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Grading the Impact of Impurities in Rich CO_2 Pipeline Fluids

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With about 195 countries signing the Paris (climate) Agreement and world leaders uniting for the planet after the United States' notification to pull out of the agreement, many carbon capture and storage (CCS) projects are expected to be executed worldwide. Captured CO_2 is not pure and may contain several impurities, which affect the flow dynamics of the CO_2 fluid in pipelines. To design efficient CO_2 pipeline transportation systems, it is imperative to understand the effect of these impurities on the flow behaviour. Aspen HYSYS (V10) and HydraFlash were used to study the behaviour of 90 mol % CO_2 and 10 mol % single impurity (N_2, CH_4, H_2, H_2S, SO_2, Ar, CO, NH_3, O_2 and H_2O). The Peng-Robinson equation of state (EoS), which has the lowest average absolute deviation (AAD) among cubic EoS for predicting CO_2 fluid properties, was used in Aspen HYSYS. Three different 50 km pipelines were simulated; one horizontal pipeline and two pipelines with +300 and -300 m in elevation between inlet and outlet respectively. The mass flow rate is 266,400 kg/h and the internal and external diameters of the pipelines are 0.289 m and 0.324 m respectively. All impurities changed the parameters of the flowing fluid. H_2 impurity caused the most pressure loss for horizontal pipelines but may cause the least pressure loss for pipelines at high inclination angles. H_2 and H_2S formed the widest and narrowest two-phase regions, respectively. The results also show that H_2 impurity resulted in the most heat loss while H_2O and SO_2 impurities had the lowest heat losses. Pipeline elevation change also affects the effect of each impurity on pressure changes. The difference in pressure drop between the impurity with the highest effect, H_2, and that with the least effect, SO_2, is 0.44 MPa for inclined pipelines, 0.77 MPa for horizontal pipelines and 1.44 MPa for declined pipelines. H_2S had the mildest effect followed by NH_3, H_2O, SO_2, CO, Ar, CH_4, O_2, N_2 and H_2.

1. Introduction

The need to protect our planet for future generations by reducing greenhouse gas emissions was highlighted by the signing of the Paris (climate) Agreement in 2016. The agreement is a United Nations non-binding document for nations to contribute their quota to the reduction of greenhouse gas emissions. Carbon dioxide (CO_2), water vapour (H_2O), Methane (CH_4), Ozone (O_3), Nitrous oxide (N_2O) and Hydrofluorocarbons (HCFCs) are the major greenhouse gases but the most important ones are CO_2, CH_4 and N_2O (Piippo et al., 2018). CO_2 is produced in large quantities by industrial processes including the burning of fossil fuels (Bare, 2011) for power generation, in automobile engines, in steel production, in cement manufacture, etc. Fossil fuels may remain the dominant source of energy for decades to come. Therefore, the need to capture CO_2 produced from large industrial plants becomes imperative. Captured CO_2 is transported to storage sites and pipelines are the economical option on land. By estimation in the IEA GHG (2014) report, as much as 360,000 km of pipelines may be required worldwide to transport the increased volume of CO_2 captured from industrial processes by year 2050. This is a huge increase from the present combined length of CO_2 pipelines of about 7,000 km. Therefore, there is need to design these pipelines for efficient CO_2 transportation.

In the process design of pipelines, density and viscosity are some of the (direct or indirect) inputs into the pressure behaviour and/or pipeline diameter equation (Lazic et al., 2014). The type and percentage of impurities in the stream affect these and several other properties of the flowing fluid. The impurities found in CO_2 streams vary depending on the type of fuel (Coal, crude oil, natural gas or biomass) and type of capture (pre-combustion, post-combustion or oxy-fuel). Therefore, evaluating fluid properties for each CO_2 stream will optimise the design of CO_2 pipelines.

