Process Simulation of Impurity Impacts on CO_2 Fluids Flowing in Pipelines

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Abstract

Captured carbon dioxide flowing in pipelines is impure. The impurities contained in the carbon dioxide fluid impact on the properties of the fluid. The impact of each impurity has not been adequately studied and fully understood. In this study, binary mixtures containing carbon dioxide and one impurity, at the maximum permitted concentration, flowing in pipelines are studied to understand their impact on pipeline performance. A hypothetical 70 km uninsulated pipeline is assumed and simulated using Aspen HYSYS (v.10) and gPROMS (v.5.1.1). The mass flow rate is 2,200,600 kg/h; the internal and external diameters are 0.711 m and 0.785 m. 15 MPa and 9 MPa were assumed as inlet and minimum pressures and 33 °C as the inlet temperature, to ensure that the fluid remain in the dense (subcritical or supercritical) phase. Each binary fluid is studied at the maximum allowable concentration and deviations from pure carbon dioxide at the same conditions is determined. These deviations were graded to rank the impurities in order of the degree of impact on each parameter. All impurities had at least one negative impact on carbon dioxide fluid flow. Nitrogen with the highest concentration (10-mol %) had the worst impact on pressure loss (in horizontal pipeline), density, and critical pressure. Hydrogen sulphide (with 1.5-mol %) had the least impact, hardly changing the thermodynamic properties of pure carbon dioxide.

Key words

CO_2 impurities; CO_2 pipelines; impact of impurities; CO_2 pressure drop; CO_2 phase envelope; binary CO_2 fluids.

1 Introduction

Surface temperatures on Earth have been rising steadily for decades, and this increase is attributed to the increase in greenhouse gases in the atmosphere. Carbon dioxide (CO_2) is a major constituent of greenhouse gases and is the most

common anthropogenic pollutant (Caravaggio et al., 2019). Humans depend on these industrial activities for survival and may continue to engage in them for many years to come. To protect the environment, industrially produced CO_2 is captured, transported and stored in underground sinks (Piippo et al., 2018). Pipelines are more cost-inefficient when transporting CO_2 over long distances (Jakobsen et al., 2017) and are preferred in the transportation of captured CO_2 on land. Up to 360,000 km of pipelines may be required to transport the volume of CO_2 captured from industrial processes alone by the year 2050 (IEA GHG, 2014). The world presently has a total CO_2 pipeline length of about 7,000 km. This means that over 350,000 km of CO_2 pipelines may be constructed between now and 2050.

Captured carbon dioxide is not 100 % pure and may contain several impurities. These impurities include nitrogen (N_2), methane (CH_4), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), oxygen (O_2), carbon monoxide (CO), ammonia (NH_3), argon (Ar), water vapour (H_2O), and hydrogen (H_2). Impurities with very low concentrations (less than 1,000 parts per million) do not significantly affect the properties of the flowing fluid and ignored in this work. However, even small quantities of the impurities might significantly affect the thermophysical properties of the CO_2 fluid (Munkejord et al., 2016). Single impurities may constitute as low as 0.001 mole percent (mol %) or as high as 10-mol %. The allowable limit of impurities depends on the geology of the storage formation (Kather and Kownatzki, 2011) or the specification for the usage. The total mol % of impurities in a carbon dioxide pipeline is rarely above 10 %; see Table 1. The maximum percentage of CH_4 considered here is 4-mol %, though it may be higher in some enhance oil recovery pipelines in the USA. For example, the Canyon Reef Carrier pipeline in the USA has up to 15-mol % of CH_4 (Patchigolla and Oakey, 2013).

The type and percentage of impurities in the stream affect the density, viscosity, pressure and temperature changes, critical pressure and temperature, phase envelope, etc. These properties when evaluated correctly for each CO_2 pipeline should optimise the design of CO_2 pipelines. Hydrates do not form under the operating conditions of pressure and temperature considered in this study and so ignored. However, the reader may refer to Chapoy et al. (2014) for hydrate modelling in CO_2 binary mixtures. The impurities and their concentrations found in CO_2 streams depend on the source of the CO_2, (i.e. natural or industrial). CO_2 impurities from industrial sources also depend on the type of fuel (gas, oil, coal or biomass) used for combustion or the type of capture (i.e. pre-combustion, post-combustion and oxy-fuel). The impurities in the fluid affect the transportation properties of the fluid. The impact may be either positive or negative, for some parameters, depending on the impurity and the pipeline profile or elevation.

Table 1: Maximum and minimum mol % of impurities in carbon dioxide pipelines (Peletiri et al., 2018a)

	CO_2	N_2	O_2	Ar	SO_2	H_2S	NO_x	CO	H_2	CH_4	H_2O	NH_3
Min.%	75	0.02	0.04	0.005	$<10^{-3}$	0.01	<0.002	$<10^{-3}$	0.06	0.7	0.005	$<10^{-3}$
Max.%	99.95	10	5	3.5	1.5	1.5	0.3	0.2	4	4	6.5	3

Impurities found in carbon dioxide streams could be classified into fuel oxidation, excess oxidation, process fluids (Porter et al., 2016) or naturally occurring. There are several sources of impurities found in CO_2 fluids. Carbon dioxide is contained in the air used for combustion and is a product of combustion. Nitrogen, oxygen and argon are contained in the air used for combustion. Carbon monoxide is a product of incomplete combustion of carbon-based compounds. Oxides of nitrogen are products of the combustion of nitrogen and water vapour is a product of hydrogen combustion. An elaborate source of impurities, the reasons for their limitations and classifications are given elsewhere (Porter et al., 2016).

