

Chapter 2

General Physical Properties of CO₂ in Compression and Transportation Processes

Andrzej Witkowski and Mirosław Majkut

Abstract Carbon dioxide properties are considerably different from other fluids commonly transported by pipeline. It is therefore necessary to use accurate representations of the phase behaviour, density and viscosity of CO₂ and CO₂ containing mixtures in the pipeline and compressor design. The Aspen Plus (Aspen, version 7.0, User Guide 2008) simulation with an extensive thermodynamic library was used to predict thermodynamic properties of the CO₂ flow at required conditions and quantify the performance of each compression chain option accordingly. Semi-empirical equations are currently available for the multiphase flow to predict the pressure profile in pipelines and wells. Within the Aspen environment three equations of state: the BWRS, the LKP and the PRBM equations were used to satisfy the needs of compression and transportation processes. The operating pressure and temperature of CO₂ pipelines were also established.

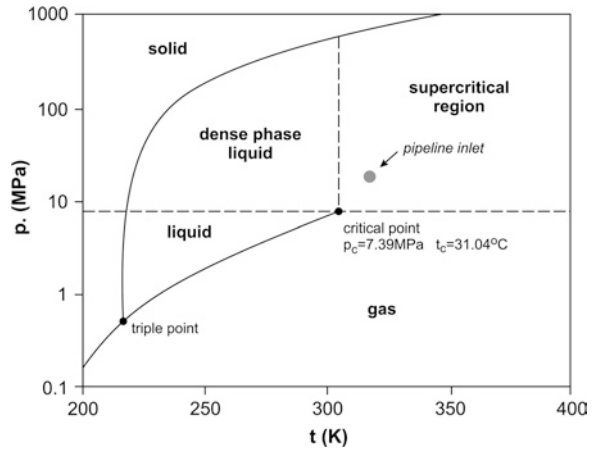
2.1 Physical Properties of Carbon Dioxide

An important characteristic of CO₂ that distinguishes it from other substances typically bulk-transported in pipelines is its low critical temperature of 31.1 °C. Technically, CO₂ can be transported through pipelines as a gas, as a supercritical fluid or as a subcooled liquid, depending on the pressure and temperature conditions in the pipeline system (Fig. 2.1). Since CO₂ is a highly corrosive medium, the water content must be reduced to less than 60 % of the saturation state (Zhang et al. 2012). In the case of intercooled compression, a portion of the moisture is removed through condensation. However, it is still necessary to provide

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Fig. 2.1 A phase diagram for CO₂



further drying after the final compressor stage (Mohitpour et al. 2012). The use of stainless steel for any components in contact with wet CO₂ eliminates the problem. The higher molecular weight of CO₂ presents additional challenges due to higher Mach numbers. Vaned diffusers, even at low solidity, can be subject to shock losses if not designed carefully.

The method of controlling the system temperature and pressure under a particular condition directly determines significant aspects of the system processes design, pressure losses, mechanical construction and, ultimately, the energy and cost efficiency. Moreover, Figs. 2.2 and 2.3 show that the compressibility and specific heat of CO₂ are non-linear in the range of pressures common for pipeline transport and highly sensitive to any impurities, as predicted by the Peng Robinson equation of state (McCoy and Rubin 2008, Lüdtke 2004). In order to reduce difficulties in design and operation, it is generally recommended that a CO₂ pipeline should operate at a pressure higher than 8.6 MPa, where dramatic changes in CO₂ compressibility can be avoided across the range of temperatures that may be encountered in the pipeline system (Farris 1983, McCoy and Rubin 2008).

In this case study it is assumed that in order to mitigate difficulties in design and operation, the pipeline should be operated at pressures of at least 9.0 MPa. Considering pressure losses and appropriate pipeline distances, the compressor discharge pressure values are required in the range of 13–20 MPa.

A pipe with ASME-ANSI 900# flanges has a maximum allowable operating pressure of 15.3 MPa at 38 °C (Mohitpour et al. 2012). Operating the pipeline at higher pressures would require flanges with a higher rating (McCoy and Rubin 2008). Considering the expected maximum transportation distance of up to 400 km and the permissible pressure drop to not less than 9 MPa, the inlet pipeline pressure of 15.3 MPa is adopted in the further analysis. It can be seen that for the compressing process calculations it is necessary to use accurate representations of the phase behaviour, density and viscosity of CO₂ in the design of the pipeline. The results presented herein are based on physical properties