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CO_2 fluids in pipelines are mostly transported at pressures and temperatures above the critical values. This is to ensure that the fluid remains in a single supercritical phase. Some researchers stated that CO_2 pipeline fluid pressures and temperatures range from 86.1 to 15.16 MPa and 12.8 to 43.3 ºC (Forbes et al., 2008), 10 to 15 MPa and 15 to 30 ºC (Patchigolla and Oakey 2013) and above 8.6 MPa (Kang et al., 2014). The minimum pressure of 8.6 MPa is above the critical pressure of pure CO_2 but the minimum temperature of 12.8 ºC is below 31.1 ºC, the critical temperature of CO_2. Temperature variations in CO_2 pipelines are not limiting considerations since CO_2 fluids remain in the dense phase (supercritical and liquid) if pressures are above critical values. The maximum and minimum pressures assumed in this study are 15 MPa and 10 MPa respectively. In declined pipelines, pressures may increase depending on fluid composition and angle of declination and pressure-reducing stations are installed to avoid encountering pressures that are too high along the pipeline. The heat transfer between the pipeline and the environment may also affect the temperature along the pipeline. In this study, there are no restriction on temperature, because a vapour phase will not form as long as pressures are above critical value.

2. Method

This paper compares the effect of common impurities in CO_2 fluids flowing in pipelines. Binary fluids of CO_2 and single impurities are simulated. Pressure changes, temperature changes, phase envelope, critical pressure and critical temperature were simulated with Aspen HYSYS (V.10), a chemical process simulator. Phase envelope was simulated with HydraFlash, a gas hydrate and thermodynamic prediction software. 90 mol % CO_2 and 10 mol % single impurity fluids are assumed. Note that only CH_4 impurities might constitute up to or above 10 mol %, mostly in enhanced oil recovery (EOR). In CCS, the total percentage of impurities is usually below 10 mol % except sometimes in oxy-fuel capture. The hypothetical pipelines have the properties listed in Table 1. Hypothetical fluids were created consisting of 90 mol % of CO_2 and 10 mol % each of N_2, CH_4, Ar, H_2S, O_2, SO_2, NH_3, CO, H_2 or H_2O. Each of these fluids were simulated separately and the results compared with that obtained with pure CO_2.

Table 1: Pipelines specification

Length (m)	50,000	Roughness (m)	4.57E-05
Elevation Change (m)	-300/0/300	Pipe Wall conductivity (W/(m×°C))	45
Outer diameter (m)	0.324	Inlet Temperature (°C)	33
Inner diameter (m)	0.289	Inlet Pressure (MPa)	15
Material	Mild Steel	Mass Flow (kg/h)	266,400

3. Effect on pressure

The effect of 10 mol % single impurity on the pressure changes in the CO_2 fluid flowing in a pipeline was simulated with Aspen HYSYS. This analysis considered three different pipeline scenarios. Pipelines with elevation change of 300 m, 0 m and -300 m from inlet to outlet. All impurities affected the pressure changes in the pipeline with the magnitude of the effect depending also on the pipeline elevation change. Figure 1 shows the results of the simulations. Positive values and the bars above zero represent pressure losses while negative values and the bars below zero indicate pressure gains. Pure CO_2, CO_2/SO_2, CO_2/H_2S, CO_2/NH_3 and CO_2/H_2O mixtures all increased in pressure in the declined pipeline. The magnitude of the effect of the impurities is different for the three pipeline scenarios. CO_2/SO_2 mixture, gave the highest-pressure gain in the downslope pipeline and the least pressure loss in horizontal pipelines but gave the second highest pressure loss in the uphill pipeline. Increasing the elevation change to just 350 m and slightly reducing the length to 46 km (for the simulation to run) will show that CO_2/SO_2 mixture causes the highest-pressure loss. Peletiri et al. (2017) concluded that H_2 and SO_2 caused the highest and lowest pressure losses respectively. This is only true for horizontal pipelines as changes in angles of inclination and declination changes the relative effect of impurities. The pressure behaviour in inclined pipelines can be explained with Eq(1) derived from Chandel et al. (2010). The second (elevation change) term on the RHS where density multiplies the gravity and elevation terms, will be negative for declined pipelines, zero for horizontal pipelines and positive for inclined pipelines. This, second term, therefore subtracts its value from the first (friction) term when Δz is negative, has no effect when the pipeline is horizontal and adds to the friction term when pipeline is inclined. Higher density fluids will have lower pressure losses or higher pressure gains in pipelines running downslope and higher-pressure losses in pipelines going uphill. The relative effect of the impurities on pressure changes was highly reduced for inclined pipelines. The pressure difference of pure CO_2 and CO_2/H_2 mixture (the highest pressure drop) is 1.44 MPa for the declined pipeline, 0.77 MPa for the horizontal pipeline and 0.44 MPa for the inclined pipeline.
In CO_2 pipeline transportation, neither pressure drop nor pressure gain is desirable. When there is pressure loss, booster stations are used to increase the pressure and when pressure increases, pressure-reducing

stations are used to control the pressure. In horizontal pipelines, H_2 impurity gave the highest loss while SO_2 gave the lowest. The relative effect of impurities on pressure also depends on the angle of elevation/declination in pipelines. Table 2 shows the percentage of deviation of pressure changes from pure CO_2 fluids in the three pipelines.

