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Thermo- and fluid-dynamical modeling of two-phase multi-component carbon dioxide mixtures

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Abstract

A method for calculating the transport and depressurization of a two-phase multi-component CO_2 mixture is presented. The thermodynamical and transport properties for mixture CO_2-CH_4 are calculated using the Soave-Redlich-Kwong equation of state (SRK). The fluid flow is described by a drift-flux model, which is solved using the multi-stage (MUSTA) centred scheme. Numerical results are shown, illustrating the effect of mixture composition and the feasibility of the approach.

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1. Introduction

An important factor in carbon dioxide (CO_2) capture and storage (CCS) is the transport between the point of capture and the point of storage. The transport in pipes will take place at high pressures, where the CO_2 is in a supercritical (liquid-like) state. Due to failure, or planned maintenance, the pipe can be depressurized. The lower pressure will cause a phase change in the CO_2, resulting in a strong cooling of the pipe. If the temperature becomes low enough, the pipe material may become brittle, causing a rupture and much damage. Therefore, for a proper pipeline design, it is necessary to be able to estimate the pipe cooling during depressurization.

Such a pipe-cooling estimation involves comprehensive *thermodynamical* and *fluid dynamical* considerations. First, information is needed about the thermodynamical and transport properties, such as phase equilibria, density, viscosity, surface tension, etc. As the CO_2 stream involves several impurities, reliable thermodynamical models for multi-component CO_2 mixtures are required. Next, it is necessary to have a transient two-phase flow model accounting for several components. Finally, a robust, accurate and efficient *numerical method* is required. Mass transport, pressure waves, and energy transfer between the gas and the liquid must be correctly captured.

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Knowledge of the thermodynamic properties of CO_2 mixtures is important for the design and operation of processes related to CCS. The calculations of the CO_2-stream conditioning process, transport and injection systems were in the past often performed with the thermodynamics of pure CO_2, although the CO_2 fluid will clearly contain impurities originating from both the feed stream (air, fuel, etc.) and the product stream (combustion products). Which components in particular will be present in the CO_2 stream depends on the type of the industrial process that is the source of CO_2, and the type of the capture process. The impurities will affect the thermodynamical properties of the CO_2 fluid and thereby influence the compression, transport and injection process design and costs. A fairly accurate thermodynamical model is therefore needed that is relatively easy to implement and robust to use in combination with flow and process calculations.

For safe and efficient design and operation of CO_2 transport and injection systems, we need to be able to perform the following kind of calculations:

- Phase equilibria, thermodynamical properties and transport properties of CO_2 mixtures at the relevant pressure and temperature ranges and for the relevant mixture compositions.
- Depressurization of a CO_2 transport pipe.
- Simulations of operational issues, for instance possible precipitations or phase transitions due to changing pressure and temperature along the transport line.

Consider the depressurization of the pipeline as an example. This will have to be done at regular intervals for maintenance. It may also happen due to an unplanned incident. The sublimation temperature of CO_2 at atmospheric pressure is about –78.5 °C. At this temperature, the tube steel may become brittle so that the tube ruptures, inflicting personal injuries or material damage. Therefore, it is important to be able to estimate the pipe temperature during depressurization. It is dependent on the local flow regime, temperature, pressure and mixture composition. Further, it is dependent on the local heat transfer to or from the surroundings.

A further example to consider is complications that may arise along the CO_2-transport pipeline due to the CO_2-mixture composition. See de Visser *et al.* [2] for a survey of effects of various impurities. For instance, the solubility of water in CO_2 decreases with decreasing pressure and temperature. Hence, a free water phase may form at one point in the pipeline, even if there was no free water present at the pipe inlet. Free water is unwanted, since it may cause corrosion. A multi-phase multi-component flow model, including heat transfer to the surroundings, is necessary to estimate the occurrence of such phenomena.

This paper presents a framework for handling the above-mentioned modeling issues. As an example mixture, we consider carbon dioxide–methane, and the thermodynamical and transport properties are modeled using the Soave-Redlich-Kwong equation of state (SRK). The pipe flow is described by a drift-flux two-phase multi-component model. Herein, each chemical component is tracked explicitly. The drift-flux model is a system of coupled non-linear hyperbolic differential equations. The pressure and mass waves inherent in the model are resolved numerically by using the multi-stage (MUSTA) centred scheme.

