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Energy Procedia 37 (2013) 3031 – 3038

Energy

Procedia

GHGT-11

PVT_x properties of a two-phase CO₂ jet from ruptured pipelineH. A. Botnen^{a*}, A. M. Omar^{b,c,d}, I. Aavatsmark^e, G. Alendal^{f,g}
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Abstract

Span and Wagner equation of state (SW EOS) have been used to investigate changes in the thermodynamic properties of CO₂ during a depressurization process from a pipeline into marine environment. The process is assumed to be isenthalpic, as only the thermodynamic change at the moment of depressurization is considered. The calculations show that the depth location of the pipeline influences greatly the density, temperature and volume changes, because of the difference in the surrounding pressures. In general the two-phase area is reached at depths shallower than 600 meters, which yields for the Norwegian Continental Shelf, as it is mainly shallower than 500 meters depth. There is a rapid decrease in density in the two-phase area causing a rapid expansion in the volume of CO₂ from 4 MPa to 1 MPa. At the shallowest depth considered (100m) the volume fraction consist almost entirely of gas, and the density change give a significant increase in volume.

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Selection and/or peer-review under responsibility of GHGT

Keywords: CO₂ pipeline transport, thermodynamics, EOS, HSH

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1. Introduction

The release of Carbon dioxide in to the atmosphere has been widely accepted to have a major impact on the earth's climate. For Carbon Capture and Storage (CCS) to be a useful tool in the mitigation of CO₂ large amounts must be captured and stored [1]. The International Energy Agency (IEA) has estimated through their BLUE map report that CCS will reduce CO₂ emissions by 9.4 Gt annually in 2050. This amounts to 19% of the total estimated CO₂ emission reduction [2].

The amount of CO₂ needed stored for CCS to be a valid mitigation process is large and causes a need for several storage sites. Utilization of these storage sites requires transportation over a significant area, i.e. North Europe. In Norway the focus have been on storage in former oil and gas reservoir, therefore will such sites be located offshore. The reservoirs have potential for more stored CO₂ than Norway will emit alone, and may therefore open for others to store CO₂ on the Norwegian Continental Shelf. In order to utilize the potential reservoirs as storage sites it will require an extensive network of pipelines from Europe and Norway into the North Sea [3]. Hence the transport will have to take place through marine environment, either by ship or through pipelines. In this work only transportation thorough pipelines will be considered. These pipelines have to be built according to precaution and safety measures to prevent any safety and environmental risks.

The potential for leakage and rupture of CCS pipelines has been discussed in several publications [4]-[8], and some state that a depressurization in this context causes significant drop in temperature causing potential for more damage to the pipeline [5,8]. However, there is little focus on the leakage from offshore pipelines into seawater. Some work have been done by Mazzoldi et al. [9] on onshore leakages from CCS pipelines, and the physical changes when CO₂ is depressurized. In these papers the formation of solid CO₂ and the dispersion of the gas is the major focus, and little focus is on the thermodynamics per say.

In oceanic water a CO₂ release may have other impacts on the environment, partially through acidification. Also, in the ocean the physical and chemical processes involved are quite different, and has so far received little attention. From Mazzoldi et al. [9] we know that an atmospheric leakage will consist mainly of gaseous CO₂, and some solid. In the ocean the surrounding will have higher pressure than the atmosphere, and also vary significantly depending on the depth at which the pipeline is located. Here the focus is on the Norwegian reservoirs, and therefore the location of the pipelines will be in the North Sea and on the Norwegian Continental Shelf, where the water depth ranges from 0 to approximately 500m. This gives reason to believe that the CO₂ will behave differently here compared to atmospheric releases.

In this work we consider only thermodynamic changes in pure CO₂. This simplifies the calculations compared to mixtures, as the composition will be constant. Since the composition is constant the saturation curves, used to identify the two-phase and single-phase areas, can be decided beforehand.

Span and Wagner equation of state (SW EOS) is used to obtain the thermodynamic properties necessary. The work done by Span and Wagner [10] include a review of experimental CO₂ data and a fitting of the equation of state (EOS) to the data presented. The fitting of the residual part of the function was based on the properties of the single-phase region, the liquid-vapor saturation curve, the speed of sound, the specific heat capacities, the specific internal energy and the Joule-Thomson coefficient. The

equation gives very accurate results, even in the region around the critical point, and is now considered the most accurate reference equation for CO₂ [11].

2. Method

The Span and Wagner equation of state (SW EOS) is used to perform the calculations of the thermodynamic properties of CO₂ during depressurization. The expansion from high pressure to low pressure is assumed to be isenthalpic, i.e. that the expansion is adiabatic. This assumption simplifies the calculation, especially in regards of temperature [12,13]. By assuming isenthalpic process the isenthalps can be used to find the thermodynamic properties as i.e. the pressure is decreased. Here we use this method to find the temperature, density and phase composition changes due to depressurization.

