Controlling evaporation of liquid CO_2 during transport as part of CCS

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Abstract:

In Europe, deployment of large-scale carbon capture and storage (CCS) with storage in an underground geological formation will in practice imply off-shore storage. This implies separation, purification and liquefaction of CO_2 and, after transport to a harbour facility, loading into a ship for transport to the storage site, a trip that may take several days. The topic of this paper is how to address the evaporation of some of the liquefied CO_2 caused by heat leaking into the storage, resulting in rising pressure and temperature that should be controlled. First, this paper will assess the dependence of liquefied CO_2 evaporation with time (boil-off rate, BOR) on starting (low, medium or high) pressures/temperatures and heat ingress, and the rate of pressure and temperature increase as a result of it. Secondly, it will suggest alternatives to re-liquefaction during the transport. The latter could involve, for example, the use of zeolite or other sorbent, or adding small amounts of a component with slightly different thermodynamic properties to the CO_2. As the first part of the paper shows, based on the behaviour of pure CO_2 there may not be a need for worries or action since the pressure rise is very modest even after several days. The work also shows that small amounts of impurities may have significant effects, emphasising the importance of pre-transport processing.

Keywords:
Carbon dioxide capture and storage (CCS), transport, liquefied CO_2, evaporation, refrigeration.

1. Introduction

In Europe, deployment of large-scale carbon capture and storage (CCS) with storage in an underground geological formation will in practice imply off-shore storage. Off the coast of Norway this has been practiced already since the mid-1990s at the Sleipner and (later) Snøhvit sites where ~ 1 Mt/yr and ~ 0.7 Mt/yr, respectively, CO_2 are separated from produced natural gas and stored under the seabed [1]. Current developments aim at expanding Norway's CCS to CO_2 from the Klemetsrud waste incinerator of Fortum Oslo Värme and Norcem's cement production facility at Brevik, for ~ 0.4 Mt/yr each. If during winter 2020/2021 Norwegian parliament makes a positive financing decision, commercial operation will start during 2023/2024, involving separation, purification and liquefaction of CO_2 and, after transport to a harbour facility, loading into a ship for transport to the storage site, a trip that may take several days.

Transport of CO_2 as part of CCS activities can involve transport of compressed gaseous or liquefied CO_2. Trucks, trains or ship can be used depending primarily on transport distance, amount and frequency of that amount [2]. One issue that needs to be considered for transport of liquefied CO_2 is the evaporation of some of the load as a result of heat leaking in from the surroundings, causing a rise in pressure that may become problematic. A recent study [3] considered re-liquefaction of boil-off gas from liquefied CO_2 transport on board a ship to be necessary and presents several process lay-outs for the implementation of an on-board refrigeration system.

This study aims at assessing the need for re-liquefaction for transport of liquefied CO_2 at a starting pressure of 15 bar (boiling point -28.1°C) rather than 7 bar (boiling point -49.3°C) as considered in [3], followed by suggestions for how to act rather than re-liquefy the boil-off gas (BOG). Obviously, although depending to some extent on the off-loading process set-up at the CO_2 underground storage site, a large amount of BOG may result in a large amount of gaseous CO_2 that needs to be transported back to its source for re-liquefaction.

2. Analysis of liquid CO_2 evaporation

2.1. Pressure and temperature rise as a result of heat ingress

This first assessment considers pure CO_2, neglecting the effect of minor amounts of contaminants. A heat ingress Q (J) into a constant volume of liquefied CO_2 with some overhead vapour (gas) will increase the enthalpy of the two-phase system. This will give a pressure change as well as a change in temperature, restricted by the constant total volume of liquid and gas combined V_{total}, and of course constant total mass m_{total}. Thus, since the constant total volume prevents work W done on or by the system, the First Law of Thermodynamics for internal energy U is simplified:

$$\Delta U = Q + W \quad \rightarrow \Delta U = Q \quad (J) \tag{1}$$

Dividing the system in a vapour (gas) phase and a liquid phase with changing amounts gives work by the increasing amount of gas on the liquid phase being balanced by work experienced by the liquid phase: $\int p \cdot dV_L = - \int p \cdot dV_G$, or $\Delta p V_L + \Delta p V_G = 0$ for the constant volume system. Then,

$$Q = \Delta U = \Delta U_L + \Delta U_G = \Delta U_L + \Delta U_G + \Delta p V_L + \Delta p V_G = \Delta H_L + \Delta H_G = \Delta H \quad (J) \tag{2}$$

Describing the state of the CO_2 by its enthalpy as function of temperature T and pressure p, *i.e.* h(T,p) (kJ/kg) gives, for the two-phase system at its boiling point, one degree of freedom according to Gibbs' phase rule. This allows for vapour mass fraction, x, defining the liquid-vapour mixture enthalpy.

