CO₂ Transportation with Pipelines - Model Analysis for Steady, Dynamic and Relief Simulation

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“Carbon dioxide or CO₂ capture and storage” (often defined by its acronym CCS) is the term used to describe a set of technologies aimed at capturing carbon dioxide emitted from industrial and energy-related sources before it enters the atmosphere, by compressing and injecting it underground in secure geological formations. The scope would be the mitigation of greenhouse effects and the reduction of related global warming and climate changes. A large number of papers have been devoted to this topic, some recent publications, also in this series, has been devoted to the risk assessment of CO₂ relief (Vianello et al. 2012) and overall risk analysis of CO₂ transportation (Samadi et al. 2012). It is not the aim of this paper to discuss the effectiveness of the technology but to only focus on the transportation of CO₂ from production points to the storage location. The only feasible way of performing this task is the use of pipelines of high-capacity. Though carbon dioxide is not very poisonous, however its relief in large quantities combined with its density higher than air could fill populated regions with large dangerous effects. This paper analyses the thermodynamic methods required for a reliable simulation of steady state as the initial requirement for the subsequent calculation of relief conditions (flow rate, pressure and temperature) as a preliminary critical step to the calculation the dispersion effects. The availability of reliable calculation methods of the most relevant CO₂ properties (enthalpy, entropy, density and viscosity) which play a key role in the fluid-dynamic calculations required by for safe and cost-effective pipeline design. These projects are usually carried out by means of commercially available process simulators (HYSYS, AspenPlus, ChemCad, etc.) and fluid-dynamics simulators (OLGA, LedaFlow, etc.). The selection of convenient equations of state and numerical methods is a key factor in engineering design as well as in the identification of possible hazards scenarios and the calculation of consequences. In summary the requirements of a reliable and high-precision simulation tool for overall engineering design are presented.

1. Thermodynamic

In the simulation of carbon-dioxide and CO₂-rich mixtures the selection of models represent a very important aspect. From a numerical solution point of view, the simulation of pure components using temperature and pressure as independent variables (TP plane) presents a discontinuous phase change from vapour to liquid. At constant pressure below the critical point and across the vapour pressure line a change of temperature as small at will can produce a complete shift from to vapour to the liquid phase or vice-versa.

Table 1: Pure carbon-dioxide thermodynamic parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature</td>
<td>30.97 °C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>73.773 bar</td>
</tr>
<tr>
<td>Triple point temperature</td>
<td>-56.6 °C</td>
</tr>
<tr>
<td>Triple point pressure</td>
<td>5.18 bar</td>
</tr>
<tr>
<td>Acentric factor</td>
<td>0.22394</td>
</tr>
</tbody>
</table>

Please cite this article as: Raimondi L., 2014, CO₂ transportation with pipelines – model analysis for steady, dynamic and relief simulation, Chemical Engineering Transactions, 36, 619-624 DOI: 10.3303/CET1436104
Some key chemical-physical parameters important for the next discussion are collected in Table 1. One of the most notable characteristic of carbon dioxide is that a normal-boiling point does not exist since no liquid phase can exist at 1 atmosphere and a solid phase is obtained when the vapour is cooled down below approximately −78.5 °C. It means that below triple point pressure, a reduction of temperature of the vapour phase (as often happens during depressurization) produces the direct formation of solid without the transient formation of an intermediate liquid phase. Practically pure carbon-dioxide is not obtained by gas purification in the CCS capture step; CO₂ is usually accompanied by small quantities of other gases. Their effect on the phase equilibrium behaviour is to lower the temperature of both the bubble point and dew point lines. For example, Figure 1 shows the phase envelope of a rich CO₂ mixture with small amounts of methane (molar composition: CO₂ 94%, CH₄ 4%, N₂ 2%) and the pure CO₂ vapour pressure curve.

Figure 1: Pure Carbon Dioxide vapour pressure line and CO₂-CH₄ mixture

The leakage of a CO₂ pipeline represents the major risk of CO₂ transportation in pipelines. In case of a leak, the CO₂ is released at a very low temperature as a mixture of cold gas and solid particles into the environment. While in case of smaller leaks, CO₂ clouds disperse after short time, in case of larger leaks, the cold gas/solid mixture forms dense-gas clouds which rest over the terrain and can gather at low points (depressions, low-situated rooms in buildings), displacing hereby the ambient air (danger of asphyxiation, toxic effects at higher concentration). The cooling effect in the CO₂ rich plume can cause localized condensation of atmospheric water into fine aerosol droplets which create regions of very low visibility that can drift with the prevailing wind. Cooling down of the pipeline material due to the leakage could result in local fragility of the pipe steel potentially forming the starting point of long running ruptures.

