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Thermal-Compositional Simulation of CO₂ Sequestration in Depleted Hydrocarbon Reservoirs

M. Wapperom, TU Delft; J. dos Santos Heringer and D. V. Nichita, University of Pau; D. Voskov, TU Delft, Stanford University

Abstract

In this work, we present a thermal-compositional simulation framework for modelling of CO_2 sequestration in de- pleted hydrocarbon reservoirs. The parametrization technique utilizes thermodynamic state-dependent operators expressing the governing equations for the thermal-compositional system to solve the nonlinear problem. This approach provides flexibility in the assembly of the Jacobian, which allows straightforward implementation of advanced thermodynamics. Taking advantage of the flexibility of operator-based linearization (OBL), multiphase thermodynamic modelling at arbitrary state specifications is implemented. The use of a hybrid-EoS approach to combine equations of state for aqueous and hydrocarbon phases and advanced initialization schemes for multi- phase equilibrium calculations improves the accuracy and efficiency of the simulation. Careful phase identifica- tion is required for the simulation of multiphase flow, in particular with the potential occurrence of multiple liquid phases in CO_2-hydrocarbon mixtures. We apply the simulation framework to model a set of CO_2 injection cases at conditions typical for depleted hydrocarbon fields. We demonstrate that important thermophysical phenomena resulting from the interaction of CO_2 and impurities with reservoir fluids can be accurately captured using the OBL approach. The consistency of compositional simulation is supported by robust and efficient modelling of multiphase equilibria between brines, hydrocarbons and CO_2. The method is shown to be robust for capturing the thermal effects related to expansion, mixing and phase transitions. This work presents a highly flexible and efficient framework for modelling of multiphase flow and transport in CCUS-related subsurface applications. Ro- bust modelling of thermodynamic equilibria at arbitrary state specification captures the complex thermophysical interactions between CO_2 and reservoir fluids.

Introduction

Geological carbon sequestration is considered one of the principal options for mitigating excessive emissions of greenhouse gases into the atmosphere and the associated negative impacts on climate change. Field pilots of CO_2 sequestration in sedimentary formations, such as saline aquifers or depleted oil and gas reservoirs, have been operating for a few decades (Kelemen et al., 2019; Ringrose, 2020). While saline aquifers globally offer the greatest potential for carbon sequestration in terms of capacity, targeting

depleted gas reservoirs for CO_2 sequestration in particular has major advantages. Injected CO_2 can replace the volumes of hydrocarbons still in place and due to the compressibility of gas in particular, pressures required to maintain injection flow rates are lower than in aquifers (Hamza et al., 2021). The injection of supercritical CO_2 has been applied in enhanced oil and gas recovery processes (EOR/EGR) to displace the fluids in place in full or partial miscibility (Blunt et al., 1993; Hamza et al., 2021). To date, most CO_2-EOR projects have used CO_2 produced from natural sources and have been optimized for oil production rather than CO_2 sequestration volumes, which could unveil large additional storage potential (Kelemen et al., 2019). In addition to the technical aspects of depleted hydrocarbon fields in comparison to aquifers, the ability to re-use a field's existing facilities and knowledge of its geological settings and containment integrity for gas storage gives a significant cost advantage (Peter et al., 2022).

The injection of CO_2 into depleted hydrocarbon reservoirs poses some challenges related to the thermodynamic properties of CO_2. Typically, the injected CO_2 is in a supercritical state that resembles liquid-like behaviour. However, adiabatic expansion into the lower-pressured reservoir can result in significant cooling, also referred to as the Joule-Thomson cooling effect. Temperatures can drop by more than 20 ∘C, which may result in sub-zero conditions. In addition, the combined pressure and temperature decrease may be sufficient to enter the two-phase region, where the reduction in temperature associated with lowering the pressure is even more pronounced due to the phase transitions (Oldenburg, 2007; Chesnokov et al., 2024). The main concerns in such conditions are that low temperatures could be sufficient to trigger ice and hydrate formation, limiting well injectivity, and that thermal stresses due to cooling could damage the near-wellbore region.

Reservoir simulation of these processes provides an important tool to assess the risks associated with CO_2 injection into depleted fields and design safe operations. Such simulators must be able to deal with highly nonlin- ear thermodynamics related to adiabatic expansion, mixing and phase transitions. A full equation of state (EoS) based approach implicitly accounts for all thermal effects to desired accuracy, but relies on a large amount of expensive phase equilibrium computations. For cold CO_2 injection problems, a thermodynamic equilibrium of up to four phases (aqueous, gas, liquid and liquid CO_2) is required at every nonlinear iteration in the simulation. The thermodynamic modelling routines must therefore be robust and efficient, as any error may propagate and lead to false solutions or no convergence at all (Petitfrere et al., 2020). Even then, convergence problems may arise in solving the flow equations when crossing narrow-boiling conditions (Zhu and Okuno, 2014).

