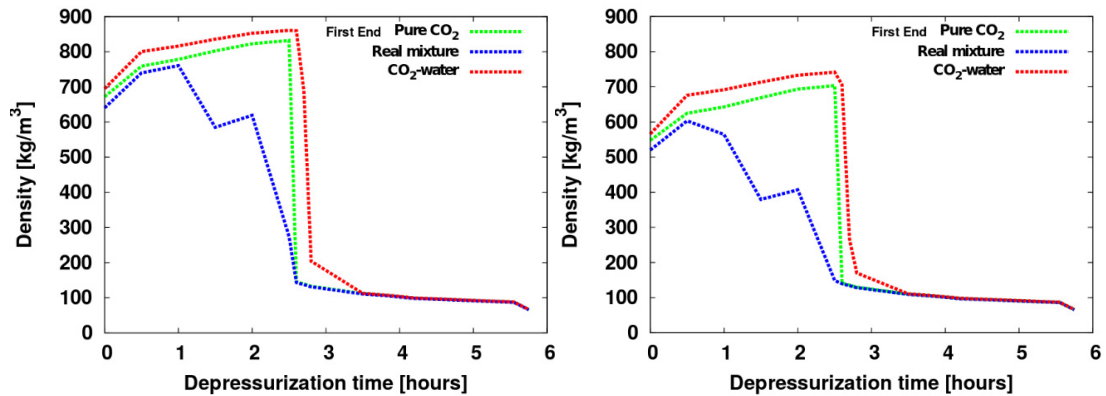


Fig. 1. Predictions of the first end density over time using (left) SPUNG EoS; (right) SRK EoS.

The comparison between the density predictions of SRK and SPUNG EoS for the pure CO₂ case is plotted in Fig. 2. The main difference lies in the heavy phase predictions, where [13, 14, 15, and 16] showed that SPUNG EoS was superior in predictions to SRK. Therefore, taking SPUNG EoS as a reference, the AAD of all the predictions was 8.1% with a maximum deviation of 18.5%.

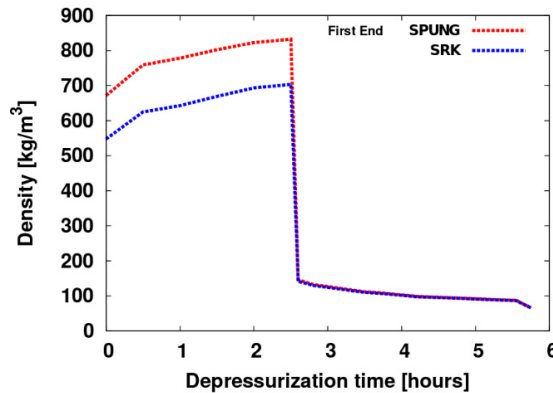


Fig. 2. Pure CO₂ density predictions over time using SPUNG and SRK EoS.

The predictions of the speed of sound for the pure CO₂ case are plotted in Fig. 3. The speed of sound using both EoSs drops as instantaneous as the mixtures changes from the heavy to the light phase. The AAD of SRK to SPUNG EoS was 6.7%, with a maximum deviation of 14.9%.

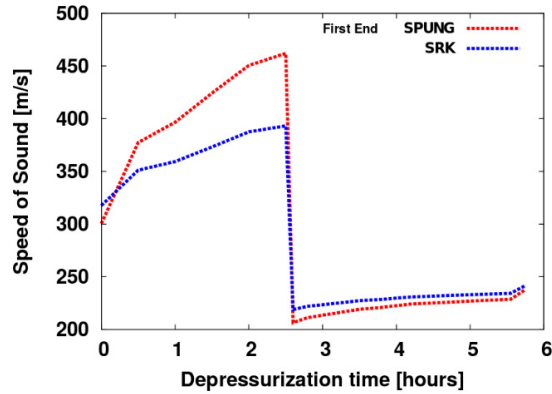


Fig. 3. Pure CO₂ speed of sound predictions over time using SPUNG and SRK EoSs.

Figure 4 shows the comparison between SRK and SPUNG EoS density predictions for the realistic mixture. The AAD of SRK to SPUNG EoS as a reference was 13.5%, with a maximum deviation of 29.7%.