The minimum pressure of a CO_2 pipeline is taken at some value, about 10 %, higher than the critical pressure of the flowing fluid (Lemontzoglou et al., 2017). This is to ensure that the fluid does not change phase while flowing in the pipeline. Carbon dioxide pipelines operate in the supercritical pressure and temperature ranges to ensure that the flowing fluid stays in the supercritical phase. The flowing fluid exists in the dense subcritical phase when temperature is below the critical value and pressure remain above the critical value. CO_2 pipeline fluid pressures and temperatures range from 8.6 to 15.1 MPa and 12.7 to 43.3 °C (Mohitpour et al., 2003), 10 to 15 MPa and 15 to 30 °C (Patchigolla and Oakey, 2013), 8.6 MPa to 15 MPa (Kang et al., 2014). All reported pipeline pressures are above the critical pressure value of pure carbon dioxide (7.39 MPa). The pipeline temperature is not always above the critical temperature of pure carbon dioxide (31.1 °C). This is because CO_2 fluids remain in the dense phase irrespective of the temperature, if the pressure is maintained above the critical value until it becomes low enough for a solid phase to form (Peletiri et al., 2018b). It has been reported that transporting liquid CO_2 is more economical than transporting supercritical CO_2 because it does not require insulation and smaller pipe sizes can be used (Teh et al., 2015).

2 Methodologies

Aspen HYSYS (V10, a chemical process simulator) was used to simulate pressure, temperature, phase envelope, density, critical pressure/temperature and viscosity. gPROMS (V4.2, a general process model builder), was used to simulate pressure, temperature, density and viscosity. Peng – Robinson (PR) equation of state was used in both the Aspen HYSYS and gPROMS analysis to calculate thermodynamic properties of CO_2 mixture state. To build confidence, results from the two software were compared. Binary fluids of CO_2 with each impurity at the maximum concentration in pipelines were simulated to determine the effect of each impurity on pressure, temperature, density, viscosity, pressure – temperature (PT) diagram, critical pressure and critical temperature. The two software gave similar results with some minor differences in some values. However, these differences in the results from the different software are not reported in this work. Specification for the hypothetical pipeline, with parameters close to the Cortez pipeline in the USA (IEA GHG, 2014), is shown in Table 2. The assumed length of 70 km is for simulation purposes only, to avoid the installation and impact of boosting stations. The minimum percentage of CO_2 is assumed to be 90-mol % because CO_2 pipelines are defined to contain fluids at supercritical conditions consisting of at least 90-mol % CO_2 (Forbes et al., 2008). The assumed inlet pressure is 15 MPa and the minimum pressure is 9 MPa, after which recompression is required. The inlet temperature is 33 ^{o}C to ensure that the fluid enters the pipeline in supercritical state. A minimum temperature is not specified because temperature changes are not limiting conditions in dense CO_2 pipeline transportation. Each binary fluid is studied at the maximum allowable percentage and deviations from pure CO_2 at the same conditions is recorded. These deviations are then graded to rank the impurities in order of the degree of impact on each parameter.

Table 2: CO_2 Pipeline specification

Length (m)	70,000	Pipe Wall Roughness (m)	4.57E-05
Inner diameter (m)	0.711	Pipe Wall conductivity (W/(m K))	45
Outer diameter (m)	0.785	Inlet Pressure (MPa)	15
Angle of elevation (^{o})	+0.37/0/-0.37	Inlet Temperature (^{o}C)	33
Material	Mild Steel	Mass Flow (kg/h)	2,200,600

3 Results and discussions

Each impurity affects the flow properties of CO_2 fluids. Some impurities may have positive impact on specific parameters. The effects of impurities, at their maximum mol %, on pressure, viscosity, temperature, critical pressure, critical temperature, phase envelope and density were studied and compared to pure CO_2 fluids as a benchmark. For the effects of equal mol % of impurities, the reader may refer to an earlier publication by the same authors (Peletiri et al., 2018b). The focus of this work is to highlight the changes in the parameters of CO_2 fluids flowing in pipelines due to the presence of impurities

3.1 Impact on Density

Both pressure and temperature affect the density of gases. Density has a positive correlation with pressure but it has a negative correlation with temperature. Pure gases at supercritical pressures and temperatures can have liquid state densities and low gaseous state viscosities (Koga et al., 2005).. Density measurements of 0.8988-mol % CO_2 and 0.1012-mol % CH_4 (Liu et al., 2017) show that temperature changes have greater effect than pressure changes within the pressure and temperature ranges of CO_2 pipelines. A 10 % increase in temperature resulted in a 26.38 % decrease in density and a 10 % increase in pressure resulted in a 6.08 % increase in density. The trend is the same for all combinations of CO_2 + CH_4 in the supercritical phase.