For transport of CO_2 with a given boil-off rate (BOR) the increase of x is defined which makes it more convenient to use h(x,p) in the energy equations. This fixes the saturation temperature (the boiling point) as function of the changing pressure. Thus:

$$h = h(x,p) = x \cdot h_G + (1-x) \cdot h_L \tag{3}$$

which for pressure changes gives

$$\frac{dh}{dp} = \left(\frac{\partial h}{\partial x}\right)_p \cdot \frac{dx}{dp} + \left(\frac{\partial h}{\partial p}\right)_x = h_G \cdot \frac{dx}{dp} + h_L \cdot \frac{d(1-x)}{dp} + x \cdot \frac{dh_G}{dp} + (1-x) \cdot \frac{dh_L}{dp}$$

$$= \frac{dx}{dp} \cdot (h_G - h_L) + x \cdot \frac{dh_G}{dp} + (1-x) \cdot \frac{dh_L}{dp} \tag{4}$$

Appendix A gives data for CO_2, giving values as polynomials for enthalpy $h_{G,sat}$ and $h_{L,sat}$ (Eqs. A.5-A.7) at the saturation state that give simple relations for dh_G/dp and dh_L/dp at the saturation state, all as function of pressure p (= p_{sat}).

Using (4), the pressure variation with time $\Delta p/\Delta t$ can be derived if the heat ingress $Q = \dot{Q} \cdot \Delta t$ during time interval Δt is known:

$$\dot{Q} = \frac{\Delta H}{\Delta t} = \frac{m_{tot} \cdot \Delta h}{\Delta p} \cdot \frac{\Delta p}{\Delta t} = m_{tot} \cdot \left(\frac{\Delta x}{\Delta p} \cdot (h_G - h_L) + x \cdot \frac{dh_G}{dp} + (1-x) \cdot \frac{dh_L}{dp} \right) \cdot \frac{\Delta p}{\Delta t} \tag{5}$$

$$\rightarrow \frac{\Delta p}{\Delta t} = \frac{\dot{Q}/m_{tot}}{\frac{\Delta x}{\Delta p} \cdot (h_G - h_L) + x \cdot \frac{dh_G}{dp} + (1-x) \cdot \frac{dh_L}{dp}} \tag{6}$$

The term $\Delta x/\Delta p$ can be determined from a mass balance combined with total volume balance, density as function of pressure relations, information on the boil-off rate (BOR) and the starting value for x. Since total volume and total mass are both constant this gives:

$$V_{total} = V_G + V_L = \frac{m_G}{\rho_G} + \frac{m_L}{\rho_L} \tag{7}$$

$$\frac{V_{total}}{m_{total}} = constant = \frac{x}{\rho_G} + \frac{1-x}{\rho_L} = \frac{x}{\rho_G(p)} + \frac{1-x}{\rho_L(p)} \rightarrow x = \frac{constant \cdot \rho_L - 1}{\frac{\rho_L}{\rho_G} - 1} \tag{8}$$

at all times, with expressions for saturation state densities $\rho_{G,sat}$ and $\rho_{L,sat}$ as function of (saturation) pressure given in Appendix A, Eqs. A.2-A.4. Thus, x is directly related to pressure from which the above mentioned $\Delta x/\Delta p$ for Eq. (6) and the (saturation) temperature can be calculated.

2.2. CO$_2$ evaporation during five days liquid CO$_2$ transport

With the thermodynamics given above, the dynamics of the evaporation of some of the liquefied CO_2 can be calculated which is here done for a five-day travel shipload of 7500 m^3 liquefied CO_2, with 99% liquid volume, starting with 15 bar pressure (CO_2 boiling point -28.1°C). This implies 7960491 kg liquid CO_2 and 2942 kg gaseous CO_2, giving $x = 3.69 \times 10^{-4}$, and a (constant) total specific volume $V_{total} / m_{total} = 9.42 \times 10^{-4}$ m^3/kg. (Note that in [3], three to four days sailing is considered "short".)