The assumptions made in regards of the calculations are based on the estimated operating conditions given by Li et al. [14], and that the pipeline is assumed to be located offshore. As the CO₂ must be kept in a dense phase throughout the transportation it must be above 7.7 MPa, so the pressure is set to be 10, 15 or 20 MPa. The temperatures are also from the estimated operating conditions [14], but it is not set lower than 280K or higher than 300K. This because the surrounding water is assumed to not be lower than 280K and we also assume there will be a heat loss thorough the pipeline causing the temperature to be no higher than 300K.

2.1 Thermodynamics

The necessary thermodynamic properties in this work are expressed in the form of specific Helmholtz free energy, $A(T,\rho)$. The reason to express the internal energy, pressure and enthalpy in this form is because when the expression of the specific Helmholtz energy is known, together with all its derivatives, all other thermodynamics properties can be found. The mentioned properties will then be given as

$$u(T,\rho) = A - T \left(\frac{\partial A}{\partial T} \right)_v \quad (1)$$

$$p(T,\rho) = - \left(\frac{\partial A}{\partial v} \right)_T \quad (2)$$

$$h(T,\rho) = A - T \left(\frac{\partial A}{\partial T} \right)_v - v \left(\frac{\partial A}{\partial v} \right)_T \quad (3)$$

In Span and Wagner [10] a non-dimensional Helmholtz function is defined, $\varphi = A / RT$, and the function is divided into an ideal-gas part, φ^0 , and a residual part, φ^r , which gives

$$\varphi(\tau,\rho) = \varphi^0(\delta,\tau) + \varphi^r(\delta,\tau) \quad (4)$$

This is called the reduced Helmholtz function, and expressed in terms of reduced density, $\delta = \rho / \rho_c$, and the inverse reduced temperature, $\tau = T_c / T$, where ρ_c and T_c are the critical density and temperature,

respectively. The R is the specific gas constant of CO₂. Equation 1-3 expressed in terms of the reduced Helmholtz function is given as

$$\frac{u(\delta,\tau)}{RT} = \tau \frac{\partial \varphi}{\partial \tau} \tag{5}$$

$$\frac{p(\delta,\tau)}{\rho RT} = 1 + \delta \frac{\partial \varphi^r}{\partial \delta} \tag{6}$$

$$\frac{h(\delta,\tau)}{RT} = 1 + \tau \frac{\partial \varphi}{\partial \tau} + \delta \frac{\partial \varphi^r}{\partial \delta} \tag{7}$$

As we are assuming the depressurization process to be at constant enthalpy, we therefore use the enthalpy to find the other thermodynamics properties such as temperature and density. The density and temperature is given by finding the roots of the calculated enthalpy at the final pressure and density, respectively.

2.2 Span and Wagner equation of state

Span and Wagner [10] produced an equation of state specific for pure CO₂ over a large temperature and pressure interval, triple-point to 1100K and pressure up to 800MPa. The EOS is in the form of a fundamental equation explicit in the Helmholtz free energy, with a residual part that was fitted to the available data.

The Span and Wagner equation of state is very precise, with accuracy close to the measurement uncertainties of the heat capacities at constant volume and pressure in the liquid and gas region [10].

$$\varphi^0(\tau,\delta) = \ln(\delta) + a_1^0 + a_2^0 \tau + a_3^0 \ln(\tau) + \sum_{i=4}^8 a_i^0 \ln\left[1 - e^{(-\tau \theta_i^0)}\right] \tag{8}$$

$$\varphi^r(\tau,\delta) = \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{34} n_i \delta^{d_i} \tau^{t_i} e^{(-\delta^{\epsilon_i})} + \sum_{i=35}^{39} n_i \delta^{d_i} \tau^{t_i} e^{(-\alpha_i (\delta - \epsilon_i)^2 - \beta_i (\tau - \gamma_i)^2)}$$

$$+ \sum_{i=40}^{42} n_i \Delta^{b_i} \delta e^{(-C_i (\delta - 1)^2 - D_i (\tau - 1)^2)} \tag{9}$$

$$\Delta = \left\{ (1 - \tau) + A_i [(\delta - 1)^2]^{1/(2B_i)} \right\}^2 + B_i [(\delta - 1)^2]^{a_i} \tag{10}$$

For more details and the coefficients a_i^0 , θ_i^0 , n_i , a_i , b_i , β_i , A_i , B_i , C_i , and D_i the reader is referred to the paper by Span and Wagner [10]. The disadvantage of this EOS is that it can only be used for pure CO₂, and therefore is not capable of solving for mixtures of CO₂. Due to this we are not including mixing with seawater in this work.