Each impurity affects density of CO_2 mixture according to its molecular weight. Lighter gases reduce the density while heavier gases increase the density. Figure 1 shows the actual density of pure CO_2 and the binary fluids and the percentage change due to impurities under the same pressure and temperature from pure CO_2. 10-mol % N_2 has the highest reduction of density at 19.4 % and 6.5-mol % H_2O has the highest increase of density at 6.11 %. H_2 at just 4-mol % reduced the density by 10.71 %. This means that H_2, at the same mol %, would have a greater reduction of density than any other impurity. Gases that increase the density result to lower pressure losses while those that reduce the density increase pressure losses. Therefore, only SO_2 with a higher molecular weight has a positive impact. 1.5-mol % H_2S had the smallest impact on the density reducing it by about -0.11 % followed by 0.2-mol % CO which reduced it by -0.37 %.

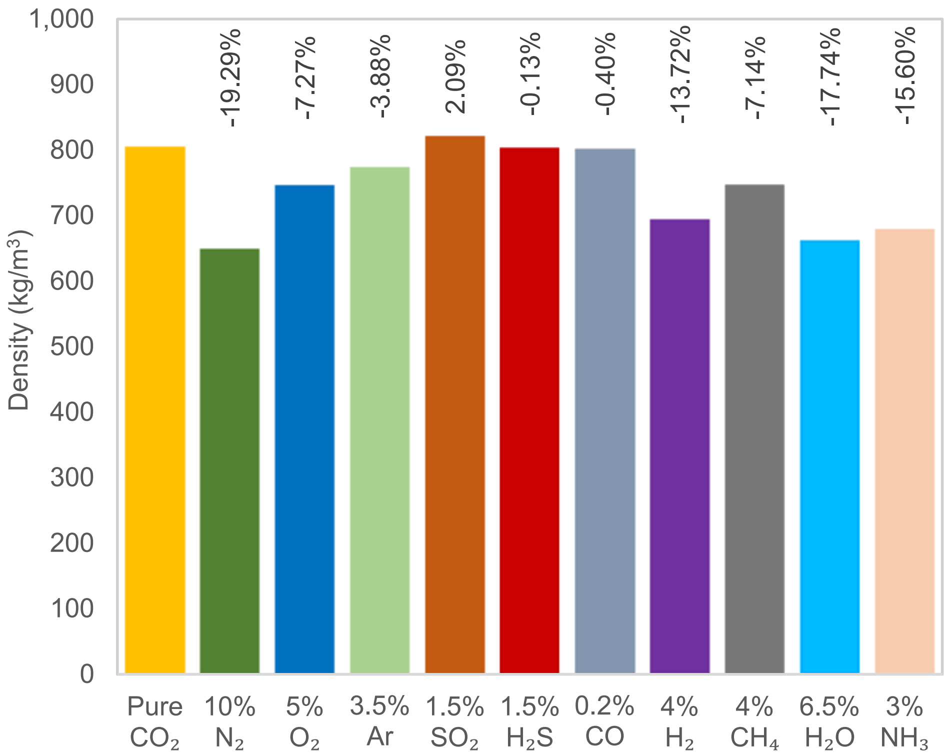


Figure 1: Densities of CO_2 binary mixtures and percentage deviation from pure CO_2.

3.2 Impact on Viscosity

Viscosity of a gas plays a role in the pressure loss calculation of CO_2 pipelines by opposing or resisting the flow. The Reynold's number used in the determination of the friction factor is a function of fluid viscosity. Temperature, pressure and composition strongly affect viscosity, an intensive property of fluids. Viscosity of CO_2 at temperatures slightly above the critical value shows nonlinearity, so a complex equation of state is recommended (McCollum and Ogden, 2006). Viscosity changes may be non-linear within the range of pressure and temperature of CO_2 pipeline transportation. Viscosity reduces with increase in temperature at high densities but increases with increase in temperature at low densities (Zabaloy et al., 2005). The viscosity of 99.44-mol % CO_2 and 0.56-mol % pentaerythritol tetra-2-ethylhexanoate (PEB3) measured at pressures between 10 and 60 MPa decreased with increase in temperature (Pensado et al., 2008). Since density is high at supercritical pressures, usually greater than 10 MPa in CO_2 pipelines, viscosity will increase with decrease in temperature. However, this behaviour was not readily verified in the simulated pipelines because both pressure and temperature decrease at the same time along the pipeline.

The effect of impurities on the viscosity of CO_2 is shown in Figure 2. 10-mol % N_2 has the highest reduction in the viscosity while 6.5-mol % H_20 has the highest increase in viscosity. A reduction in viscosity reduces the friction between fluid molecules and allows the fluid to flow more freely. Higher pressure losses are expected with fluids with higher viscosity. Therefore, SO_2, H_2S and H_2O had a negative impact on the ease of fluid flow.