Several full-EoS thermal-compositional simulators have been proposed. Zaydullin et al. (2014) developed three-phase EoS-based simulations of steam injection in the AD-GPRS simulator (Voskov and Zhou, 2015), an approach that was later extended to four-phase CO_2 injection problems (Petitfrere et al., 2020). Brantferger (1991) and later Heidari (2014) proposed compositional simulation for thermal processes with an isenthalpic flash, taking enthalpy as primary variable rather than temperature to improve the convergence. Moncorge et al. (2022) employed a similar thermal-compositional formulation based on full-EoS isenthalpic flash, this time applied to model pure CO_2 and CO_2 mixtures in depleted reservoirs.

In this work, we combine the unified in-house thermal-compositional Delft Advanced Research Terra Simula- tor (DARTS) framework (Voskov et al., 2024) with accurate thermodynamic modelling procedures for multiphase reservoir mixtures with CO_2 and brine (Wapperom et al., 2025). The abundance of water in target reservoirs and the importance of its interaction with CO_2 in particular requires careful thermodynamic modelling. Most EoS-based compositional simulators rely on cubic equations of state to model all fluid phases. Such cubic EoS have proven accuracy for thermodynamic calculations of nonpolar mixtures, yet they are not adequate for aqueous mixtures. By employing a hybrid-model approach with a fugacity-activity model for the brine, using an activity model based on Henry's constants for the dissolved gases (Akinfiev and Diamond, 2003; Ziabakhsh-Ganji and Kooi, 2012) and a separate expression for water fugacity (Jager

et al., 2003), we maintain the simplicity of a flash with cubic equations while greatly improving the thermodynamic accuracy for simulation.

Using the operator-based linearization (OBL) parameterization technique (Voskov, 2017), the implementation of multiphase physics in DARTS is straightforward. In addition, the OBL approach requires only a limited number of phase equilibrium calculations, which could be particularly beneficial for advanced multiphase compositional simulations. In this paper, we investigate scenarios of CO_2 injection into depleted hydrocarbon reservoirs at various conditions of interest and demonstrate that the thermal effects related to Joule-Thomson cooling, mixing and phase transitions are captured effectively.

Simulation framework

Here we briefly describe a nonlinear formulation in Delft Advanced Research Terra Simulator (DARTS) which we use here for simultion. We assume that fluid flow is governed by advective-diffusive multiphase multicomponent formulation. For a domain with volume Ω, bounded by surface Γ, the mass and energy conservation can be expressed in a uniformly integral way, as

$$\frac{\partial}{\partial t}\int_\Omega M^c d\Omega + \int_\Gamma \mathbf{F}^c \cdot \mathbf{n} d\Gamma = \int_\Omega Q^c d\Omega. \tag{1}$$

Here, M_c denotes the accumulation term for the cth component ($c = 1,…, n_c$, indexing for the mass components and $c = n_c + 1$ for the energy quantity); $\mathbf{F}_c$ refers to the flux term of the cth component; $\mathbf{n}$ refers to the unit normal pointing outward to the domain boundary; Q_c denotes the source/sink term of the cth component.

The mass accumulation term collects each component distribution over n_p fluid phases in a summation form,

$$M^c = \varphi \sum_{j=1}^{n_p} x_{cj} \rho_j s_j, \quad c = 1, …, n_c, \tag{2}$$

where φ is porosity, s_j is phase saturation, ρ_j is phase density [kmol/m³] and x_{cj} is molar fraction of c component in j phase.

The energy accumulation term contains the internal energy of fluid and rock,

$$M^{nc+1} = \varphi \sum_{j=1}^{n_p} \rho_j s_j U_j + (1 - \varphi)U_r, \tag{3}$$

where U indicates specific fluid internal energy [kJ/kmol], U_r indicates the rock internal energy [kJ/m³]. The rock is assumed compressible and represented by the change of porosity through:

$$\varphi = \varphi_0(1 + c_r(p - p_{ref})), \tag{4}$$

where φ_0 is the initial porosity, c_r is the rock compressibility [1/bar] and p_{ref} is the reference pressure [bars].