The rest of this paper is organized as follows. Section 2 gives an overview of the employed fluid dynamical and thermodynamical models, while Section 3 outlines the numerical method. Section 4 presents an example calculation demonstrating the feasibility of the suggested approach, and Section 5 concludes the paper.

2. Model formulation

This section briefly presents the employed models describing the two-phase flow of CO_2 mixtures.

2.1. Fluid dynamics

The motion of a strongly coupled gas (g) and liquid (ℓ) phase can be described by the *drift-flux model*. In the present case, each phase consists of n components, i. We then obtain n component-balance equations,

$$\frac{\partial}{\partial t}(\rho_{\mathrm{m}} z_i) + \frac{\partial}{\partial x}(\alpha_{\mathrm{g}}\rho_{\mathrm{g}} u_{\mathrm{g}} z_{\mathrm{g},i} + \alpha_\ell \rho_\ell u_\ell z_{\ell,i}) = 0\,, \tag{1}$$

a balance equation for the mixture momentum,

$$\frac{\partial}{\partial t}(\alpha_{\mathrm{g}}\rho_{\mathrm{g}} u_{\mathrm{g}} + \alpha_\ell \rho_\ell u_\ell) + \frac{\partial}{\partial x}(\alpha_{\mathrm{g}}\rho_{\mathrm{g}} u_{\mathrm{g}}^2 + \alpha_\ell \rho_\ell u_\ell^2 + p) = 0\,, \tag{2}$$

and one for the mixture total energy:

$$\frac{\partial}{\partial t}(\alpha_{\mathrm{g}}\rho_{\mathrm{g}} e_{\mathrm{t,g}} + \alpha_\ell \rho_\ell e_{t,\ell}) + \frac{\partial}{\partial x}\left\{\alpha_{\mathrm{g}}\rho_{\mathrm{g}} u_{\mathrm{g}}(h_{\mathrm{g}} + 1/2u_{\mathrm{g}}^2) + \alpha_\ell \rho_\ell u_\ell (h_\ell + 1/2u_\ell^2)\right\} = 0\,. \tag{3}$$

Herein, ρ denotes mass density, u velocity, p pressure, e inner energy, $h = e + p/\rho$ enthalpy and $e_{\mathrm{t}} = e + 1/2u^2$ total energy. $\rho_{\mathrm{m}} = \alpha_{\mathrm{g}}\rho_{\mathrm{g}} + \alpha_\ell\rho_\ell$ is the gas-liquid mixture density. Further, $z_{k,i} = \rho_{k,i}/\rho_k$ is the mass fraction of component i in phase k. z_i is the total mass fraction of component i,

$$z_i = \frac{\alpha_{\mathrm{g}}\rho_{\mathrm{g}} z_{\mathrm{g},i} + \alpha_\ell \rho_\ell z_{\ell,i}}{\alpha_{\mathrm{g}}\rho_{\mathrm{g}} + \alpha_\ell \rho_\ell}\,. \tag{4}$$

We also have the relation

$$\sum_{i=1}^{n} \rho_{\mathrm{m}} z_i = \rho_{\mathrm{m}}\,, \tag{5}$$

and the volume fractions satisfy

$$\alpha_{\mathrm{g}} + \alpha_\ell = 1\,. \tag{6}$$

Since the momentum equation (2) is for the mixture, a relation is needed for the relative velocity between the phases – the *slip*. Slip relations contain empirical information of the prevailing flow regime, and they are often of the form

$$u_{\mathrm{g}} - u_\ell = \Phi((\alpha\rho)_{\mathrm{g}}, (\alpha\rho)_\ell, u_{\mathrm{g}})\,. \tag{7}$$

In this work, we assume no slip, for simplicity: $\Phi = 0$. This is often referred to as homogeneous flow. Further, since this is a conceptual study, effects like wall friction and heat transfer to the surroundings are not considered. However, such effects can be included relatively easily by adding terms to the right-hand sides of (1)–(3).