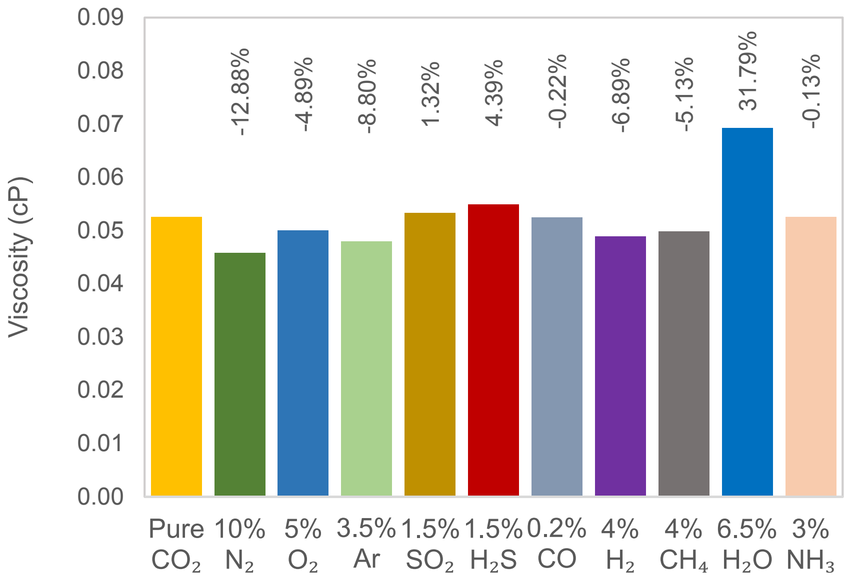


Figure 2: Viscosity of binary CO_2 fluids at 15MPa and 33 ºC and percentage change from pure CO_2.

3.3 Impact on Pressure

Pressure changes in fluids flowing in pipelines is dependent on density, viscosity (Tan et al., 2015) and velocity among other minor effects. At equal mass flow rates, lighter fluids result in higher pressure losses than denser fluids in horizontal pipes (Peletiri et al., 2017). This is due to increase in velocity in the pipeline for lighter fluids. For non-horizontal pipelines, the effect of density may outweigh the effect of velocity due to the elevation component. A high-density fluid will result in higher pressure losses in inclined pipelines but may result in lower pressure losses in horizontal pipelines and higher pressure gains in declined pipelines. Equation 1 (Chandel et al., 2010) presents frictional and elevation components of the common pressure drop equation. The acceleration component of pressure drop is usually ignored in the calculation of pressure losses.

$$\Delta P = \frac{f \rho l v^2}{2D} + \rho g \Delta z \qquad (1)$$

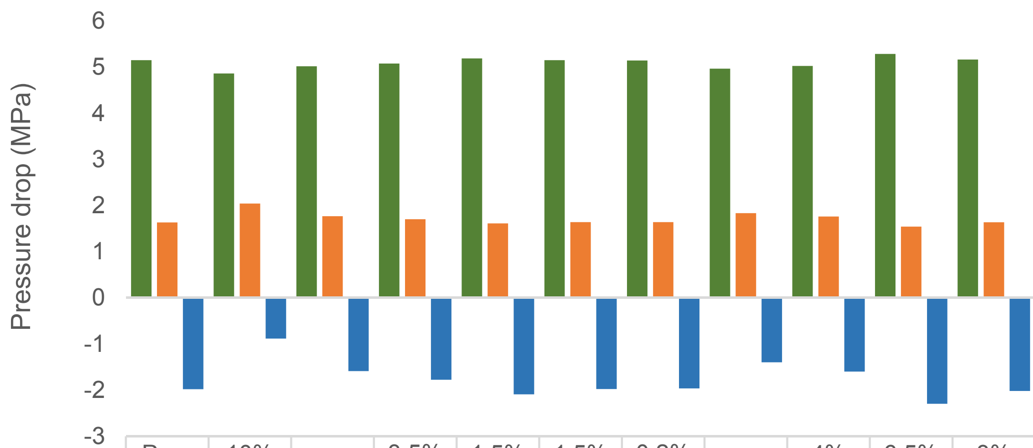
where ΔP is pressure drop (Pa), f is friction factor, l is the length (m), v is velocity (m/s), D is the pipeline internal diameter (m), ρ is the fluid density (kg/m^3), g is acceleration due to gravity (m/s^2) and Δz is change in elevation (m).

In horizontal pipelines, gases lighter than CO_2 increase the pressure losses while denser gases reduce the pressure losses. This effect is due to the fact that a higher volume of lighter gases are required to make up the same mass flow, which consequently increases the velocity of fluid flow. This increased velocity when squared (see Equation 1) outweighs the reduced density. The loss of pressure during flow determines the length of flow before recompression is required and may increase the cost of pipelines. The cost of CO_2 pipelines increases when there are high pressure losses resulting to higher capital cost (installation of more boosting stations) and higher operational cost in running the increased number of boosting stations. Techniques for designing minimum cost pipelines is given in (Benson and Ogden, 2003), a model for transport cost is given in (Elahi et al., 2014) and a cost optimisation model for transportation is given in (Kemp and Sola Kasim, 2010). The analysis of the cost impact of impurities is a theme for our future work. Flowing pressures and pressure loss are the most important flow parameters in CO_2 pipeline design. Therefore, pipelines are designed to avoid high pressure losses. However, pipelines running downhill may increase in pressure. The increase in pressure may affect pipeline joints/seals, cause pipeline wall erosion, leakages, or necessitate the installation of pressure reducing stations.

Only SO_2 and H_2O impurities resulted to lower pressure losses than pure CO_2 in horizontal pipelines. It means that in horizontal pipelines, CO_2 fluids with these impurities will flow for longer distances before recompression is required, thereby reducing the cost of transportation. The percentage change in horizontal pipes was least at 0.9 % with 3-mol % NH_3 while the largest change was 25.01 % with N_2. 10-mol % N_2 also resulted to the highest pressure loss of 2.04 MPa while 6.5-mol % H_2O resulted to the lowest pressure loss of 1.54 MPa. A single impurity of 6.5-mol % H_2O would enable the fluid flow for 5.8 % longer distance while 1.5-mol % SO_2 would enable the fluid travel 1.3 % longer distance compared to pure CO_2 before recompression. Conversely, 10-mol % N_2 will cause the fluid to travel only 80 % of the distance a pure CO_2 fluid would travel before requiring recompression.