The mass flux of each component is represented by the summation over n_p fluid phases,

$$\mathbf{F}^c = \sum_{j=1}^{n_p} (x_{cj}\rho_j \mathbf{u}_j + s_j \mathbf{J}_{cj}), \quad c = 1, …, n_c. \tag{5}$$

Note that the energy accumulation term consists of the total internal energy in a control volume and the energy fluxes has enthalpy contributions. The first law of thermodynamics states that a change in internal energy in a closed system equals the heat absorbed by the system and the work done on the system (Michelsen and Mollerup, 2007):

$$dU = Q + W = TdS - PdV + \sum_i \mu_i dn_i. \tag{6a}$$

The enthalpy equals the internal energy minus the energy equivalent to the *PV* properties of the system (Michelsen and Mollerup, 2007):

$$H = U - V \left. \frac{\partial U}{\partial V} \right|_{S,\mathbf{n}} = U + PV \tag{7}$$

The advective energy fluxes therefore only account for the flow of heat and do not include *PV*-work. Combining all terms, the mass and energy conservation equations can be written in residual form as

$$\left(\frac{\partial}{\partial t} \varphi \sum_{j=1}^{np} \rho_j s_j x_{cj} \right) + \nabla \cdot \left(\sum_{j=1}^{np} x_{cj} \rho_j u_j + s_j \rho_j \mathbf{J}_{cj} \right) = 0 \quad c = 1, \, \ldots, n_c, \tag{8}$$

$$\frac{\partial}{\partial t} \left(\varphi \sum_{j=1}^{np} \rho_j s_j U_j + (1 - \varphi) U_r \right) + \nabla \cdot \left(\sum_{j=1}^{np} H_j \rho_j u_j - \kappa \nabla T \right) = 0. \tag{9}$$

he nonlinear equations (8) - (9) are discretized using finite volume discretization with a two-point flux approxi- mation and upstream weighting on a general unstructured mesh in space and a backward Euler approximation in time. The set of discretized equations are then solved utilizing the operator-based linearization (OBL) approach, which simplifies the solution of the nonlinear system of equations by introducing algebraic operators that capture all complex physics and nonlinear terms. Instead of keeping track of each property and its derivatives with respect to nonlinear unknowns, abstract algebraic operators representing the physics can be constructed and assembled into the set of Jacobian and residuals defined at each iteration. The OBL approach has been described in more detail in previous works (Voskov, 2017; Lyu et al., 2021).

Thermodynamic modelling

In the compositional formulation used in this study, thermodynamic modelling determines the robustness and accuracy of the simulation. We investigate scenarios of CO_2 injection into depleted hydrocarbon fields, where one typically encounters light to heavier hydrocarbon fractions, impurities and brines. A multiphase hybrid- model approach is employed to accurately describe the interaction between reservoir fluids and brine, including the occurrence of multiple non-aqueous liquid phases.

Thermodynamic equilibrium

At thermodynamic equilibrium, pressure and temperature are uniform throughout the system. Furthermore, the Gibbs free energy of an equilibrium mixture is at a global minimum. The Gibbs free energy is given by:

$$\overline{G} = G / RT = \sum_{k=1}^{np} \sum_{i=1}^{n_c} n_{ik} \ln f_{ik} \tag{10}$$

with n_{ik} the number of moles of species i in phase k. At the global minimum, the change in Gibbs energy for any transfer of material must be zero:

$$\frac{\overline{\partial G}}{\partial n_{ik}} = \ln f_{ik} - \ln f_{iR} = 0, \quad i = 1, \, \ldots, n_c; k = 1, \, \ldots, n_p; k \ne R, \tag{11}$$

where the reference phase R can be any phase. Hence, this yields the equality of fugacity of each component i throughout all phases k as a necessary condition for equilibrium.

Since it is generally not known in advance how many phases coexist at a global minimum, a sequence of phase stability and split routines must commonly be performed to find the correct equilibrium state. The stability test and phase split problems have similar mathematical structures. In a recent work (Wapperom et al., 2025), we adapted the procedures described by Petitfrere and Nichita (2015a,b) for hybrid models. A stability test indicates whether the Gibbs energy surface is either at or above the mixture tangent hyperplane throughout the entire compositional space (Baker et al., 1982; Iranshahr et al., 2012). Michelsen (1982) developed a mathematical implementation of this "tangent plane distance" (TPD) criterion. The common

approach to finding the minima of the TPD function is to apply local optimization over a set of initial guesses. The corresponding phase compositions can be used as an initial estimate in further phase split calculations.

In the phase split procedure, the dimensionless Gibbs energy (10) is minimized with respect to mole numbers. In addition, in SSI iterations or if lnK are used as independent variables in the Newton method, the material balance must be satisfied, generally done so by solving the Rachford-Rice (RR) system of equations:

$$R_k \equiv \sum_{i=1}^{n_c}(x_{ik} - x_{iR}) = \sum_{i=1}^{n_c} \frac{z_i(K_{ik} - 1)}{\sum_{p=1}^{n_p}\theta_p^{(K_{ip}-1)}} = 0, \quad k = 1, \ldots, n_p; k /= R. \tag{12}$$

The solution to the RR equations yields the phase fractions $\theta = (\theta_1, \ldots, \theta_k)_T$ and phase compositions $\mathbf{x}_k$. For two phases, the RR equation can solved using convex transformations, as proposed by Nichita and Leibovici (2013), leading to a significant increase in solution speed in difficult cases. For multiphase systems, Michelsen (1994) proposed a minimization approach, which was later extended to negative flashes (Leibovici and Nichita, 2008; Yan and Stenby, 2012).