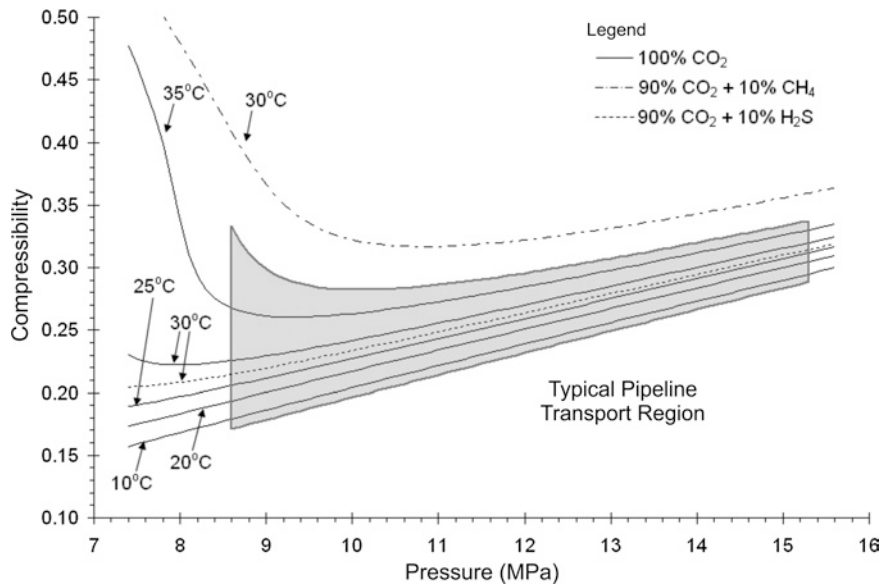


Fig. 2.2 Non-linear compressibility of CO₂ in the range of pressures common for pipeline transport. Prediction: Peng-Robinson Equation of State (Courtesy of McCoy and Rubin 2008)

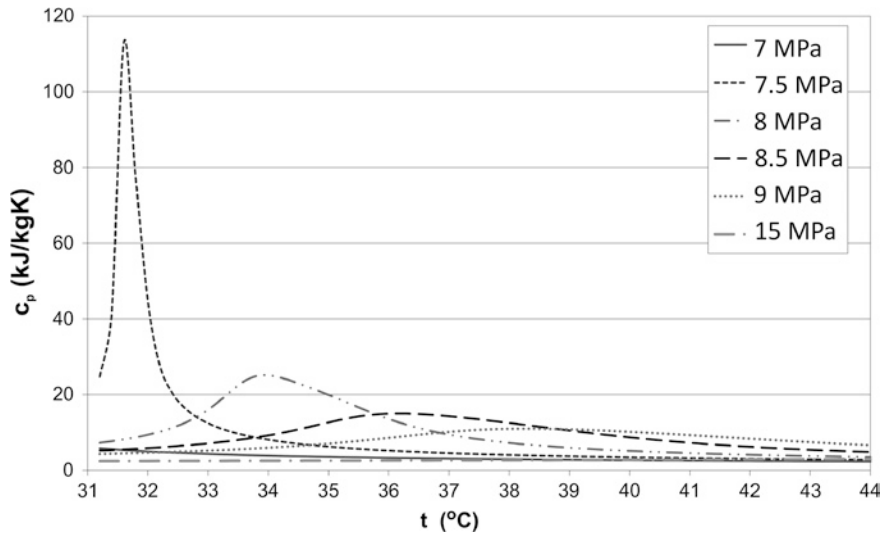


Fig. 2.3 Non-linear specific heat c_p of CO₂ in the range of temperatures and pressures common for pipeline transport

of CO₂-containing mixtures. The Aspen Plus (Aspen Plus, Version 7.0 [2008](#)) simulation with an extensive thermodynamic library was used to predict thermodynamic properties of the CO₂ flow at required conditions and quantify the performance of each compression chain option accordingly. Within the Aspen environment, three equations of state (EOS) were used for comparison of the calculation results:

- Redlich and Kwong equations augmented by Soave, who proposed a novel virial equation (Lee and Kesler [1975](#)) modified by Plocker et al. ([1978](#)), known as the LKP equations of state for real gases within relevant ranges of pressure and temperature for the process compressor (Edmister and Lee [1984](#))
- The cubic equation of state with the Peng and Robinson ([1976](#)) parameters with the Boston-Mathias modifications as the base thermodynamic property estimator for CO₂, known as the PRBM equations of state (Peng and Robinson [1976](#), Reid et al. [1987](#)). This formula is commonly used in simulations of the transportation processes by other authors (Zhang et al. [2006](#), McCoy and Rubin [2008](#)).
- The Benedict, Web, and Rubin equation with extension by Starling, known as the BWRS equations of state (Edmister and Lee [1984](#)). The BWRS equation of state is one of the most accurate equations of state that are applicable to vapour and liquid phases (Edmister and Lee [1984](#)). This equation of state is applied in the temperature range of 10–50 °C and the pressure range of 5–60 MPa for pure CO₂ (Mohitpour et al. [2012](#), George [1982](#), Starling [1973](#)). The BWRS coefficients have been tested extensively for hydrocarbons and carbon-derived compounds and can therefore be used to calculate properties of such fluids (Reid et al. [1987](#)).