The effect of impurities on pressure also depends on pipeline profile. Impurities in pipelines at inclined positive angles tend to have reduced effects. The maximum impact resulting from 10-mol % N_2 in pressure change for the inclined pipeline is -5.62 %, for horizontal pipeline is 25.01 % and for the downhill pipeline is -55.46 %. Impurities heavier than CO_2 increase pressure losses in the uphill pipeline and increase pressure gain in the downhill pipeline. H_2O had the highest pressure loss in the inclined pipeline and highest pressure gain in the declined pipeline. In the inclined pipeline, 10-mol % N_2 had the highest positive change, reducing the pressure loss by about 0.29 MPa. In the declined pipeline, (assuming that pressure gain is also not desirable), 10-mol % N_2 had the greatest positive change by reducing the pressure gain by about 1.1 MPa while H_2O increased the pressure gain by about 0.32 MPa. Overall, 1.5-mol % H_2S had the least impact, changing the pressure behaviour from that of pure CO_2 by about 0.03 %, 0.49 % and -0.30 % on the uphill, horizontal and downhill pipelines respectively.

The pressure changes in the three pipeline profiles are shown in Figure 3 and the percentage change from the pressure drop of pure CO_2 is shown in Table 3. Negative values in Table 3 indicate a reduction in pressure loss and in the case of a downhill pipeline, a reduction in pressure gain. Any impurity that reduces pressure increase or pressure decrease has a positive impact. The negative values (bars) in Figure 3 indicate pressure gain. Table 4 shows the minimum dip (negative) angles for this pipeline to gain in pressure. All fluids including pure CO_2 increased in pressure along the downhill pipeline. Downhill pipelines with binary CO_2 fluids at the maximum specified mol % of impurities flowing in a pipeline with the assumed specifications at angles to the horizontal greater than the values shown will increase in pressure along the direction of flow. Increases in CO_2 fluid pressure during flow of fluids in pipelines is also not desirable because pressure reducing stations may be required be control the pressure. A minimal pressure loss along the length of pipelines transporting CO_2 fluids is desired.



	Pure CO_2	10% N_2	5% O_2	3.5% Ar	1.5% SO_2	1.5% H_2S	0.2% CO	4% H_2	4% CH_4	6.5% H_2O	3% NH_3
Angle (0.37%)	5.15	4.86	5.02	5.08	5.19	5.15	5.14	4.97	5.02	5.28	5.16
Angle (0 %)	1.63	2.04	1.77	1.70	1.61	1.64	1.64	1.84	1.76	1.54	1.63
Angle (-0.37 %)	-1.98	-0.88	-1.59	-1.78	-2.09	-1.98	-1.96	-1.40	-1.60	-2.30	-2.02

Figure 3: Pressure drop of CO_2 binary fluids in uphill, horizontal and downhill pipelines.

Table 3: Percentage change of pressure drop of uphill, horizontal and downhill pipelines.

Angle of inclination	+ 0.37⁰	0°	- 0.37°
10% N_2	-5.62	25.01	-55.46
5% O_2	-2.53	8.15	-19.82
3.5% Ar	-1.38	4.12	-10.38
1.5% SO_2	0.77	-1.34	5.50
1.5% H_2S	0.03	0.49	-0.30
0.2% CO	-0.13	0.38	-0.97
4% H_2	-3.54	12.36	-29.50
4% CH_4	-2.42	7.83	-19.33
6.5% H_2O	2.63	-5.45	15.89
3% NH_3	0.31	0.09	1.83

Table 4: Minimum dip angle (to the horizontal) of pipeline to gain in pressure.

Impurity	Pure CO_2	6.5 % H_2O	3 % NH_3	1.5 % SO_2	0.2 % CO	1.5 % H_2S	3.5 % Ar	4 % CH_4	5 % O_2	4 % H_2	10 % N_2
Dip Angle (degrees)	0.17	0.15	0.25	0.16	0.17	0.17	0.18	0.19	0.20	0.23	0.26

3.4 Impact on Temperature

As CO_2 flows in the pipeline, heat is transferred from the flowing fluid to the soil or surrounding. Heat transfer out of the pipeline is in three components, convective heat transfer between the fluid and the inner pipeline wall, the heat conduction from the inner pipeline wall to the outer pipeline wall and the heat emission to the surrounding (Na et al., 2012). The maximum temperature of CO_2 fluids occur immediately after exiting the compressor. This heat is transferred to the environment as the fluid flows in the pipeline. Fluid temperature is not a limiting factor in CO_2 pipeline design because the fluid stays in the dense phase as long as the pressure is above the critical value. During depressurisation, heat may be transferred from the surrounding to the pipeline since the CO_2 cools due to vaporisation and the Joule-Thompson effect (de Koeijer et al., 2011). This reverse heat transfer may occur only during start-up or shut down for a short period or during a leak. CO_2 pipelines may be pressured with N_2 at start-up before introducing the CO_2 fluid into the pipeline to avoid the cooling effect of expanding fluid. The bulk of heat transfer is from the flowing fluid, which increases in heat after compression, to the surrounding. The temperature of binary components at the maximum allowable impurity concentration from the pipeline inlet to the outlet were studied.