In systems that are known to form two phases at maximum, converging to a non-trivial solution with a negative flash indicates the single-phase stability of the feed with the same certainty as a traditional phase stability test (Whitson and Michelsen, 1989). However, this approach is limited to liquid water conditions and cannot handle the transition from liquid water to steam. More importantly, a negative flash corresponds to a local minimum in the Gibbs energy surface (which becomes a saddle point at the convergence locus), rather than a global minimum (Whitson and Michelsen, 1989; Nichita et al., 2007). Consequently, a standalone negative flash procedure is not adequate in multiphase systems and a full Gibbs energy minimization procedure is required.

Hybrid-EoS approach
Cubic equations of state have proven reliable for thermodynamic calculations of nonpolar mixtures but are not adequate to predict the interaction between associating particles in aqueous solutions and fail to describe the behaviour close to infinite dilution. Using a hybrid-model approach (Wapperom et al., 2025), thermodynamic models can be combined to represent different phase types. The implementation of a separate model for the aqueous phase maintains the simplicity of solving phase equilibrium problems with cubic equations of state while obtaining an accurate thermodynamic description of the aqueous phase. For the aqueous model, we combine activity coefficient models based on Henry's law constants for the dissolved species (Akinfiev and Diamond, 2003; Ziabakhsh-Ganji and Kooi, 2012) and a separate fugacity model for the H_2O component (Jager et al., 2003) to calculate the aqueous phase fugacities.

The cubic EoS is valid for all compositions, but the aqueous fugacity model is limited to a H_2O-rich phase. For a practical implementation of mixed models for aqueous systems, it is important to distinguish the vapour- and liquid-like roots of the cubic equation of state to correctly identify the minima of the Gibbs free energy surfaces in water-rich compositions. We can identify these roots using the characteristics of the cubic polynomial (Kamath et al., 2010). Furthermore, one can take advantage of the convexity of the Gibbs energy surface that the aqueous phase model exhibits throughout the relevant range of compositions. We therefore have only a single local minimum of the Gibbs energy, which allows the use of a specific initial guess for the aqueous model. The hybrid-model approach introduces a thermodynamic inconsistency that is mostly pronounced close to critical conditions. Far from brine criticality, however, robust, accurate and efficient solution procedures are obtained. Figure 1 shows the solubilities of CH_4 and CO_2 in brine (zoomed to 97-100% of H_2O overall molar fraction) calculated using the described approach, validated with experimental data (Dhima et al., 1999).
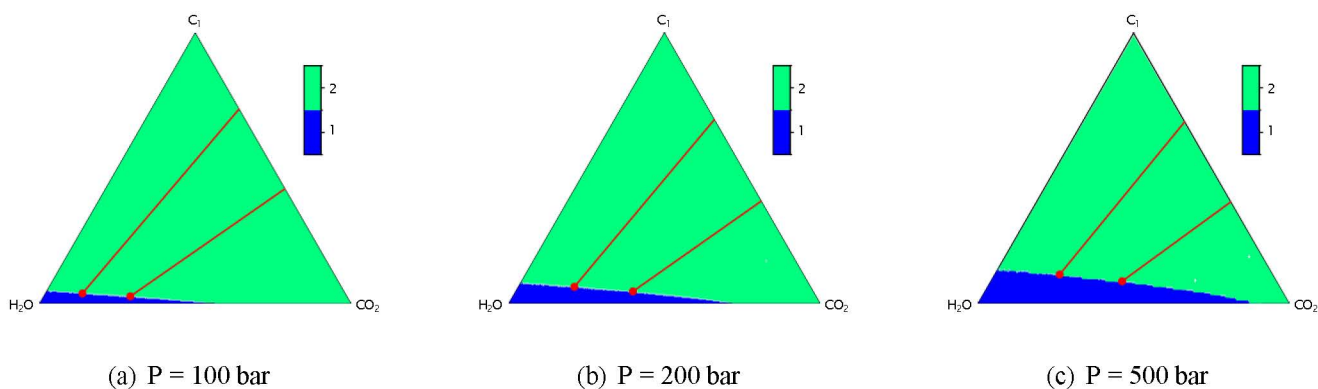
(a) P = 100 bar   (b) P = 200 bar   (c) P = 500 bar

Figure 1—Ternary diagram for H_2O-CH_4-CO_2 mixtures at 344 K, zoomed in to 97-100% H_2O. Blue and green indicate single- and two-phase regions, respectively. Solubility data from Dhima et al. (1999).