As input data, an evaporation rate of 0.1 % of the liquid CO$_2$ per day is assumed, within the 0.05 – 0.15 %/day range typical for LNG transport [4]. This implies that each hour a fraction $0.1 \times 10^{-2}/24$ ((kg/kg)/h) of the liquid volume but also of the liquid mass goes from the liquid phase to the gas phase. With this, the changing mass of gas and its mass fraction x as function of time can be quantified for time step $\Delta t = 1$ h (where $\Delta x/\Delta t$ equals $x^{i+1} - x^i$:

$$m_G^{i+1} = m_G^i + (m_{tot} - m_G^i) \cdot \frac{0.001}{24} \tag{9}$$

$$x^{i+1} = \frac{m_G^{i+1}}{m_{tot}} = \frac{m_G^i + (m_{tot} - m_G^i) \cdot \frac{0.001}{24}}{m_{tot}} = x^i + (1 - x^i) \cdot \frac{0.001}{24} \tag{10}$$
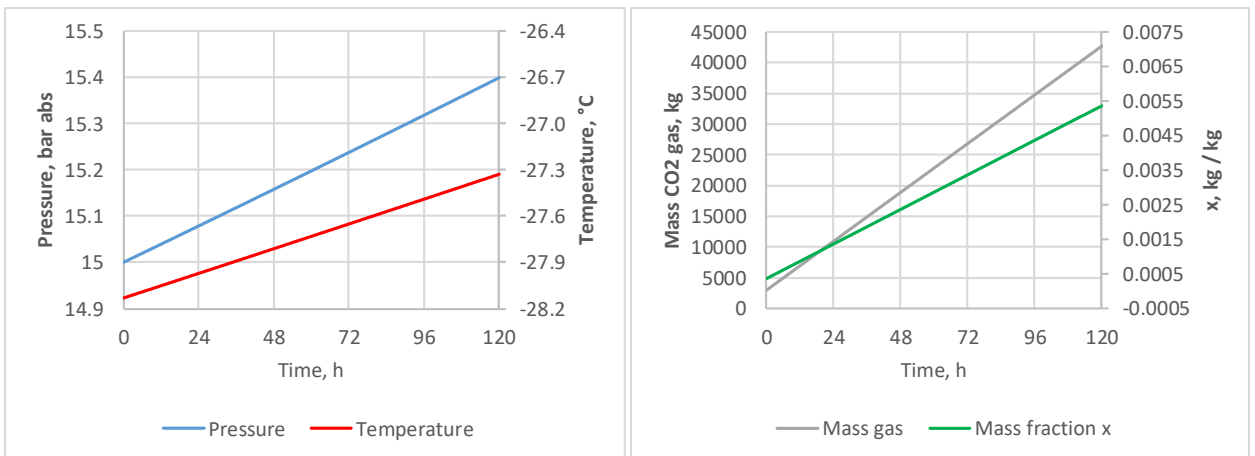

Fig. 1 Increasing pressure and temperature (left) and amount of CO$_2$ vapour (right) versus time during a five-day transport for the reference case (15 bar and 1% volume as gas at the start, BOR 0.1 %/day)

For these system dynamics the variation of pressure, gas mass and mass fraction CO_2 and temperature can be calculated, with results as in Figs. 1. Clearly, a dramatic rise in pressure is hardly to be expected even during a five-day transport while also the temperature rises only with 0.8°C. Gas max fraction x increases from < 0.04% to < 0.5% (mass). One may question whether any special measures are needed when this occurs.

2.3. CO_2 evaporation parameter sensitivity

While the results in Fig. 1 do not seem to call for special measures like collection and re-liquefaction of the BOG, a sensitivity analysis may shed light on how starting conditions and process system parameters affect the behaviour of the liquefied CO_2.