The energy equation (3) constitutes an assumption of thermal equilibrium between the phases. The gas and liquid compositions, as well as the volume fraction, are then determined by a thermodynamical model, as outlined in the following. A drift-flux model similar to the one described here, was also studied in [6].

2.2. Thermodynamics

The objective here is to provide the flow model with the necessary thermodynamical functions and properties so that multi-component CO_2 mixtures can be handled. The importance of this task has been recognized by several research groups, and a few attempts have been made to find a suitable equation of state (EOS) model for CO_2 mixtures [3,4,7,8,10].

An EOS is a constitutive relation between the state variables pressure, specific volume and temperature (PVT) for pure components, and PVT and composition in mixtures. It describes the state behavior of the fluid and is also applied to calculate other thermodynamical properties. The EOS is specified by its mathematical form and the applied values of adjustable parameters. The various models differ in the quality of the results at high pressures (non-ideal gas), in the liquid phase, and for polar fluids. Further issues are the possibility to extend the model to mixtures, and the computational efficiency. The choice of a suitable EOS is in general governed by following criteria:

- Availability of experimental data
- Character of the fluid (polar/non-polar etc.)
- Area of application; temperature and pressure range

The choice of appropriate mixing rule is the determining factor for mixtures.

Austegard *et al.* [1] performed a study on mutual solubilities in H_2O-CO_2-CH_4 mixtures by using three different models:

- Soave-Redlich-Kwong equation of state with common van der Waals mixing rules (SRK-vdW)
- Soave-Redlich-Kwong equation of state with Huron-Vidal mixing rules (SRK-HV)
- Cubic Plus Association equation of state (CPA)

Experimental data for binary mixtures were collected and their quality and consistency were evaluated prior to the evaluation of binary interaction parameters by regression. It was concluded that the SRK-HV model is the most useful one, providing good results and being relatively simple in structure compared to the CPA model. Figure 1 illustrates the effect of CH_4 on water solubility in CO_2. The lines are calculated results obtained with the SRK-HV model and the points are experimental data by Song and Kobayasi [14]. In the present work, the SRK-HV EOS was applied. However, the Huron-Vidal mixing rules are of no importance for CO_2-CH_4 mixture, since CO_2 and CH_4 are not polar molecules.

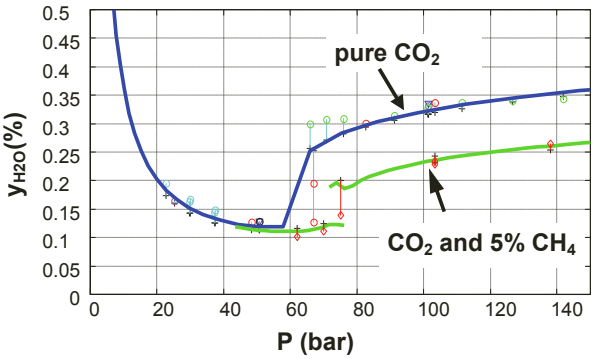

Figure 1: Water solubility in pure CO_2 and in CO_2-CH_4 mixture.

The Soave-Redlich-Kwong (SRK) EOS is a cubic equation of state, i.e., third order with respect to volume and density. It is a relatively simple equation with only a few adjustable parameters and it is easily applicable for mixtures and phase-equilibrium calculations. Cubic EOS'es are in general poorly suited to describe the liquid phase, polar components, and complex mixtures. For the problem with the liquid-phase volume, the solution is to use a volume shift, which is a correction in liquid volume that is evaluated based on experimental data.