$$\Delta P = \frac{\rho\, f\, L\, v^2}{2\, D} + \rho\, g\, \Delta z \tag{1}$$

where ΔP is change in pressures between inlet and outlet (Pa), *f* is the friction factor, *L* is the length (m), *v* is the 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 Δ*z is* elevation change between inlet and outlet of pipeline (m).

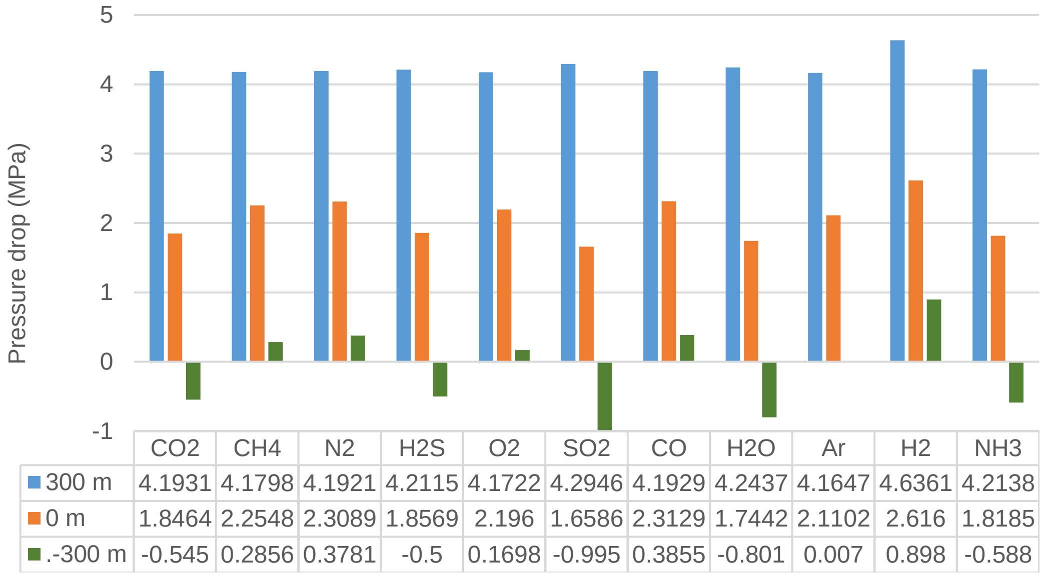

Figure 1: Pressure change along inclined, horizontal and declined pipelines

Table 2: Percentage of pressure change due to impurities in different elevation profiles

Elevation change	N_2	CH_4	O_2	Ar	SO_2	H_2S	CO	H_2	H_2O	NH_3
-300 m	168.2	151.4	130.3	100.5	82.12	8.21	169.7	263	46.7	7.85
0 m	25.01	22.08	18.93	14.27	10.15	0.54	25.23	41.67	5.53	1.52
300 m	0.05	0.33	0.52	0.69	2.43	0.43	0.02	8.83	1.22	0.5

4. Effect on temperature

The temperature change in the pipelines was simulated with Aspen HYSYS assuming ambient temperature of 25 °C and inlet pressure of 15 MPa. The pipeline is uninsulated and 33 °C assumed as the input temperature. The results show that H_2 resulted in the highest temperature loss while H_2O and SO_2 have the lowest losses (see Figure 2).

The CO_2 pipeline fluid remains in the dense phase irrespective of temperature if pressures remain above the critical value. Decrease in temperature is not desirable if the fluid is to remain in supercritical state. However, temperature is not a serious consideration as long as pressures are above the critical value. The advantages of transporting supercritical CO_2 over liquid CO_2 in pipelines is not quite clear. Liquid CO_2 has some advantages over supercritical CO_2 including use of pipelines with smaller diameter and thinner wall thickness (cost saving), the use of pumps instead of compressors (energy saving) (Teh et al., 2015) and higher density (increased volume flow) (zhang et al., 2006). Table 3 shows the percentage of temperature deviations from pure CO_2.