Fig. 2 shows the outcome for a lower starting pressure of 10 bar, which would require refrigeration to -40.6°C. With a 0.1%/day BOR and 1% of the transport volume filled with gaseous CO_2 above the liquefied CO_2 again a pressure rise < 0.5 bar is seen after 5 days with a temperature rise of 1.3°C. The increase of gas mass and gas mass fraction x are not changed compared to the reference case.
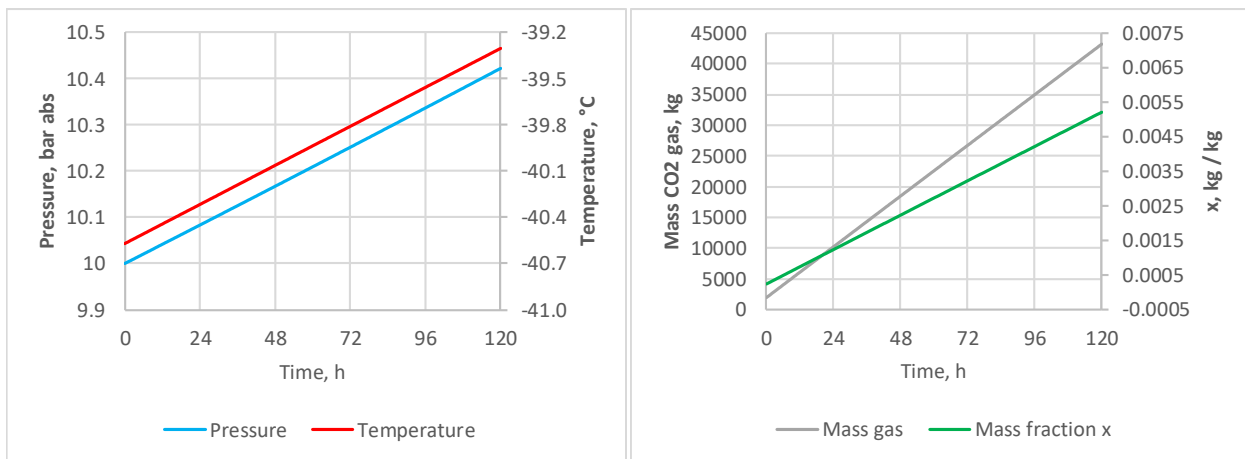

Fig. 2 Increasing pressure and temperature (left) and amount of CO_2 vapour (right) versus time during a five-day transport for a lower pressure case (10 bar and 1% volume as gas at the start, BOR 0.1 %/day)

The same modest differences are found for a higher starting pressure of 20 bar which would require refrigeration to -19.3°C: a pressure rise < 0.4 bar and a temperature rise < 0.5°C, as shown in Fig. 3. A lower temperature obviously gives a larger driving force for heat ingress, which is approx. 13.3 W per kg transported CO_2, comparable to 12.5 W for the reference case (Fig. 1) and 11.7 W for the previous case (Fig.2). Also for this third case the increase of gas mass and gas mass fraction x are not changed.