Fluid thermodynamic and transport properties

Apart from calculating the equilibrium phase fractions and phase compositions at the given state specification, the thermodynamic modelling procedures are used as inputs to evaluate the fluid properties in the different terms of the conservation equations. Phase densities, viscosities and enthalpies are calculated based on the phase compositions. Furthermore, some of these properties are available directly from the equations of state.

For phases that are calculated with an equation of state that have an expression for $P = (V, T, \mathbf{n})$, such as the cubic EoS (Peng and Robinson, 1976) used for the non-aqueous phases, densities can be obtained directly from the EoS. In addition, an expression for the residual Helmholtz free energy $A^r(V, T, \mathbf{n})$ can be derived from the pressure equation, which allows one to calculate the thermodynamic equilibrium properties (Michelsen and Mollerup, 1986).

In multiphase systems, consistent phase identification is important to assign flow properties (relative perme- abilities, capillary pressure curves, etc.) and keep track of the different possible phases during simulation. In the hybrid-EoS approach, the identification of the aqueous phase among the multiphase flash output is straight- forward. For the non-aqueous phases, however, one needs to distinguish vapour(-like) and potentially multiple liquid(-like) phases. In our approach, we can take advantage of the characteristics of the cubic polynomial to determine the phase type at a given composition (Kamath et al., 2010).

Phase enthalpies are calculated as the sum of an ideal H^{id} and a residual part H^r. Residual enthalpies can be obtained from partial derivatives of the fugacity or fugacity coefficient:

$$-\frac{H^r(P, T, \mathbf{n})}{T} = nRT \left.\frac{\partial \ln f_i}{\partial T}\right|_{P,\mathbf{n}} = nRT \left.\frac{\partial \ln \phi_i}{\partial T}\right|_{P,\mathbf{n}} \tag{13}$$

For equations of state from which an expression for Helmholtz free energy can be derived, the fugacity coefficient and its partial derivatives can be derived from the reduced residual Helmholtz energy $F = A^r(V, T, \mathbf{n})/RT$, as was shown by Michelsen and Mollerup (1986); Mollerup and Michelsen (1992). In such models, the derivative of the fugacity coefficient with respect to temperature reads:

$$\left.\frac{\partial \ln \phi_i}{\partial T}\right|_{P,\mathbf{n}} = \frac{\partial^2 F}{\partial T \partial n_{i_V}} + \frac{1}{RT} \frac{1 - \frac{\partial P}{\partial n_i (V,T)} \frac{\partial P}{\partial T (V,\mathbf{n})}}{\frac{\partial P}{\partial V (T,n)}} + \frac{1}{T} \tag{14}$$

The aqueous phase enthalpy can also be calculated from the respective thermodynamic model. It involves different expressions for water and dissolved components. For the water component, one can directly obtain enthalpy by evaluating the derivative of water fugacity with respect to temperature. For the dissolved species, the fugacity can be written in terms of Henry's constants. Models based on Henry's constants are asymmetric activity coefficient models, which means that infinite dilution of the solute is taken as the

reference state for the activity coefficient: $h_i^\infty \equiv f_i(P, T)\gamma_i^\infty(P, T, n_k)$ Following the discussion by Michelsen and Mollerup (2007), the fugacity of component i in terms of the asymmetric activity coefficient $\tilde{\gamma}_i$ is:

$$f_i(P, T, \mathbf{n}) = h_i^\infty(P, T, n_k)\tilde{\gamma}_i(P, T, \mathbf{n})x_i \tag{15}$$

where $\tilde{\gamma}_i(P, T, \mathbf{n}) \equiv \gamma_i(P, T, \mathbf{n})/\gamma^\infty(P, T, n_k)$. In the models considered in this study, the interaction between dis- solved components in the aqueous phase is neglected and $\tilde{\gamma}_i(P, T, \mathbf{n})$ is only dependent on brine salinity. Con- sistently with the other models, enthalpy can be calculated by taking the derivative of fugacity with respect to temperature (13).