Table 3: Percentage deviation of temperature change due to 10 mol % single impurity

Impurities	H_2S	NH_3	H_2O	SO_2	Ar	O_2	CH_4	N_2	CO	H_2
% deviation	-3.4	-18.5	-26.3	-25.5	56.2	67.5	59.3	85.0	84.9	146.5

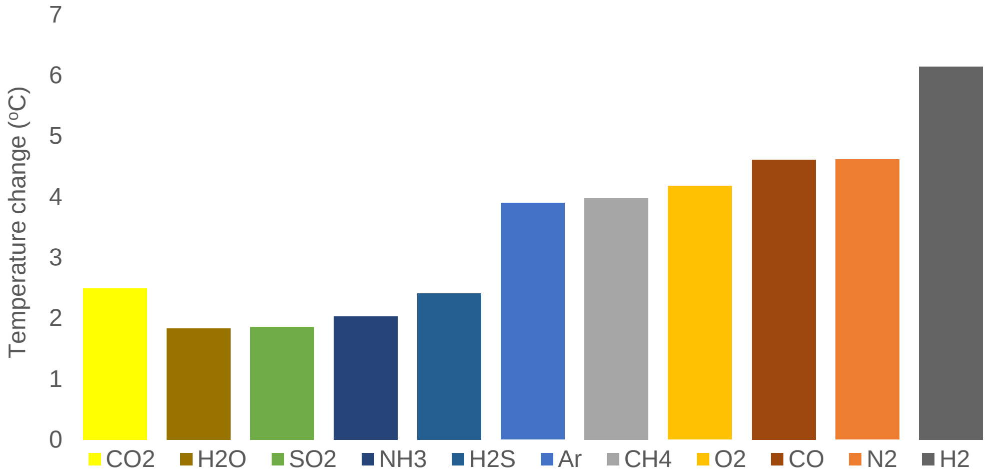

Figure 2: Temperature drop of CO_2 binary mixtures along the horizontal pipeline

5. Effect on phase envelope, critical pressure and critical temperature

Both Aspen HYSYS and HydraFlash were used to study the effect of impurities on the phase envelope of CO_2 fluids and both simulations gave similar results. H_2 created the widest two-phase region (Figure 3 insert) while H_2S created a negligible two-phase. The simulation of critical pressure and temperature with Aspen HYSYS showed similar results with the earlier publication by Peletiri et al. (2017) and is presented here in Table 4. All impurities caused an increase in critical pressure. An increase in critical pressure increases the energy penalty to compress the fluid to supercritical state. CO_2/H_2 mixture had the highest critical pressure while CO_2/H_2S mixture had the lowest critical pressure.