As may be expected, a more dramatic effect follows from a higher BOR: Fig. 4 shows the results obtained with a doubled, relatively high [4] BOR of 0.2 % per day. This corresponds to a heat ingress of 25 W per kg transported CO_2. Final mass of gas is almost doubled while the final gas mass fraction x is > 0.1, as shown in Fig. 4. Pressure rise is 1.4 bar while the temperature rise is doubled to 1.5 ° C from 0.8 °C for the reference case.
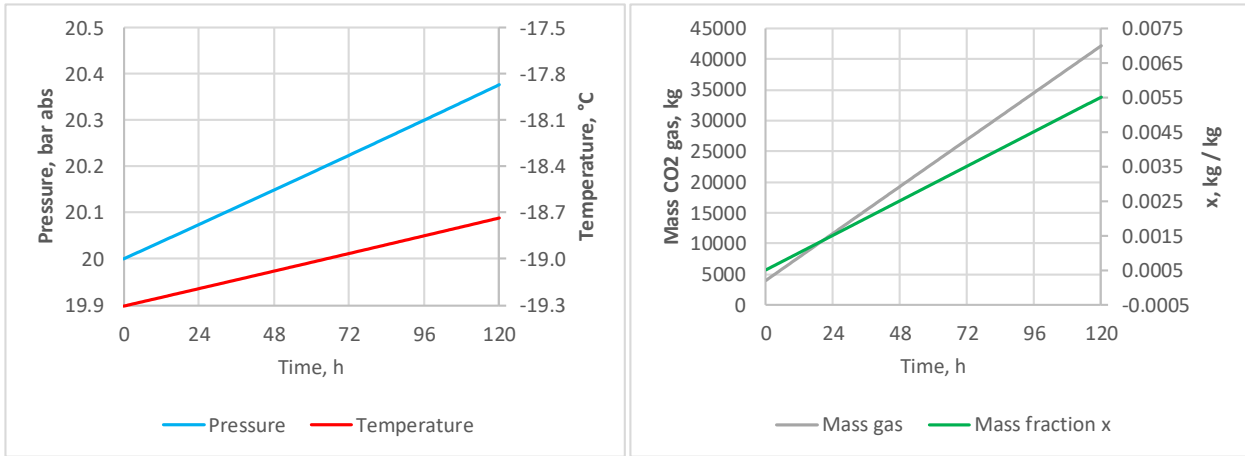
Fig. 3 Increasing pressure and temperature (left) and amount of CO_2 vapour (right) versus time during a five-day transport for a higher pressure case (20 bar and 1% volume as gas at the start, BOR 0.1 %/day)
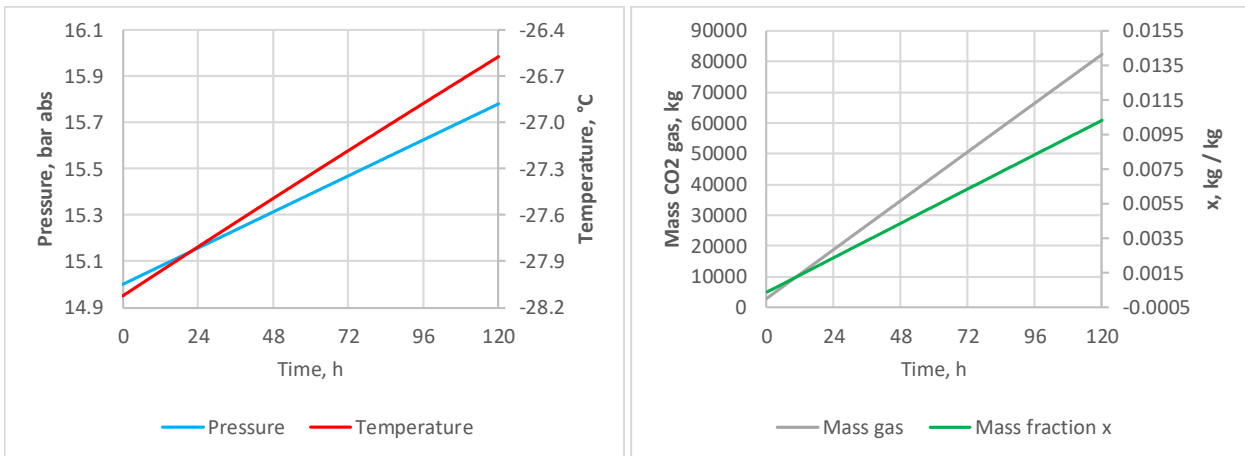

Fig. 4 Increasing pressure and temperature (left) and amount of CO_2 vapour (right) versus time during a five-day transport for a higher BOR case (15 bar and 1% volume as gas at the start, BOR 0.2 %/day)

The final case simulated was a larger amount of initial volume filled with gas above the liquefied CO_2 when starting the transport, being 3% of the storage volume rather than 1%. While this does have some effect on the amount of gas transported versus time and its mass fraction there is hardly a difference from the reference case when it comes to pressure and temperature rise, as shown in Fig. 5. The heat ingress is also practically the same at around 12.5 W per kg transported CO_2.