The SRK model can be cast in the form given by Reid *et al.* [12]:

$$p = \frac{RT}{v - b_i} - \frac{a_i}{v \cdot (v + b_i) + b_i \cdot (v - b_i)} \tag{8}$$

where p is pressure, T is temperature, v is the mixture molar volume, and R is the universal gas constant. The two state constants a_i and b_i are evaluated as follows, for each component, i, in the mixture:

$$b_i = \frac{\Omega_b RT}{p_{ci}}; \quad a_i = \alpha_i \cdot \frac{\Omega_a (RT_{ci})^2}{p_{ci}} . \tag{9}$$

Herein, p_{ci} and T_{ci} are the critical temperature and pressure, respectively, of component i. The following standard relation was applied for the parameter α_i:

$$\alpha_i = \left[1 + m_i\left(1 - \sqrt{T_{ri}}\right)\right]^2; \quad T_{ri} = \frac{T}{T_{ci}} \tag{10}$$

$$m_i = \alpha + \beta \cdot \omega_i - \gamma \cdot \omega_i^2$$

where T_{ri} is the reduced temperature and ω_i is the acentric factor. Values for the other parameters are summarized in Table 1.

Table 1: Coefficients of Soave-Redlich-Kwong equation of state (SRK EOS).

α	0.48
β	1.574
γ	0.176
Ω_a	0.42748
Ω_b	0.08664

3. Numerical method

The drift-flux model of Section 2 can be written in the following form:

$$\frac{\partial \boldsymbol{q}}{\partial t} + \frac{\partial \boldsymbol{f}(\boldsymbol{q})}{\partial x} = \boldsymbol{0}, \tag{11}$$

where $\boldsymbol{q}$ is the $n + 2$-vector of unknowns:

$$q_i = \rho_m z_i \text{ for } i = 1,\ldots,n, \tag{12}$$

$$q_{n+1} = \alpha_g \rho_g u_g + \alpha_\ell \rho_\ell u_\ell, \tag{13}$$

$$q_{n+2} = \alpha_g \rho_g e_{t,g} + \alpha_\ell \rho_\ell e_{t,\ell}. \tag{14}$$

The model (11) can be integrated over a control volume to yield the semi-discrete formulation

$$\frac{d}{dt}\boldsymbol{q}_j(t) = -\frac{1}{\Delta x}\left(\boldsymbol{f}_{j+1/2} - \boldsymbol{f}_{j-1/2}\right). \tag{15}$$

A simple way of integrating (15) in time is to use the Forward Euler method:

$$\boldsymbol{q}_j^{m+1} - \boldsymbol{q}_j^m = -\frac{\Delta t}{\Delta x}\left(\boldsymbol{f}_{j+1/2} - \boldsymbol{f}_{j-1/2}\right). \tag{16}$$

Herein, $\boldsymbol{q}_j^m$ denotes the numerical approximation to the cell average of the vector of unknowns $\boldsymbol{q}(x,t_m)$ in control volume j at time step m. Quantities without a time index are evaluated at time step m.

The most difficult part of solving (15) is to find an approximation to the cell-interface flux vector, $\boldsymbol{f}_{j+1/2}$. For an accurate numerical solution, it would be desirable to have an upwind resolution of all the waves inherent in the model (1)–(3), for instance by constructing an approximate Riemann solver of the type of Roe [13]. However, this is relatively complex, even for simpler types of drift-flux models than the one considered here [5]. The multi-stage centred (MUSTA) scheme was formulated by Toro and coworkers [16,15] to approach the accuracy of upwind schemes while maintaining the simplicity of centred schemes. The idea is to find a numerical approximation to the cell-interface Riemann problem by solving a simple, first-order scheme on a local grid. It was shown that in the case of linear advection, for an increasing number of pseudo-time steps on the local grid, the MUSTA flux approaches that of the Godunov method [15]. Titarev and Toro [15] considered the Euler equations of single-phase flow.

Munkejord *et al.* [9] explored the MUSTA scheme for a drift-flux model without an energy equation. Even though the present model is considerably more complex, it has the same form as the one in [9], so the MUSTA scheme can be applied rather directly.

The scheme (16) is of first order. Second-order accuracy can, for instance, be obtained by considering the semi-discretization (15) and using the monotone upwind-centred scheme for conservation laws (MUSCL) [17,11]. More details can be found in Munkejord *et al.* [9]. In the following, we employ the MUSCL-MUSTA scheme with four local stages and four local cells.