Figure 4 shows the temperature drop of each binary mixture flowing in a horizontal pipeline and the percentage change from that of pure CO_2. 6.5-mol % H_2O content reduced the temperature loss by a maximum of -25.5 % and 10-mol % N_2 increased the temperature drop by a maximum of 87.2 %. A low temperature is desired because it results in increased volume transported due to increased density and lower pressure loss in CO_2 pipelines (Zhang et al., 2006). It therefore implies that impurities that increase heat loss have positive effect. Pipelines need not be insulated (except to protect them from external corrosion) to enable rapid heat loss, which may result to reduced pressure loss.

The most heat loss (4.03 ^oC) was due to 10-mol % N_2, increasing the heat loss by about 87.19 %. This loss is as a possible effect because it will result to denser fluid and consequently lower pressure losses. The lowest heat loss (1.60 ^oC) was due to 6.5-mol % H_2O reducing the heat loos by about -25.51 % less heat loss compared to pure CO_2. 1.5-mol % H_2S had a negligible change on temperature variation at -0.11 %.

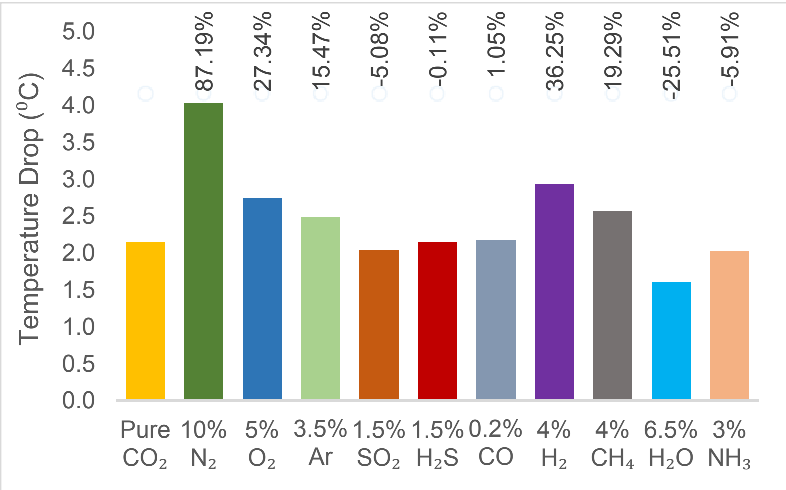


Figure 4: Temperature drop of binary mixtures with percentage deviation from pure CO_2.

3.5 Impact on Phase envelope

The binary fluids formed two – phase envelopes under different pressure and temperature combinations. Fluids with different boiling points have different pressure and temperature combinations to exist as a liquid or gas. A two – phase region forms when one gas is in vapour state while the other is in liquid state. CO_2 pipelines are designed to operate under pressures and temperatures above the critical values to avoid two – phase flow. Figure 5 shows the two – phase envelope created by each impurity with the upper (solid) line representing the bubble point curve and the lower (dash) line representing the dew-point curve. 4-mol % H_2 created the widest two – phase envelope while 1.5-mol % H_2S created the smallest two – phase envelope. At the same mol %, in increasing magnitude of the phase envelope is, H_2O, H_2S, CO, NH_3, SO_2, Ar, O_2, CH_4, N_2 and H_2 (Peletiri et al., 2018b). The presence of impurities in the fluid increases the possibility of two-phase flow in the pipeline as the pressure and temperature decline during transportation. Therefore, all impurities have negative impacts for creating two-phase regions. Table 5 shows the (relative) dimensionless area enclosed by the bubble and dew point lines and a vertical line drawn at 0 ºC to intersect both lines.