Altogether, it can be concluded that for transport of pure CO_2 in liquid form, neglecting the effect of contaminants, hardly a problematic rise in temperature or pressure would arise for a BOR of 1% per day. It does not agree with "*the tank will explode unless the BOG is removed or reliquefied. Thus, treatment of the BOG is a must to consider in designing a CO_2 transport ship.*" as stated in [3].
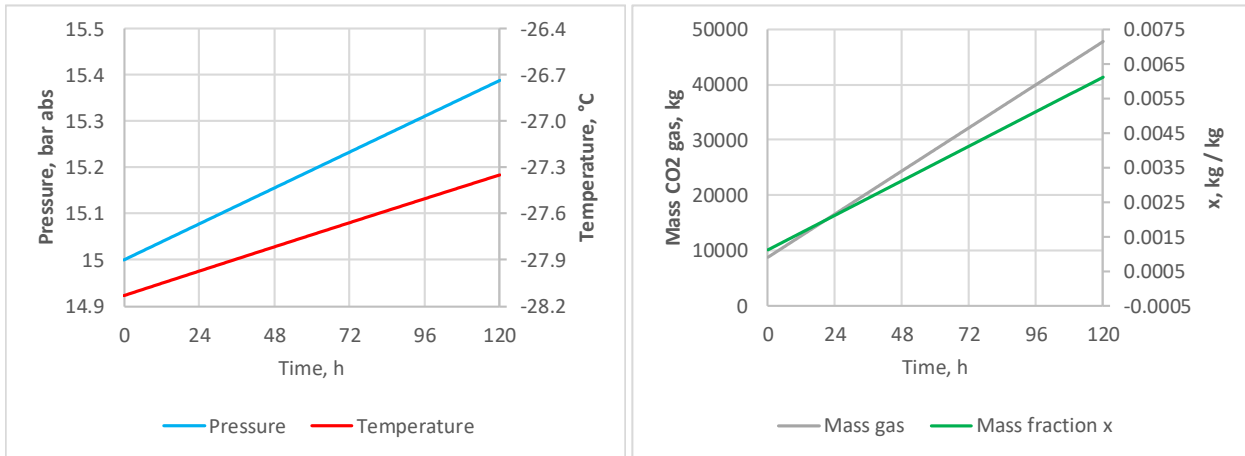
Fig. 5 Increasing pressure and temperature (left) and amount of CO_2 vapour (right) versus time during a five-day transport for a higher gas phase starting volume case (15 bar and 3% volume as gas at the start, BOR 0.1 %/day)

3. Suggestions for controlling pressure and temperature rise

Somewhat surprisingly, the analysis given above for a shipment of pure liquefied CO_2 does not show a significant or dramatic rise of pressure or temperature. The above reference case with 0.1%/day BOR gives ~ 330 kg/h gas production. The work in [3,5] considers 1000 kg/h BOG processing from 0.05 %/day BOR from a 50000 m³ storage capacity vessel (much larger than the 7500 m³ considered above), evaporating at 7 bar (where the boiling point for CO_2 is -51.5 °C), while transporting 99.5%/0.5% vol/vol CO_2/N_2 liquid. That gave a 64%/36% vol/vol CO_2/N_2 boil-off gas, as a result of a much higher relative volatility for N_2. Unfortunately [3,5] do not report neither a pressure or temperature rise nor the rate of these.

As shown above, a lower CO_2 transport temperature gives a larger heat ingress simply as a result of a larger temperature difference driving force. Moreover, a higher transport pressure would require a stronger (thicker walls) CO_2 storage which probably gives better heat insulation as well (although a higher pressure does give a somewhat lower density for the liquefied CO_2, increasing the necessary volume.) Thus, it seems that BOR can be reduced by operating at higher pressures rather than low temperatures, also from an energy efficiency point of view if the energy penalty of re-liquefaction can be avoided.

The presence of contaminants has a significant influence on the composition of the BOG as the work in [3] shows. Nitrogen has a lower heat of evaporation and a much lower boiling point than CO_2 for a given pressure, and a lower liquid density as well. It would preferably occur near the liquid – vapour interface and show a higher rate of evaporation than CO_2. The gas phase will nonetheless contain a large CO_2 fraction and simply purging the BOG is not an option. Similarly, increasing the fraction of nitrogen in the liquefied CO_2 until a, say, > 95% nitrogen BOG is obtained is not an option.