By conserving phase internal energies consistently, the simulation implicitly accounts for energy and temper- ature changes related to mixing and dissolution, phase transitions, and isenthalpic compression and expansion (also referred to as Joule-Thomson effect). Figure 2 shows the *PH*-diagram for mixtures of CO_2-CH_4. It indicates that an isenthalpic pressure drop is accompanied by a significant decrease in temperature, which is the result of a combined effect of (Joule-Thomson) expansion cooling in single-phase conditions and a phase transition. It can be observed that across the phase transition, a small change in temperature causes a large change in enthalpy. The isotherms in the *PH*-diagrams are nearly horizontal (exactly horizontal for the extreme case of pure CO_2), known as narrow-boiling conditions (Zhu and Okuno, 2014). This introduces difficulties for a *PT*-based simulator and in such systems a *PH*-based formulation is preferred.
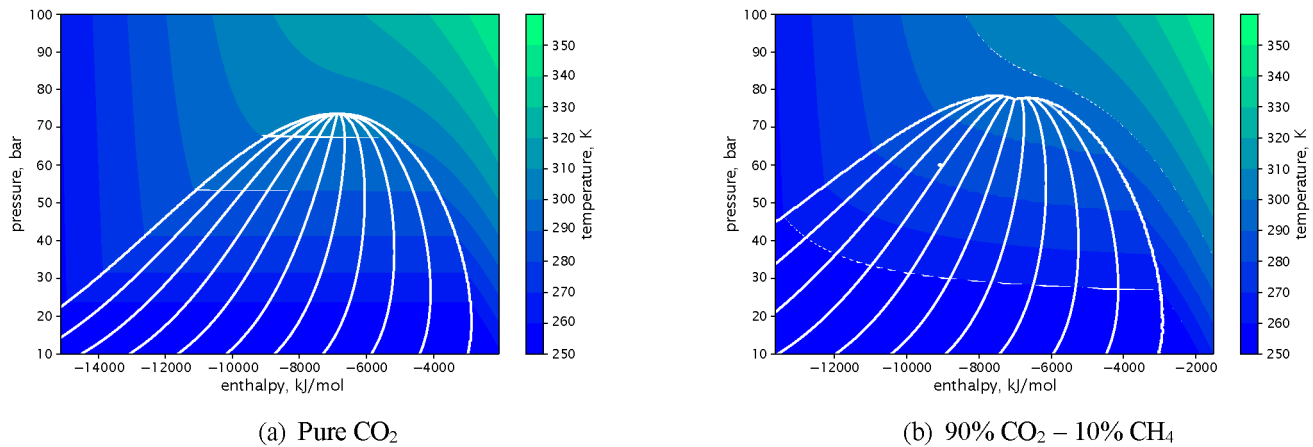

(a) Pure CO_2 (b) 90% CO_2 − 10% CH_4

Figure 2—*PH*-diagram of injected mixtures of CO_2-CH_4 at depleted gas field conditions.

Finally, a few properties have not directly been obtained from thermodynamic equilibrium modelling. Since in this work, the cubic EoS is not used to model the aqueous phase and its predictions of aqueous density are poor, we employ the correlation from Spivey et al. (2004) for brine density and take into account the effect of dissolved CO_2 on its volume (Garcia, 2001). In addition, we model the phase viscosities of based on different correlations (Fenghour et al., 1998; Islam and Carlson, 2012). Molecular diffusion coefficients and phase thermal conductivities are taken to be constants.

Results

In this section, we investigate typical conditions for CO_2 injection into depleted fields. We consider a depleted gas reservoir saturated with CH_4 and residual brine. This model is inspired by the Porthos project in the Netherlands offshore of the North Sea (Neele et al., 2019). A simple radial reservoir model with a high-permeable strike (100 mD) and a lower-permeable zone (20 mD) is considered, with impermeable over- and underburden. We test the feasibility of modelling such type of reservoirs using binary or ternary representations of reservoir fluids.

In this example, we inject gaseous CO_2 into the depleted field. The reservoir is depleted to 20 bar and uniformly saturated with brine at a residual saturation of 25% We compare two scenarios: a simplified binary model when in-situ methane is represented by gaseous CO_2 and a full-physics ternary case with CH_4-H_2O originally in place. In both cases, pure CO_2 is injected with a pressure of 60 bar and a temperature of 310 K. The 2D radial plots of pressure and temperature in the full-physics model after one year of injection are present in Figure 3. Here, the expansion of CO_2 and corresponding cooling below the injection temperature can clearly be observed.

(a) 3D view of pressure profile   (b) 3D view of temperature profile
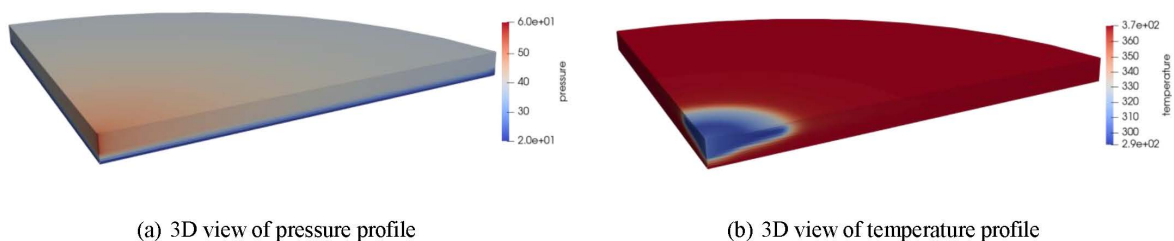
Figure 3—3D view of pressure and temperature profile after one year of simulation (lower half of the reservoir).