3. Depressurization results

Figure 1(a) gives the pressure and density changes when the CO₂ is depressurized from different initial pressures and temperatures. The overall shape of the lines gives a distinct break point in the lines between 6 and 4 MPa at high densities, and a gathering of the lines towards low pressure. This break point line gives the liquid limit of the two-phase area, which is located towards the left from these points. The gas limit of the two-phase area is not reached in these calculations. However, the limit is not far away from 1MPa as the highest volume fraction of gas here is found to be 0.97.

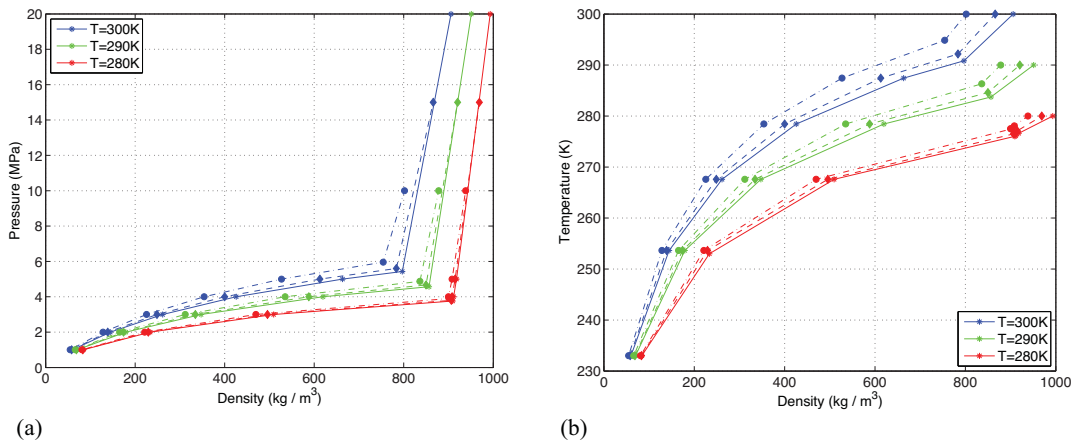


Fig. 1. (a) Changes in density of CO₂; (b) and changes in temperature and density of CO₂ according to pressure changes. In both figures the CO₂ is depressurized isenthalpic from 10 MPa (circle points), 15MPa (diamond points), and 20MPa (asterisk points). The different colors represent different initial temperatures 300K (blue), 290K (green), and 280K (red)

The decrease in density is very rapid in the two-phase area compared to the liquid area. We can also see that the highest initial pressure and lowest initial temperature give the most rapid density decrease in the two-phase area. While the lowest initial pressure and highest initial temperature give the least rapid decrease. From the figure it is also seen that these two cases reach the two-phase area at different pressures and densities.

Figure 1(b) gives the temperature and density changes according to the pressure changes shown in Fig. 1(a). In this figure the two-phase area is also identified by the break points between 295 and 275K.

The figure shows that the temperature changes are the same for the different initial pressure and temperatures, except from the limit to the two-phase area. The difference is related to the densities the CO₂ has at the same temperatures. The higher initial temperature has a lower density at the same

temperature than the lower initial temperatures. However, they are all reaching towards the same density at the lowest temperature. This temperature is associated with the end pressure of 1 MPa.

For a better overview of the two-phase area the data is presented in table 1. Here we can see the difference in the pressure, temperature and density, at which the two-phase area is reached for the different initial pressures and temperatures. The lowest temperature gives the lowest pressures where the two-phase area is reached. However, within these the lowest initial pressure gives the highest two-phase pressure. This yields for all temperatures.

Table 1: The pressure, temperature and density at which the two-phase area was reached for the different initial pressures and temperatures.

Initial P	Initial T	Two-phase P	Two-phase T	Two-phase ρ
20	300	5.43	290.8	796.8
20	290	4.57	283.8	856.6
20	280	3.76	276.0	909.4
15	300	5.60	292.2	783.4
15	290	4.67	284.6	849.7
15	280	3.80	276.5	906.3
10	300	5.96	294.9	754.2
10	290	4.87	286.3	836.3
10	280	3.90	277.5	899.7

From figure 1(a) and 1(b) we see significant changes due to the depressurization. The most distinct change is found in the density of the CO₂. From the densities it is possible to calculate the volume changes that would result from a depressurization. In figure 2(a) the volume changes is given more generally for CO₂ as dm³ / mol. It is shown that the highest initial temperature and the lowest initial pressure give the largest change in volume.