Besides nitrogen, contaminants that are more volatile than CO_2 are methane, hydrogen, argon and carbon monoxide. These are flammable or (argon) inert and some methane (as LNG) or ethane (with a boiling point similar to CO_2) may be added to the transported liquefied CO_2 so that a flammable BOG mixture is obtained for the engines that drive the ship (or transport vehicle in general). See [6] for low-temperature CO_2-N_2, CO_2-CH_4, CO_2-C_2H_6 and several other CCS-relevant phase diagrams (and a discussion on the importance of mixing enthalpy).

Alternatively, adsorption of BOG CO_2 on molecular sieves or active carbon can be considered: when pressure is reduced during off-loading of CO_2 at the point of underground storage the adsorbed CO_2 would be released and become available for storage as well. If ammonia, NH_3 is available at an

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attractive cost an gaseous overhead space of ammonia above the liquefied CO_2 may give production of ammonium (bi)carbonate (ABC, AC) similar to the chilled ammonia process (CAP) for removal of CO_2 from flue gas at ~ 5°C [7]. Formation of AC and/or ABC powder will effectively suppress a rising pressure. Again, these solid salts will decompose during a pressure reduction in the storage tank upon off-loading for storage.

Most of the above deserves further analysis, for example experimentally (e.g [8]). At this point no urgency seems to exist if not very long (more than a week) duration CCS travel with liquefied CO_2 is planned. If impurities in the liquefied CO_2 become a critical or expensive factor during transport then a better on-shore pre-processing before transport is the most cost-effective solution. Goos et al. recommend no free water and limited concentrations of contaminants and non-condensable gases [9].

4. Conclusions

For a better understanding pressure and temperature rise during transport of liquefied CO_2 as part of a CCS process train, the thermodynamics of a liquid/vapour pure CO_2 system is analysed. Based on this it can be concluded that for pure CO_2 a significant rise in pressure and temperature is not to be expected when starting of at 15 bar (- 28 °C) and a boil-off rate (BOR) of 0.1%/day. Comparison with (scarce) literature suggests that these conditions are preferable over 7 bar (- 49°C) conditions to start with, as a larger temperature difference with the surroundings apparently increase the BOG rate. The role of impurities that have a higher volatility than CO_2 warrants more study. For example, adsorbents like zeolite or active carbon may adsorb BOG CO_2, and so can ammonia form solid (bi)carbonate: these sorbents or salts would re-release the CO_2 during a pressure reduction at CO_2 off-loading. If impurities in the liquefied CO_2 become a critical factor during transport then a better (on-shore) pre-processing is recommended.

Appendix A – Thermodynamic data CO_2

For this paper, thermodynamic data for CO_2 as a two-phase system of saturated liquid and saturated vapour is considered for the pressure range 10 – 25 bar (abs). This corresponds to -40 - -16 °C. A log pressure – enthalpy diagram for CO_2 as can be found on-line [10] is given below; for the calculations using data on the saturated states an on-line calculator [11] was used that gave data as collected in Table A.1.