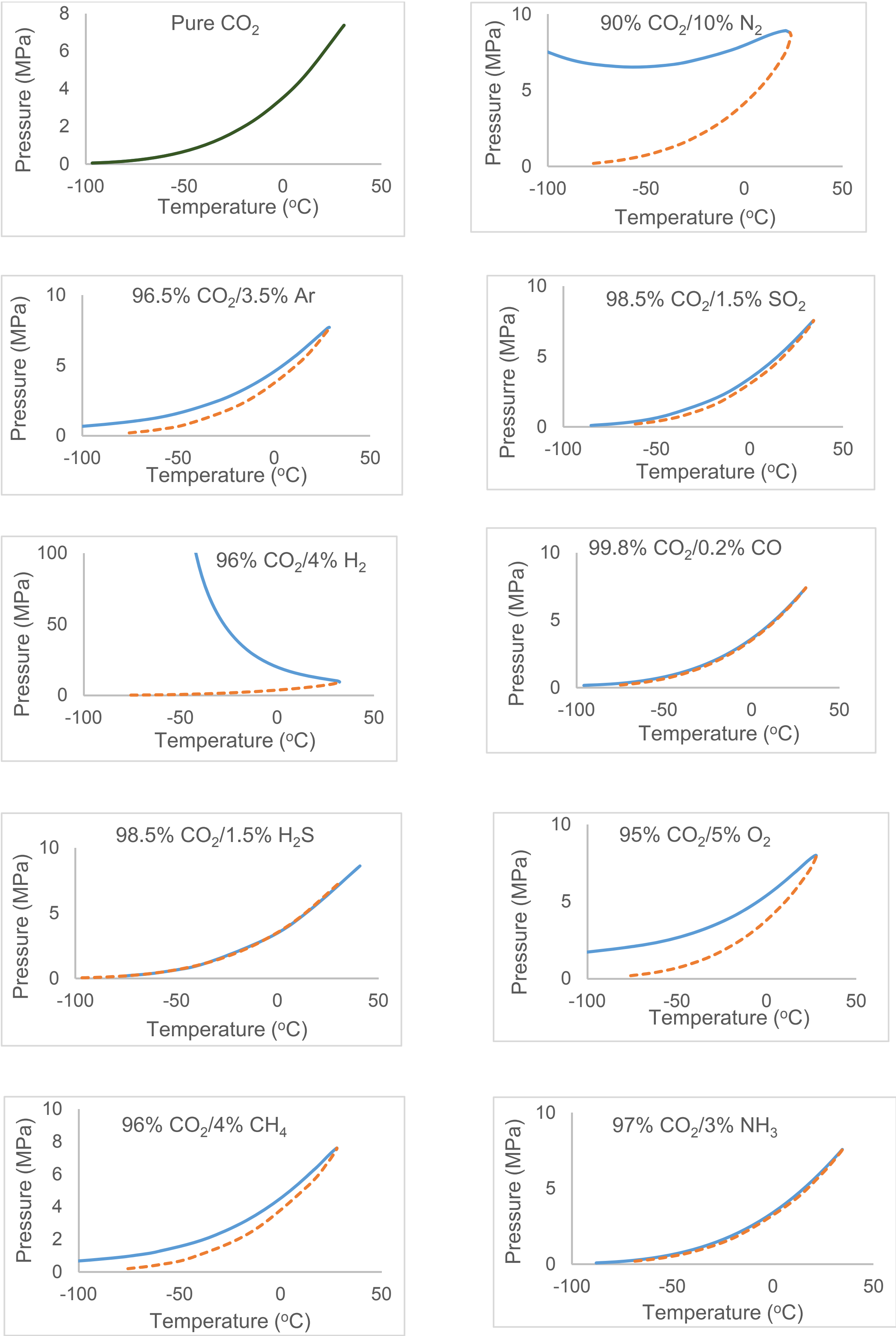


Figure 5: Phase envelope of binary CO_2 fluids. The solid line is the bubble point curve and lower dotted line is the dew point curve.

Table 5: Dimensionless area of two-phase region from 0 °C to critical temperature.

Impurity	10% N_2	4% CH_4	3.5% Ar	1.5% SO_2	1.5% H_2S	5% O_2	4% H_2	0.2% CO	3% NH_3
Dimensionless area	59.0	17.5	17.7	12.8	1.6	31	258	1.2	3.9

3.6 Impact on critical pressure and temperature

To keep the fluid in a supercritical state, the temperature and pressure must be above the critical values. To achieve this, the fluid is compressed and the pipeline heated or insulated to reduce the heat transfer from pipeline to the surrounding. Fluid compression and heating, where it is applied, are costly. Lower critical pressures require less compression and consequently less energy cost. All impurities increased the critical pressure above that of pure CO_2. An increase in critical pressure may increases the minimum pipeline pressure, which in turn increases the cost of operation of CO_2 pipelines. The cost of energy of compression increases with increase in critical pressure. 10-mol % N_2 has the highest critical pressure while 1.5-mol % H_2S has the lowest value. At equal mol %, H_2 has the highest critical pressure while H_2S has the lowest critical pressure (Peletiri et al., 2018b). The minimum pressure of a CO_2 pipeline is stipulated to be slightly above the critical pressure. Minimum pressures are chosen slightly above (about 10 % higher than) the critical pressure. Impurities that cause increases in critical pressure may result to an increase in the cost of fluid transportation, as more compression energy is required to compress the gas to supercritical condition. All impurities increased the critical pressure with N_2 having the highest increase at more than 19.6 % while H_2S increased it by just 0.11 %.

Three impurities, SO_2, H_2S and NH_3, increased the critical temperature while all others decreased the critical temperature. The temperature ranges for supercritical flow decreases with increase in critical temperature. However, temperatures within the operational range of CO_2 pipeline pressures is not a limiting consideration. An increased critical temperature may result in lower pressure losses when the flowing fluid temperature reduces below the critical value and enter the subcritical state or liquid state. CO_2 fluids at subcritical or liquid state result to increased density and lower pressure losses. Therefore, an increase in critical temperature is a positive impact if supercritical flow is not a requirement. 10-mol % N_2 resulted to the lowest critical temperature of 23.61 °C representing -23.72 % lower than pure CO_2 and 3-mol % NH_3 impurity resulted to the highest critical temperature of 34.26 °C, about 10.7 % higher than that of pure CO_2. A high critical temperature may be desired to ensure that the fluid stays in the dense subcritical state rather than the supercritical state. However, where supercritical flow is specified, a lower critical temperature is desired to avoid heating the fluid to reach supercritical state. Table 6 shows the critical pressure and critical temperature of the CO_2 fluids.