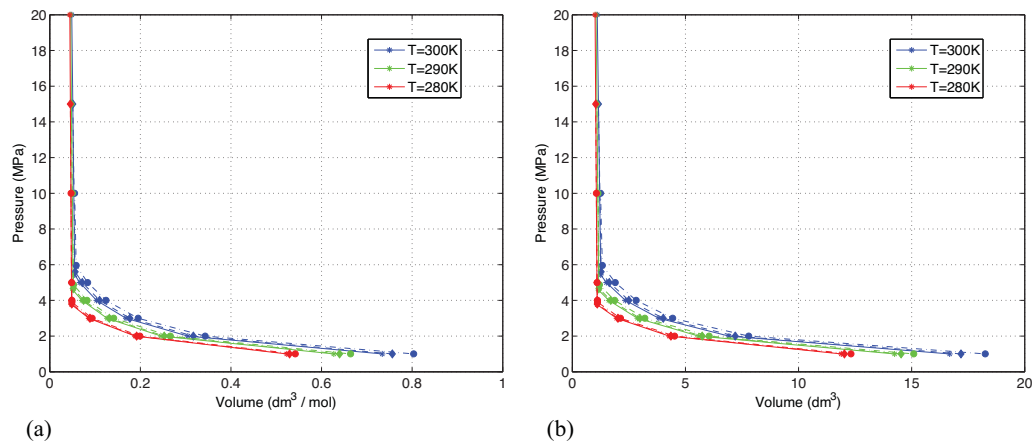


Fig. 2. (a) Pressure and volume (dm³ / mol) changes in CO₂; (b) Pressure and volume (dm³) changes in 1 kg CO₂. Both as CO₂ depressurize isenthalpic from 10 MPa (circle points), 15MPa (diamond points), and 20MPa (asterisk points). The different colors represent different starting temperatures 300K (blue), 290K (green), and 280K (red)

To get an impression of how the volume change would evolve the changes in 1 kg of CO₂ has been calculated, and is shown in figure 2(b). Here it is shown that the largest volume change will be from approximately 1 dm³ to 18.5 dm³, and the smallest will be an expansion to 12 dm³. These volume changes are the result if the pipeline is depressurized into surroundings of 1 MPa, which is approximately adequate to 100 meters ocean depth. If the leakage is located at greater depths, higher pressure, it can be seen from the figures that the volume change will be significantly smaller. The largest difference in volume is found between 1 and 2 MPa, and there are hardly any changes at pressures higher than 5 MPa.

4. Discussion

The aim of this paper was to use SW EOS to calculate the thermodynamic changes resulting from the depressurization of a CCS transport pipeline into the ocean. The depressurizations are kept isenthalpic in order to simplify the calculations, and give an assumed appropriate estimate for the thermodynamic properties. The assumption of constant enthalpy has been made before by Katz and Lee [15], and has also been used by Oldenburg [13] and Pruess [14], in order to simplify the calculation of temperature changes as a result of depressurization. With this assumption the Joule-Thomson coefficient can be applied in the calculation giving a good estimate of the temperature.

The question remains if this is an accurate assumption in this context, as there will be friction and there will be a heat exchange with the surrounding given time. It can be argued that the process should be viewed as an isentropic process instead. However, the difference between these processes is the presence of friction, and here we only consider the expansion at the moment of depressurization, so friction is ignored at this point.

In this work we have looked at two stable states, the initial state and the fully expanded state at end of the depressurization. The density and following volume expansion of the CO₂ given in these calculations are idealized and may differ from the real event. How much is not easy to answer at this point, and it needs further investigation.

However, the results show that the changes in the thermodynamic properties are dependent on the location of the pipeline when it depressurizes. If it is located in shallow waters with a depth of 100 m there will be larger temperature, density and volume changes compared to leakages at greater depths. The difference is increasing significantly from 4 MPa to 1 MPa, showing that the depressurization will have significant effect on the thermodynamic properties of CO₂ when leaked on the Norwegian Continental Shelf.

From the location of the two-phase area it can be assumed that there will only be liquid CO₂ if the leakage is at a depth of 600 m or deeper. As the Norwegian Continental Shelf is located on shallower depths than this it can be assumed that there will be gaseous CO₂ present no matter the initial pressure and temperature.

The calculations of the new volumes after a depressurization show that we can expect a large volume expansion on the shelf. However, at this point we cannot say at which distance from the pipeline the volume expansion is completed, and the CO₂ is in thermal equilibrium with its surroundings. The distance will depend on the velocity of the expansion and of the expanding material. In these calculations we have not considered the speed of the expansion, which will be interesting when considering the further development of the CO₂ plume.

5. Further work

In this work the depressurization process is very simplified, not considering the surrounding water, the speed of the expansion or hydrate and ice formation. In further work all these aspects should, as they probably will influence the thermodynamics and, further, the hydrodynamics.

As mentioned in the discussion, the speed of the expansion in order to identify the distance from the pipeline where the CO₂ is in thermodynamical equilibrium with the surrounding will also be important to investigate. This will provide a broader understanding of a leakage, and the potential environmental consequences it may cause.

Acknowledgements

This work is part of the SECURE project support from the Norwegian Research program CLIMIT and the Research Council of Norway.

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