2. Equations of State and Thermodynamic Models

The selection of suitable equations of state is very important step in the design of a CCS project due to the impact in many areas from steady state and dynamic simulation, HSE risk evaluation including pipeline depressurization either during planned operations or in case of unforeseen events. In these fields the use of commercial simulators such as HYSYS (Aspen Technology or Honeywell versions) and AspenPlus is a common practice. Standard cubic equations of state as the Soave-Redlich-Kwong SRK (Soave, 1974) and Peng-Robinson PR (Peng and Robinson, 1978) are proposed as default choices and are usually assumed to be the most reliable tools. For the simulation of pure CO₂ transport, one of the leading fluid-dynamics simulation software (OLGA) has recently introduced the use of the Wagner equation (Span and Wagner, 1996). The assessment of simulation results in the frame of feasibility studies or more detailed engineering projects represent a problem due to the lack of experimental data in this field. As a substitution of experimental data, the use of the Span-Wagner or GERG equations of state is a possible solution. With
respect to the Span-Wagner equation which applies only to pure CO₂, the GERG model can be applied also to CO₂ mixtures containing light hydrocarbons (C1, C2, C3 etc.) and inert gases (N₂ and O₂), etc. The GERG-2004 equation of state has been developed and published (Kunz et al., 2007) as a research project supported by the "Groupe Européen de Recherches Gazières". The natural gas industry requires the accurate knowledge of the thermodynamic properties of natural gases and other mixtures of natural gas components for the basic engineering, performance assessment of existing plants, gas metering, transmission, and storage. Processing, transportation, and storage of natural gas requires property calculations for a wide range of mixture compositions and operating conditions in the homogeneous gas, liquid, and supercritical regions, and also for vapor-liquid equilibrium states. Most of the standard natural gas applications, such as gas transmission and storage, are located in the “classical” natural gas region, i.e. the gas phase at temperatures from 250 K to 350 K and pressures up to 30 MPa, this range is of main interest for the calculation of thermodynamic properties and is addressed by this new equation. To reproduce experimental values, for both pure components and mixtures, within experimental errors, the GERG-2004 equation uses a larger number of regressed parameter with respect to cubic equations of state.

The GERG-2004 equation of state is explicit in the Helmholtz free energy with density and temperature as independent variables:

\[ a(\rho, T) = a^0(\rho, T) + a'(\rho, T) \]  

(1)

where \( a^0 \) represent the ideal part and \( a' \) the residual part. Usually, the Helmholtz free energy is used in dimensionless form and by introducing the adimensional variables \( \tau = T/T_c \) and \( \delta = \rho/\rho_c \) is finally written as:

\[ a(\delta, \tau) = a^0(\delta, \tau) + a'(\delta, \tau) \]  

(2)

There is no sufficient space here to detail how the GERG-2004 equation expands the ideal and residual Helmholtz energy parts by means of a large number of complex polynomial and exponential terms. The level of complexity of the equation can be guessed by noting that it uses up to 110 parameters to define the pure fluid behavior and 89 binary coefficients for each component-component interaction. These figures are astonishingly high when compared to 3 pure component parameters and one interaction coefficient used by cubic equations of state.

### 3. Carbon-dioxide transportation

To compare the selected equations of state and models, we have chosen a complex case of a long distance pipeline, about 525 km long, designed to transport pure carbon dioxide generated by some electric-power-plant located on a sea coast to an oil field at higher elevation. At the delivery point CO₂ will be either stored or used for enhanced oil recovery. The profile of the transfer line is shown on the next Figure 2. Transported fluid is assumed to be pure CO₂ and the very small impurities are excluded from the simulation. At the pipeline inlet the fluid is received at 55°C and at 250 bar. The initial flow-rate considered is 600,000 kg/h and number of calculations with different internal diameters are performed to select a viable combination. The target final pressure should be nearer but not over 120 bar. As a usual practice in flow-assurance analysis, two different scenarios (summer and winter) characterized by different ambient temperature are simulated. An internal diameter equal 0.463 m represents a possible solution for the specified flowrate and is used to perform sensitivity calculation with the selected thermodynamic models. Calculation are performed using the XPSIM (eXtended Process SIMulator, 2013) simulation software which allows the selection of other complex equations of state in addition to the standard cubic equations such as SRK and PR. The results are shown on Table 2 and the values calculated using the GERG equation would be considered as the reference experimental data.