Figure 4 shows the 2D profiles in logarithmic scale for the binary and ternary system simulation after one year of injection. The simulation shows a pronounced cooling front in the reservoir due to the CO_2 expansion seen in the density plot. A temperature drop of more than 20 ◦C can be observed with most of the cooling at the tip of the thermal front. The saturation profile reflects non-uniform distribution due to the layer heterogeneity structure. Surprisingly, the simulation results in the full-physics ternary system (see Figure 4b) share the same dynamics with only insignificant changes in the saturation and density profiles.
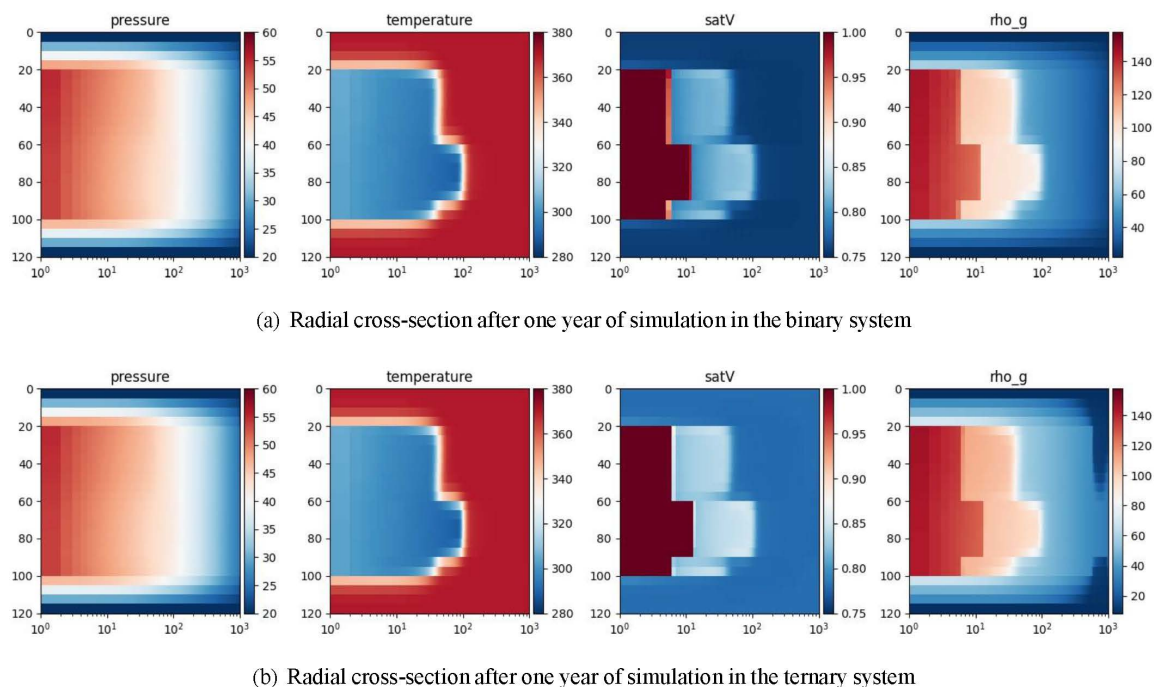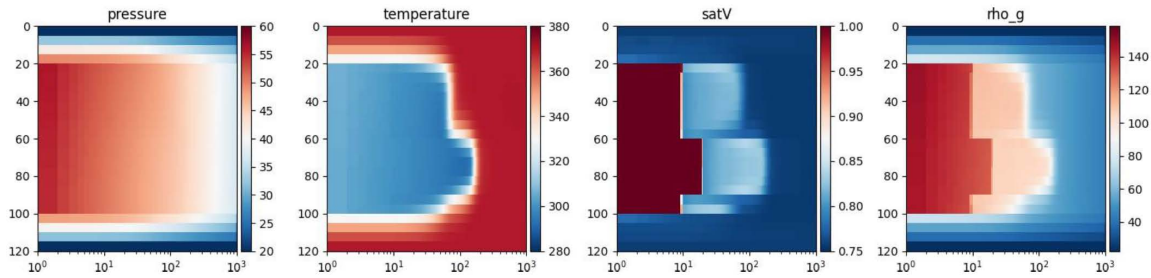

(a) Radial cross-section after one year of simulation in the binary system

(b) Radial cross-section after one year of simulation in the ternary system

Figure 4—Simulation results after one year of pure CO_2 injection at 60 bar into radial depleted gas reservoir.

In Figure 5, one can see the late time dynamics after 3 years of injection. Here, the pressure is built up in the permeable part of the reservoir (far side pressure is around 40 bars). The thermal cooling is less pronounced after the reservoir is pressurized. Comparing these results with simulation in the ternary system still reflects quite a good match with the binary results.