After each time step, the MUSTA solver returns the vector $\boldsymbol{q}$ (12)–(14) of composite variables. However, the primitive variables (pressure, temperature, gas volume fraction, phasic velocities, phasic inner energies, as well as gas and liquid mixture composition) are also needed. Due to the complex thermodynamical relations, they have to be found by iteration.

4. Numerical simulation

In this section, we will show an example calculation that illustrates the effect of the CO_2-mixture composition. We consider a mixture of CO_2 and methane. The test case consists of a tube of length 100 m, closed at $x = 0$ m, and with a membrane at $x = 100$ m, see Figure 2. Initially, the pressure is $p_0 = 60$ bar, and the mixture is at rest, at a temperature 0.5 K above its bubble point. At time $t = 0$, the membrane ruptures. The external pressure is $p_e = 30$ bar, so a depressurization wave starts propagating into the fluid, which then starts flowing towards the exit. Some of the liquid evaporates, and the temperature sinks.

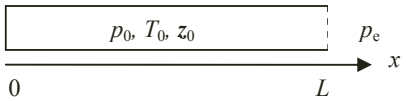

Figure 2: Test-case setup.

Calculations have been performed using the MUSCL-MUSTA scheme with a Courant-Friedrichs-Lewy (CFL) number of 0.5 on a 800-cell grid. Two different mixtures have been considered, one with $z_{CO2} = 99$ % and the other with $z_{CO2} = 95$ %. Figure 3 displays results calculated at $t = 1$ s. The left plot shows the pressure. It can be seen that the pressure-propagation speed (or mixture sonic speed) is higher for the 99 % CO_2 mixture. One can also note that the mixture sonic speed is in the order of 70 m/s, which is significantly lower than the speed of sound for each of the mixture components, both in the gas and the liquid phase.

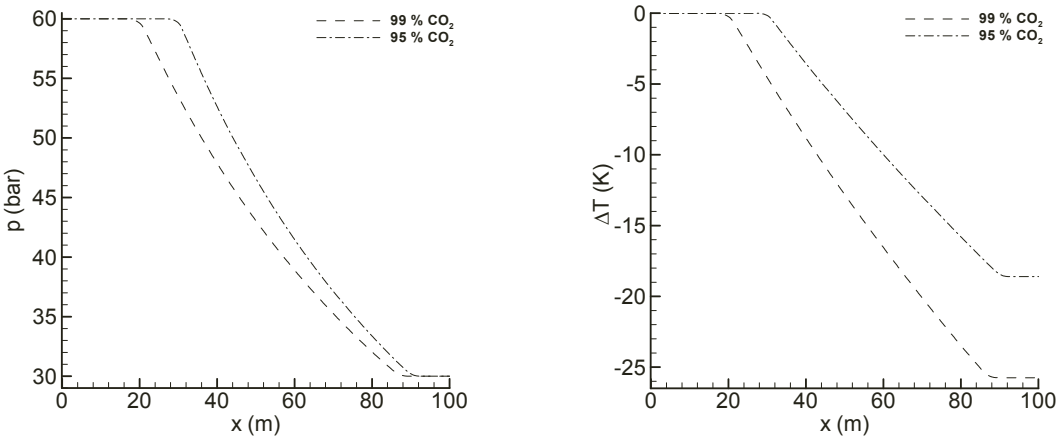

Figure 3: Depressurization of a carbon dioxide-methane mixture. Pressure (left) and difference between initial and final temperature (right).

The right-hand-side part of Figure 3 shows the initial temperature subtracted by the final temperature. The cooling effect of the evaporation is highest for the mixture with the highest CO_2 content.

5. Conclusion

We have proposed to employ a two-phase multi-component drift-flux model to model the transport and depressurization of CO_2 mixtures. Calculations have been performed for a CO_2-CH_4 mixture using the Soave-Redlich-Kwong equation of state to compute the mixture properties. The multi-stage centred (MUSTA) scheme was employed for the numerical solution of the drift-flux model and produced accurate results even for this complex model.

The results confirm that the mixture composition influences the pressure-propagation speed and the amount of cooling exerted by depressurization. These issues should be taken into account for the design and operation of CO_2 transport systems.

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