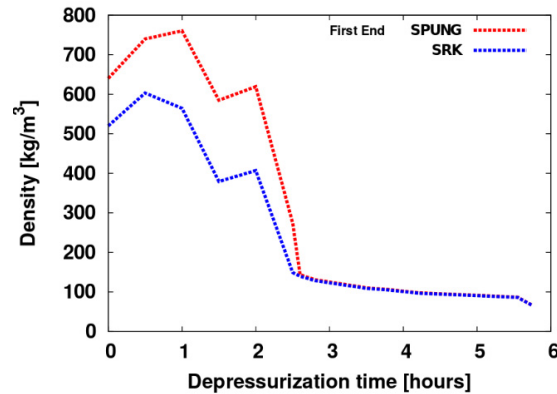


Fig. 4. The density predictions of the realistic mixture of CO₂, N₂, CH₄ and water over time using SPUNG and SRK EoSs.

The comparison between SRK and SPUNG EoS density predictions for the CO₂-water mixture is shown in Fig. 5. The AAD for this case was 13.8%, with a maximum deviation of 21.4%.

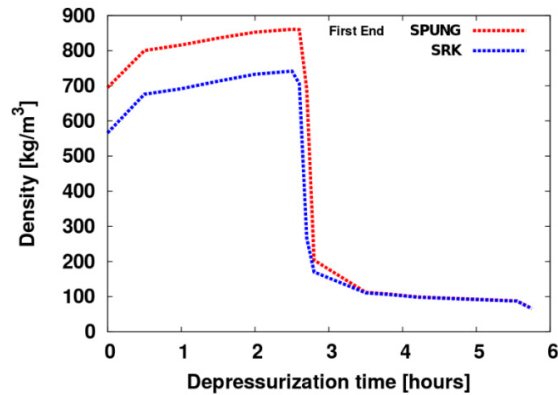


Fig. 5. The 98% CO₂ - 20% water density predictions over time using SPUNG and SRK EoSs.

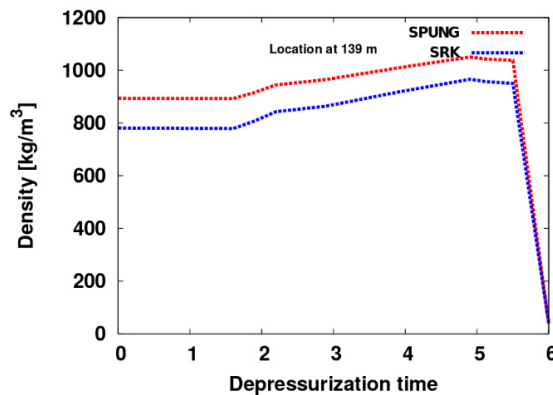


Fig. 6. The density predictions at de Koeijer et al. [12] temperature and pressure pairs.

Figure 6 shows the comparison between SRK and SPUNG EoS density predictions for the pure-CO₂ case of de Koeijer et al. [12]. The AAD was 10.3%, with a maximum deviation of 12.8%.

A 1-D flow solver will always include models that are fitted to recover pipeline measurements, which would increase or decrease the relevance of thermodynamics depend on how new the investigated setup is. Therefore, this work was conducted to isolate this model fitting effects on the relevance of EoSs and impurities. The results showed how the density and speed of sound profiles look like for a set of real depressurization conditions taken from experiments. This density reflects on the mass fractions, pumping power, etc. The speed of sound will influence the pressure wave propagation for a full simulation. Consequently, the crack propagation speed in a case of fracture. The results showed that including impurities is important from the thermodynamics behavior point of view. Moreover, the results also showed that the accuracy of an EoS is as important as the inclusion of impurities and can have a strong impact on the final dynamic simulation results. A coupling to a 2-D flow solver is planned for future work.

5. Conclusions

The SPUNG EoS was used for prediction of thermodynamics properties over a real depressurization TP conditions. The phase fraction and composition was computed using TP-flash routines. The results were compared to SRK. We conclude that the inclusion of impurities is very important, but using an accurate EoS is also very crucial for the accuracy of the simulation.

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