According to Lüdtkke ([2004](#)), the results for the carbon dioxide compression process are as follows: the BWRS best agreement for $p_{\max} < 5$ MPa (>99.8 %), the LKP best agreement for 5–25 MPa (>98 %), (Lüdtkke [2004](#)). The phenomena occurring at CO₂ transport, the supercritical state transport and the subcooled liquid transport are also simulated using the ASPEN PLUS v7.0 software, which is a useful tool of the design process.

However, it is necessary to mention that for CO₂ mixtures containing significant levels of impurities, the used equation of state should be adjusted using experimental data or, as a minimum, it should be validated with experimental data to evaluate the level of uncertainty in the calculations. The recommended practice (Mohitpour et al. [2012](#)) also cautions against using an equation of state close to the critical point as this point is associated with non-linearity.

2.2 Effects of Impurities on the CO₂ Phase Diagram

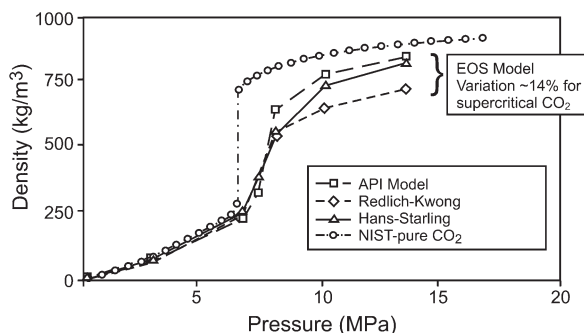
Any carbon dioxide capture and sequestration (CCS) system retrofitted to a typical pulverized coal-fired (PC) power plant must pressurize relatively pure CO₂ captured from flue gases in a gaseous state to its supercritical liquid state before storing it underground in stable geological formations.

It is anticipated that “captured” CO₂ will include a series of impurities depending on the capture technology. Race et al. (2007) discuss the potential effects of these impurities (SO_x, NO_x, H₂, and Ar) on the CO₂ phase diagram. Moreover, one of the conclusions reached by the Workshop participants (Wolk 2009) was that the currently available versions of the equations of state (EOS) used to predict the properties of supercritical CO₂ contaminated with other compounds (i.e. N₂, O₂, CO, NH₃, H₂S) at conditions near the critical point were not reliable enough to design the compression system precisely. Small amounts of impurities in CO₂ change the location of the supercritical line. The equations of state are also not good enough if water condensation occurs. Due to deficiencies in the available data, larger margins of safety than may be necessary are used by designers and manufacturers in their products. Better equations of state have the potential to be used to lower equipment costs.

Generally, impurities in CO₂ have the following effect (Rabindran et al. 2011):

1. Suction pressure settings and the compression strategy need to be adjusted to avoid operation in the two-phase region.
2. The concentration of impurities may determine the safe exposure limits for the fluid instead of CO₂ concentration.
3. Impurities reduce the pipeline transport capacity.

Fig. 2.4 Variation in predicted gas density for CO₂ mixture (Courtesy of Moore 2009)



4. A rise in vapour pressure necessitates a higher minimum value of the inlet pressure or a shorter spacing of subsequent recompression/booster stations to keep the fluid in the dense phase.
5. The vapour pressure sets the decompression pressure at a pipeline rupture. Thus a high value of decompression pressure can facilitate further propagation