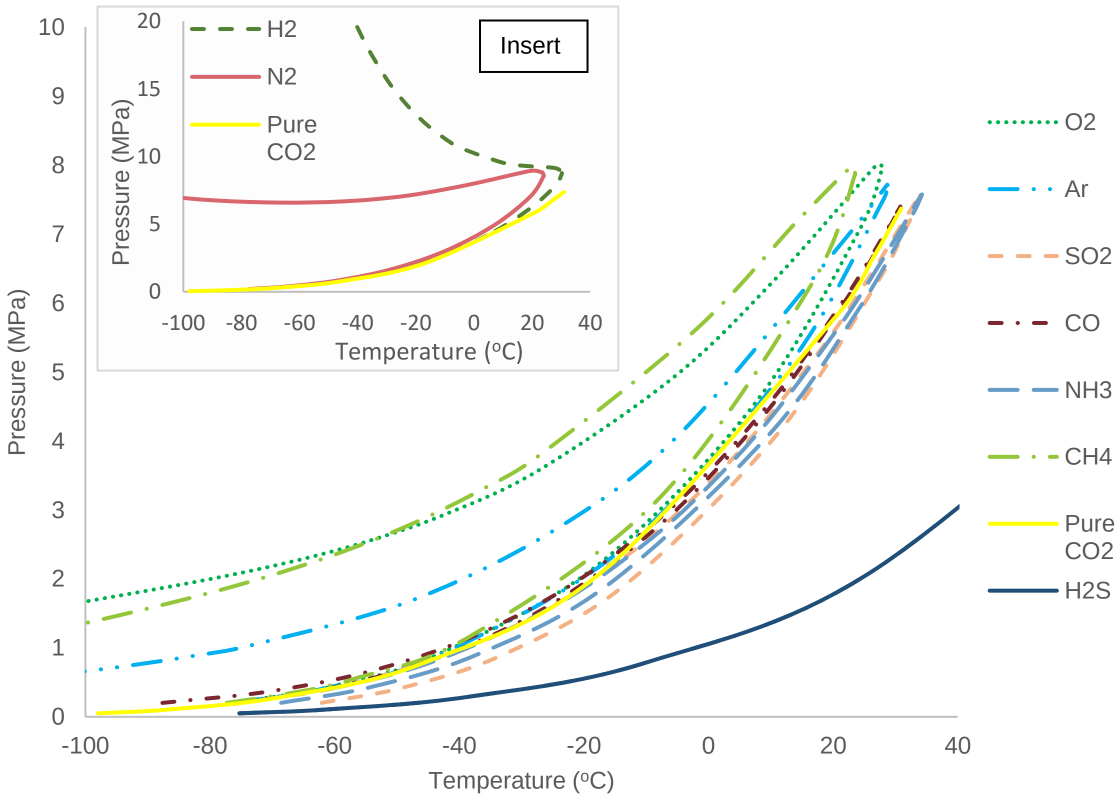

Figure 3: P-T diagram of CO_2 fluid with 10 mol % single impurity

Table 4: Critical pressure and critical temperature of 90 mol % CO_2 and 10 mol % single impurity

Impurity	Pure CO_2	H_2S	CH_4	NH_3	Ar	SO_2	O_2	CO	N_2	H_2O	H_2
Pc (MPa)	7.37	7.45	7.94	8.04	8.37	8.51	8.64	8.78	8.82	8.85	10.77
Tc (^oC)	30.9	33.29	23.25	41.91	15.6	49.84	24.4	23.4	23.61	24.8	28.3

The simulation of critical pressure and temperature with Aspen HYSYS is presented in Table 4. Only H_2S, NH_3 and SO_2 increased the critical temperature of the binary fluids. A low critical temperature is beneficial for supercritical transportation as it increases the temperature range of supercritical phase. Where the critical temperature is very high, heating may be required to raise the temperature to supercritical values. This may increase both the capital and operational costs of CO_2 pipelines. CH_4 impurity caused the lowest reduction of critical temperature and SO_2 impurity caused the highest increase of critical temperature.

6. Results and discussions

Results of two software used in the study of the effects of single impurities in CO_2 pipeline fluids were analysed for pressure changes, temperature changes, phase envelope, critical pressure and critical temperature. The pressure effect of impurities also depend on pipeline elevation change. For horizontal pipelines, the CO_2/SO_2 fluid has the highest pressure saving with 10.3 % less pressure loss than pure CO_2. This means that the CO_2 fluid with 10 mol % SO_2 would be transported for 10.3 % longer distance before the need for recompression compared to pure CO_2, resulting to power savings of about 10 %. H_2 caused 41.6 % higher pressure loss than pure CO_2, requiring recompression at about 70 % of the length for pure CO_2. When pressure drops to the minimum design value (usually slightly higher than the critical pressure), recompression is required. CO_2 pipeline fluids with 10 mol % H_2 impurity would therefore require about 141 % more compression power than pure CO_2. The impurities caused only small variations in temperature changes from pure CO_2. H_2 impurity resulted to the maximum temperature loss of 0.62 MPa representing 1.48 % deviation from pure CO_2. Most impurities reduced the critical temperature, expanding the temperature range for supercritical flow. Only SO_2, NH_3 and H_2S increased the critical temperature increasing the range for liquid phase flow. All impurities created two phase regions. Any component with critical pressure and temperature higher or lower than pure CO_2 will respectively form a two phase region expanding below or above the vapour liquid equilibrium (VLE) line of pure CO_2 (Race et al., 2012). H_2S created a negligible two phase region below the VLE line of pure CO_2 while H_2 created the widest two phase region above the VLE line of pure CO_2. A high critical temperature is desired for liquid phase flow while a low critical temperature is desired for supercritical flow. However, both supercritical and liquid phases are in the dense phase and can be handled under similar conditions.