Table A.1. Data for saturated CO_2 liquid and vapour

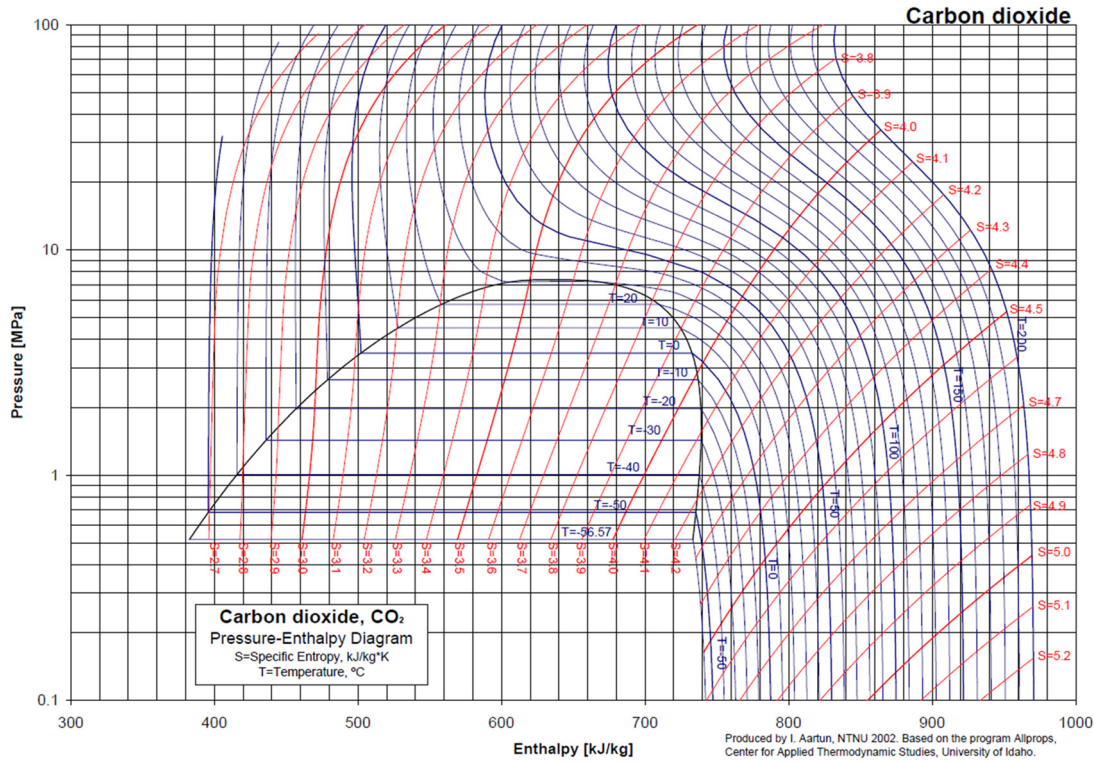| Pressure, bar abs	T_{sat}, °C	$\rho_{L,sat}$, kg/m^3	$\rho_{G,sat}$ kg/m^3	ρ_{Lsat} / $\rho_{G,sat}$, -	$h_{L,sat}$ kJ/kg	$h_{G,sat}$ kJ/kg	$h_{G,sat}$ -$h_{L,sat}$ kJ/kg
10	-40.14	1116.55	25.99	42.96	112.62	435.27	322.65
13	-32.76	1087.06	33.76	32.20	127.63	436.52	308.89
16	-26.56	1061.25	41.67	25.47	140.52	436.97	296.45
19	-21.18	1037.29	49.78	20.84	151.97	436.96	284.99
22	-16.37	1014.66	58.14	17.45	162.39	436.46	274.07
25	-12.01	993.17	66.79	14.87	171.97	435.7	263.73

Fig. A.1 Pressure – enthalpy diagram for CO₂   (taken from [10]).

This data was further processed into simple polynomials for the purpose of this paper, with results as given in Table A.2, valid for the temperature/pressure ranges as in Table A.1.

Table A.2. Expressions for saturated CO₂ liquid and vapour properties versus pressure

Parameter	Unit	Polynomial as function of	R^2	Equation
T_{sat}	°C	$30.683 \times \ln(p) - 111.23$	0.9987	A.1
$\rho_{L,sat}$	kg/m³	$-8.172 \times p + 1194.7$	0.9967	A.2
$\rho_{G,sat}$	kg/m³	$2.717 \times p - 1.52$	0.9996	A.3
$\rho_{L,sat} / \rho_{G,sat}$	-	$0.1077 \times p^2 - 5.5726 \times p + 87.342$	0.9963	A.4
$h_{L,sat}$	kJ/kg	$3.9284 \times p + 75.77$	0.9932	A.5
$h_{G,sat}$	kJ/kg	$-0.0275 \times p^2 + 0.9805 \times p + 428.29$	0.9832	A.6
$h_{G,sat} - h_{L,sat}$	kJ/kg	$-3.9097 \times p + 360.22$	0.9973	A.7

Nomenclature

ABC Ammonium bicarbonate

AC Ammonium carbonate

BOG Boil-off gas

BOR   Boil-off rate, %/day

CAP Chilled ammonia process

CCS Carbon capture and storage

H enthalpy, J

h specific enthalpy, kJ/kg

LNG Liquefied natural gas

p pressure, Pa or bar

Q heat, J

$\dot{Q}$ heat rate, W or W

T temperature, °C or K

t time, h

U internal energy, J

W work, J

x mass fraction gas (vapour), kg/kg

Greek symbols

Δ difference

ρ density, kg/m^3

Subscripts and superscripts

G gas (or vapour)

L liquid

sat saturated

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