(a) Radial cross-section after three years of simulation in the binary system

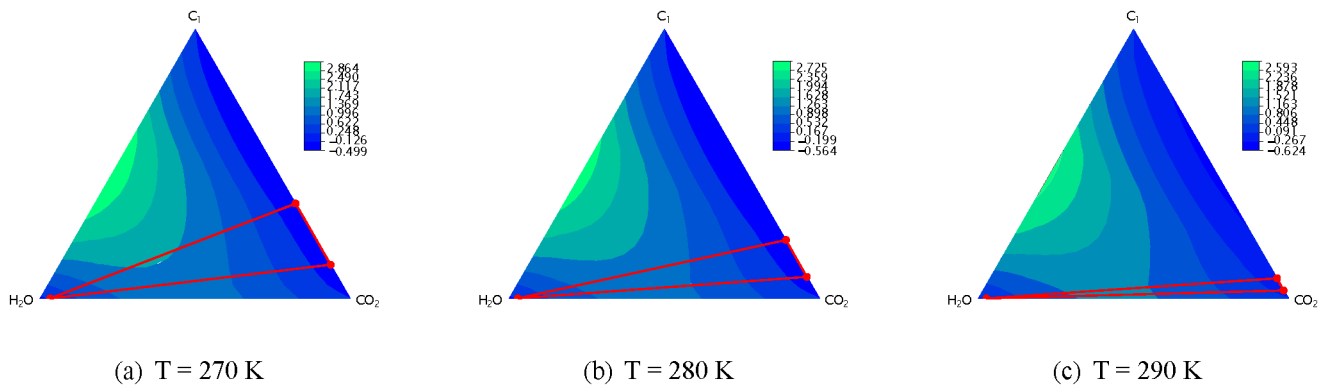(b) Radial cross-section after three years of simulation in the ternary system

Figure 5—Simulation results after three years of pure CO_2 injection at 60 bar into radial depleted gas reservoir.

In these simulations, we did not consider the differences between the liquid CO_2-rich phase and the gaseous phase. However, in many real-world applications, the three-phase split with a second liquid phase cannot be ignored. Depending on the reservoir and injection conditions, sufficient isenthalpic cooling (Figure 2) can bring the system in three-phase conditions, as depicted in Figure 6. In such systems, the CO_2-rich phase should be modeled using a three-phase relative permeability model and other phase-related properties. The CO_2-rich phase will guide the injection conditions and the displacement front will follow more complex three-phase characteristics (LaForce and Johns, 2005).

(a) T = 270 K   (b) T = 280 K   (c) T = 290 K

Figure 6—Gibbs energy of mixing surfaces for H_2O-CO_2-CH_4 mixtures at 60 bar. The red lines indicate the three-phase region (Aq-V-LCO2), which degenerates with increasing temperature.

In addition, the more pronounced thermal effects related to phase transitions pose problems for a *PT* formula- tion where small changes in temperature cause a large difference in enthalpies (Zhu and Okuno, 2014; Moncorgé et al., 2022). Besides, the cooling of the field depends on the particular reservoir geometry and structure which need to be considered for a practical dynamic simulation. These important considerations are the focus of our future work.

Conclusion

In this work, we have presented a thermal-compositional simulation framework for modelling of CO_2 sequestra- tion in depleted hydrocarbon reservoirs. Taking advantage of the flexibility of the operator-based linearization approach, a multiphase thermodynamic formulation has been employed to accurately describe the interaction between reservoir fluids and brine, including the occurrence of multiple non-aqueous liquid phases. We use a hybrid-EoS approach to combine thermodynamic models for aqueous and hydrocarbon phases and advanced ini- tialization schemes for multiphase equilibrium. These ingredients improve the accuracy and efficiency of the fully coupled simulation.

We have applied the simulation framework to model CO_2 injection cases at conditions typical for depleted gas fields. We have demonstrated that important thermophysical phenomena resulting from the interaction of CO_2 with reservoir fluids can be accurately captured using the OBL framework. The consistency of compositional simulation is supported by robust and efficient modelling of multiphase equilibria between brine, hydrocarbon components and CO_2. For the particular scenario considered in this study, a pseudo-binary representation of the ternary system (CO_2-CH_4-H_2O) provides an accurate approximation and can be used for simulation of CO_2 injection into depleted gas fields.

The proposed formulation proves to be capable of capturing the thermal effects related to expansion, phase change and mixing in the fully coupled dynamic simulation. However, upon severe cooling, the transition from two- to three-phase conditions with the occurrence of a liquid CO_2-rich phase cannot be captured effectively using a *PT*-based simulation. For such conditions, a *PH*-formulation with isenthalpic flash should be considered which is the topic of our future investigation.

Acknowledgements

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