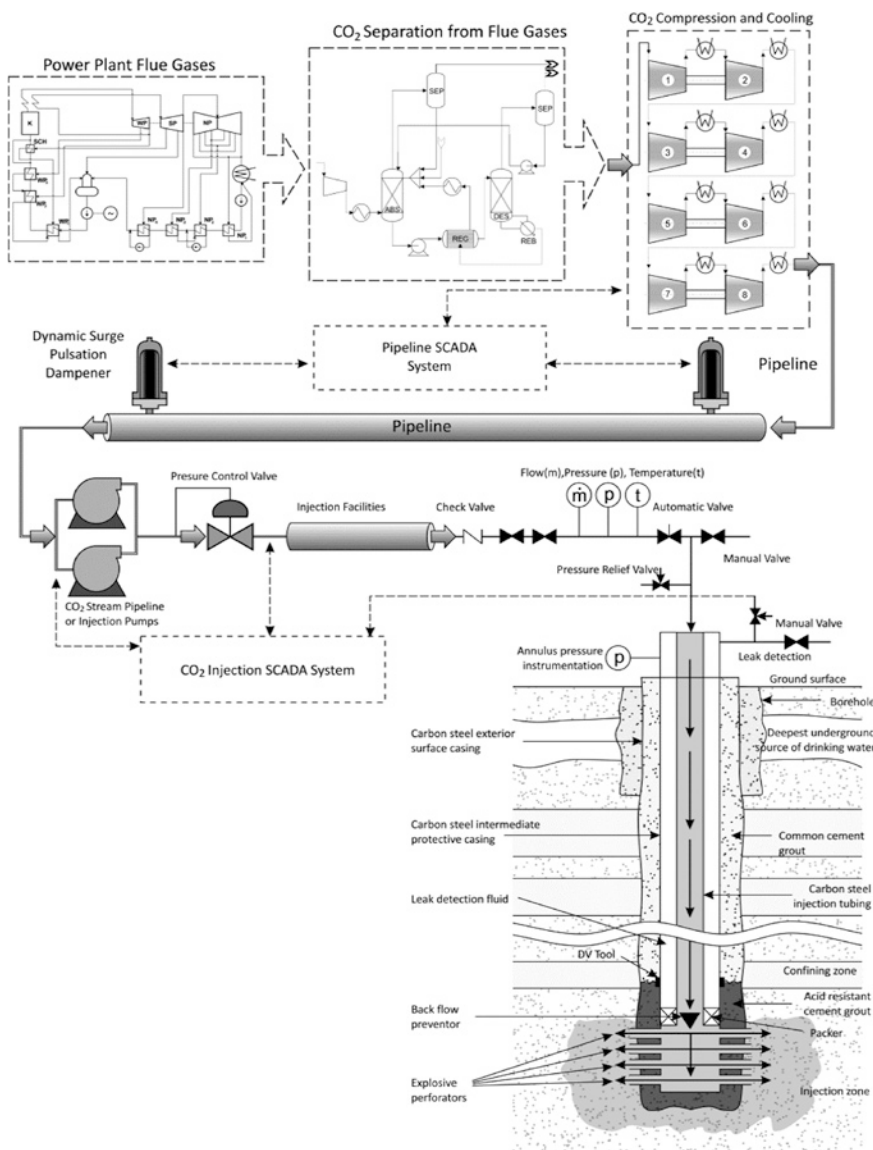


Fig. 2.5 Pipeline and sequestration systems for compression, transportation and injection of CO₂ (adapted from Mohitpour et al. 2012)

of a fracture. The presence of atomic hydrogen can lead to hydrogen embrittlement of the pipeline steel or hydrogen-induced cracking.

6. Due to water solubility and hydrate formation conditions, the gas stream remains extremely dry. Because the medium in the pipeline should be non-corrosive, the content of impurities should be minimized.

Impurities generally increase the width of the phase envelope and result in the formation of a two-phase gas-liquid region. Some impurity combinations tend to cause a large increase in the envelope (e.g. H₂ and NO₂) whilst others have a much smaller impact (e.g. N₂ and H₂S).

As one illustration of the differences, Fig. 2.4 (Wolk 2009) shows the variation in predicted density of CO₂ obtained with various prediction methodologies.

2.3 Establishing CO₂ Pipeline Pressure

In CO₂ dense phase transport, a compressor is required to increase the pressure of CO₂ to a value that ensures that CO₂ stays in the dense phase along the pipeline until CO₂ is either injected or re-pressurized. The exact discharge pressure thus varies depending on the pipeline length, operating conditions, booster pump stations and storage conditions.

In most CCS approaches, CO₂ is transported by pipeline to a porous rock formation where it is injected underground. When injected over 800 meters deep into a typical storage site, CO₂ becomes relatively dense due to atmospheric pressure and it is less likely to migrate out of the formation.

The pipeline delivery pressure requires the knowledge of the injection pressure. In order to determine the operating pressure at the top of the well leading to underground reservoirs (Fig. 2.5), it is necessary to consider:

- the pressure at the bottom of the well to force CO₂ into the injection zone,
- the pressure increase in the pipe due to the height of the CO₂ column, the pressure loss related to the flow in the pipe.

For sequestration purposes, CO₂ is generally injected to depths well over 1000 m. Typically, the CO₂ injection pressure is about 9 to 18 % above the in situ bottom value (Mohitpour et al. 2012). Thus, at a 1000 m depth and the lowest acceptable pressure at the top of the wellhead of 9.0 MPa and with the mean value of CO₂ density of 800 kg/m³, the required injection pressure will be 9.0 MPa + (1000 m depth × 800 kg/m³/100,000) = 17 MPa. Taking account of a 9 % loss, the pressure at the ground reservoir level will be 15.47 MPa (Witkowski et al. 2013)

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