Table 5 shows the percentage variations of parameters from pure CO_2 caused by 10 mol % single impurity. Critical temperature is omitted in the general grading of impurities in Table 5 because pressures are maintained above the critical value. Negative percentage values indicate improved performance due to the impurity while positive percentages indicate worse conditions. Arranged in increasing order of negative impact from left to right, Table 5 ranks the impurities. H_2S has the mildest effect while H_2 has the worst effect. Race et al. (2012) also concluded that H_2 resulted to largest pressure and temperature drops among the impurities studied. The classification of the impurities is only in general terms, as the inclusion or omission of any single parameter may change the relative ranking of the impurities. For example, including T_C in the analysis would move H_2S from position 1 to 3 or excluding phase envelope will move SO_2 from position 4 to 2. Generally, H_2S has the least impact and H_2 the worst impact.

Table 5: Grading of impurities in horizontal CO_2 pipeline

Parameters	1 H_2S	2 NH_3	3 H_2O	4 SO_2	5 CO	6 Ar	7 CH_4	8 O_2	8 N_2	10 H_2
Pressure change (%)	0.54	-1.6	-5.4	-10.3	24.9	14.1	21.6	18.9	24.8	41.6
Temperature change (%)	-0.04	-0.2	-0.28	-0.24	0.84	0.56	0.60	0.68	0.84	1.48
Phase envelope (%)	0	5.0	0	11.0	3.6	26.8	49.7	48.6	109.1	181.8
P_C (%)	1.1	9.2	20	15.5	19.1	13.6	7.7	17.3	19.6	46.1
Average % change	0.3	2.5	2.9	3.2	9.7	11.0	15.9	17.1	30.9	54.2

7. Conclusions

This paper has considered the most important parameters in CO_2 pipeline process design but does not claim to be exhaustive. A comparison of the impact each impurity has on CO_2 fluids flowing in pipelines is made and the following conclusions can be drawn.

- Effects of impurities on pressure also depend on pipeline elevation change along the pipeline.
- Deviations of pressure changes from pure CO_2 is smallest in pipelines with positive elevation (uphill pipelines) and largest in pipelines with negative elevation change (declining pipelines).
- H_2 has the worst effect on phase envelope, temperature loss and critical pressure.
- SO_2 has the worst effect on critical temperature.

Generally, H_2 was found to have the worse impact while H_2S was found to have the mildest impact on CO_2 pipeline fluids.

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References

Bare J., 2011, TRACI 2.0: the tool for the reduction and assessment of chemical and other environmental impacts 2.0. Clean Technologies and Environmental Policy, 13(5), 687-696.

Chandel M.K., Pratson L.F., Williams E., 2010, Potential economies of scale in CO_2 transport through use of a trunk pipeline. Energy Conversion and Management, 51(12), 2825-2834.

Forbes S.M., Verma P., Curry T.E., Bradley M.J., Friedman S.J., Livermore L., 2008, CCS guidelines for carbon dioxide capture, Transportation, and Storage. WRI, Washington DC, USA.

IEAGHG, 2014, CO_2 Pipeline infrastructure. IEAGHG, Stoke Orchard, UK.

Kang K., Huh C., Kang S.G., Baek J.H., Noh, H.J., 2014, Estimation of CO_2 pipeline transport cost in South Korea based on the scenarios. Energy Procedia, 63, 2475-2480.

Lazic T., Oko E., Wang M., 2014, Case study on CO_2 transport pipeline network design for Humber region in the UK. Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering, 228(3), 210-225.

Patchigolla K., Oakey J.E., 2013, Design overview of high pressure dense phase CO_2 pipeline transport in flow mode. Energy Procedia, 37, 3123-3130.

Peletiri S.P., Rahmanian N., Mujtaba I.M., 2017, Effects of impurities on CO_2 pipeline performance. Chemical Engineering Transactions, 57, 355 - 360.

Piippo S., Lauronen M., Postila H., 2018, Greenhouse gas emissions from different sewage sludge treatment methods in north. Journal of Cleaner Production, 177, 483-492.

Race J.M., Wetenhall B., Seevam P.N., Downie M.J., 2012, Towards a CO_2 pipeline specification: defining tolerance limits for impurities. Journal of Pipeline Engineering, 11(3), 173-190.

Teh C., Barifcani A., Pack D., Tade M.O., 2015, The importance of ground temperature to a liquid carbon dioxide pipeline. International Journal of Greenhouse Gas Control, 39, 463-469.

Zhang Z.X., Wang G.X., Massarotto P., Rudolph V., 2006, Optimization of pipeline transport for CO_2 sequestration. Energy Conversion and Management, 47(6), 702-715.