Table 6: Critical pressure and temperature of CO_2 fluids

Impurity	Pure CO_2	10% N_2	4% CH_4	3.5% Ar	1.5% SO_2	1.5% H_2S	5% O_2	4% H_2	0.2% CO	3% NH_3
P_c (MPa)	7.37	8.82	7.99	7.71	7.56	7.38	7.40	7.86	7.60	7.57
T_c (^{O}C)	30.9	23.6	27.8	28.8	34.0	31.2	30.8	28.5	28.0	34.3

3.7 Grading of impurities

All impurities reduce the volume of CO_2 transported by taking up a portion of the volume. The following ranking can be made in order of increasing (from left to right) magnitude of negative impact of each impurity on the transportation of CO_2 fluids in pipelines. It should be noted that some impurities (at the beginning) might have positive impacts. Table 7 shows a summary of the percentage changes from pure CO_2 resulting from each impurity.

- Pressure – H_2O, SO_2, NH_3, CO, H_2S, Ar, CH_4, O_2, H_2, N_2
- Temperature Heat loss – N_2, H_2, O_2, CH_4, Ar, CO, H_2S, SO_2, NH_3, H_2O
- Density – H_2O, SO_2, H_2S, NH_3, CO, Ar, CH_4, O_2, H_2, N_2
- Viscosity – H_2O, N_2, Ar, H_2, CH_4, O_2, CO, NH_3, SO_2, H_2S
- Phase envelope – H_2O, H_2S, CO, NH_3, SO_2, CH_4, Ar, O_2, N_2, H_2
- Critical pressure – H_2O, H_2S, CO, SO_2, NH_3, CH_4, Ar, H_2, O_2, N_2
- Critical temperature – H_2O, NH_3, SO_2, H_2S, CO, Ar, H_2, CH_4, O_2, N_2

Table 7: Percentage deviation of thermodynamic properties due to impurities.

Impurities	10% N_2	4% CH_4	3.5% Ar	1.5% SO_2	1.5% H_2S	5% O_2	4% H_2	0.2% CO	10% N_2	6.5% H_2O
Pressure loss	25.0	7.8	4.1	-1.3	0.5	8.2	12.4	0.4	0.1	-5.5
Heat loss	87.2	19.3	15.5	-5.1	-0.1	27.	36.3	1.1	- 5.9	-25.5
Pc increase	19.6	3.2	4.6	2.6	0.1	8.4	6.7	0.4	2.8	-
Tc increase	-23.7	-9.6	-7.1	9.8	0.9	-	-8.0	-0.44	10.7	-
Density increase	-19.4	-5.8	-3.9	2.1	-0.1	-7.3	-10.7	-0.4	-0.3	6.1
Viscosity increase	-12.9	-5.1	-8.8	1.3	4.4	-4.9	-6.9	-0.2	-0.1	-31.8
Phase envelope*	60.0	18.0	22.0	12.4	2.3	31.	260	2.4	6.5	-

* The unit of phase envelope is dimensionless area.

4 Conclusion

This paper analyses the impact of common impurities at their maximum allowable concentrations in the transportation aspect of CCS operations. The impact of each impurity on the transportation of CO_2 in pipelines at the maximum allowable concentrations has not been investigated before. Both positive and negative impacts of the impurities on pipeline transportation and the percentage deviations from pure CO_2, under the same operating conditions, were studied. The authors recognise that CO_2 pipelines with single impurities were not found in the literature and that the effects of the multiple impurities would be more complex than the single impurities presented here. Investigating the effect of each impurity in the presence of other impurities is an option for future work.

Pressure changes were graded only for horizontal pipelines because the effect of impurities on pressure is also dependent on the angle of inclination/declination for non-horizontal pipelines. Though the highest pressure drop occurs in inclined pipelines, the impact of the impurities is reduced. The worst impact of impurities occurs in pipelines running downhill. Impurities lighter than CO_2 reduce the pressure loss in inclined pipelines, increase the pressure loss in horizontal pipelines, and decreases pressure gain in declined pipelines. Impurities heavier than CO_2 show the opposite trend. It should be noted that pressure may decline in pipelines running downslope at very small declination angles (see Table 4).

From this work, it has been shown that at the specified maximum concentration of impurities, N_2 has the worst impact followed by hydrogen. 10-mol % N_2 increased the pressure loss by 25.0 %, heat loss by 87.2 %, critical pressure by 19.6 %; and reduced the critical temperature by -23.7 %, density by -19.4 % and viscosity by -12.9 %. H_2S has the smallest impact closely followed by CO on the transportation of CO_2 fluids. 1.5-mol % H_2S increased the pressure loss by 0.5 %, critical pressure by 0.1 %, critical temperature by 0.9 %, viscosity by 4.4 %; and reduced the heat loss and density by -0.1 %.

Though allowable concentrations of the impurities also depend on the specifications for CO_2 storage or usage, the findings here can be used to modify the maximum allowable concentrations for each impurity and help in sensitivity analysis of CO_2 pipelines. For example, the permitted concentration of N_2 could be reduced because it has a high impact on the transport properties. The impact of H_2S is small, so a higher concentration may be allowed to save the cost of purifying the stream to a very low concentration. This work can serve as a guide during the design of CO_2 pipelines because it shows both the negative and positive parameters affected by each impurity. A pipeline designed to transport pure CO_2 may be overdesigned for CO_2 fluids with impurities having positive impact but under designed for impurities having negative impact. It is advisable to design each parameter of CO_2 pipeline transportation with a knowledge of the impact of each impurity found in the fluid.

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