**Table 2: Carbon-dioxide transport results (winter case)**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Final Pressure bar</th>
<th>Final Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GERG</td>
<td>116.08</td>
<td>0.32</td>
</tr>
<tr>
<td>LK</td>
<td>115.92</td>
<td>-0.30</td>
</tr>
<tr>
<td>SRK</td>
<td>115.47</td>
<td>-0.07</td>
</tr>
<tr>
<td>PR</td>
<td>116.31</td>
<td>-0.26</td>
</tr>
</tbody>
</table>
The fluid is transported in the dense gas phase region; the pressure is always above the critical pressure and the crossing of the critical temperature at 31 °C does not show any discontinuities in the calculated fluid properties. Formally the fluid is vapour at the pipeline inlet and liquid at the pipeline outlet. In this case, calculated final pressure and temperature are quite similar and the cubic equations of state perform well.

Figure 2: Pipeline elevation profile

The profile of pressure and temperature along the pipeline is shown on the next Figure 3. From the model testing point of view, the above simulation is not much interesting. A more interesting simulation is when the pure CO₂ enters the two-phase region and some segments of the pipeline will operate in two phase flow exhibiting liquid hold-up and thermal effects associated to condensation and evaporation.

Figure 3: Pressure and temperature profile – Single phase transport case

For the thermodynamic simulation of CO₂ transport some simulators use the Span-Wagner equation of state (Span, 1996). This equation has some drawbacks since it can strictly applied only to pure CO₂.
Using XPSIM the GERG-2004 model can be used; it provides thermodynamic values for pure CO\textsubscript{2} with the same precision of the Span-Wagner model, in addition it can be used to simulate fluids not composed of pure CO\textsubscript{2}: light hydrocarbons, water, nitrogen and other gases are treated by the GERG-2004 equation of state.

The simulation of pure fluid transport in dense phase is not a difficult task. More interesting and difficult simulations are encountered when the formation of coexisting vapour and liquid phases appear along the pipeline. In this case the formation of an equilibrium phase entrains the evaluation of the liquid holdup and isenthalpic flash calculation are required to evaluate the pressure-temperature profile.

This case can be obtained by decreasing the inlet pipeline pressure from 250 bar to 210 bar and keeping the initial temperature at 55 °C. This produces an higher pressure drop with corresponding lower final pressure. So at about 473 km the fluid crosses the critical temperature and soon after enters in the two-phase coexistence region. As shown in the next Figure 4, at this point the liquid hold-up sharply increases to 1.0 and then diminishes with the pressure lowering reaching a value of 0.25 at pipeline exit.

In this case the simulation shows important differences when the equations of state are changed. Results are shown on the next Table 3. The difference in the values obtained for the final pressure become critical from the engineering design point of view. While the two non-cubic models (GERG and LK) show coherent results the two cubic equations (PR and SRK) sharply diverge in the final calculated pressure, temperature and hold-up values.

### Table 3: CO\textsubscript{2} transport – Summer case with 2-phase flow

<table>
<thead>
<tr>
<th>Case</th>
<th>Equation</th>
<th>Final Pressure, bar</th>
<th>Final Temperature, °C</th>
<th>Vapour Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GERG, k=SRK</td>
<td>62.61</td>
<td>23.84</td>
<td>0.4545</td>
</tr>
<tr>
<td>2</td>
<td>LK, k=SRK</td>
<td>63.40</td>
<td>24.39</td>
<td>0.4697</td>
</tr>
<tr>
<td>3</td>
<td>SRK</td>
<td>53.81</td>
<td>17.36</td>
<td>0.4881</td>
</tr>
<tr>
<td>5</td>
<td>PR, k=PR</td>
<td>59.50</td>
<td>21.64</td>
<td>0.4397</td>
</tr>
</tbody>
</table>

![Figure 4: Pressure and temperature change – Two phases transport case](image)

4. Pipeline Depressurization

Another point where the selection of equation and models represent a critical point is the simulation of pipeline depressurization. Since the depressurization of a long distance pipeline can last many days, the analysis of the effect of the various models in this field has been performed by considering a pipeline section 4 km long, with nominal diameter of 24", and the leak or pressure-safety-valve size is assumed to have a diameter equal to 50 mm. The initial conditions are assumed to be 150 bar and 30 °C. Two sets of the simulation results performed using the GERG and Peng-Robinson models are summarized by the
curves presented in Figure 5. Pressure differences can be considered relatively small while a significant temperature difference is found at the end of the simulation.

Figure 5: Pipeline depressurization – Pressure and temperature profiles for PR and GERG models

5. Conclusions

Though the use of widely popular cubic equations of state, as implemented in commercial simulators, supplies in general reliable simulation results, in the case of CCS projects, they can produce large differences when applied in regions where vapour and liquid phases coexist. The use of more complex models such as the GERG equation of state becomes an almost mandatory step for the general verification of thermodynamic simulation in the CCS application field and research.

References


