CO_2 Freezing in Low-temperature Distillation of Natural Gas

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Abstract. Natural gas is a source of low-carbon energy. However, increasing demand directs the exploration towards CO_2-rich gas reserves. Exploitation of CO_2-rich reserves requires the CO_2 to be separated and sequestrated. This study investigated low-temperature distillation to remove CO_2 to 50 ppm, to meet liquefied natural gas specifications. Distillation can produce natural gas and liquid CO_2 suitable for sequestration, but low-temperatures causes CO_2 freezing and require energy-intensive refrigeration. This study also investigated the thermodynamic behaviour of methane-carbon dioxide mixtures to understand conditions of which CO_2 freezing occurs during distillation. Aspen HYSYS was used to explore the feasibility of CO_2 removal considering binary, ternary and multicomponent mixtures and whether freezing occurs in the column. This study found that the condenser and first stage of the first column in a two-column separation system and some stages near the reboiler of the second column are vulnerable to freezing.

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Keywords Natural gas purification, low-temperature distillation, CO_2 removal, CO_2 freezing, thermodynamic validation

Introduction

Natural gas, which is predominantly methane gas, is a cleaner fossil fuel than coil and oil as it emits less carbon dioxide upon combustion. The use of natural gas may be key to reducing greenhouse gas emissions and improving energy security (Mohammad et al., 2021). Natural gas demand is expected to continue to rise and expected to be 14% higher in 2030 and 28% more in 2050 compared to demand in 2020 (Key World Energy Statistics, 2021). Higher natural gas production is essential to meet the increasing demand for natural gas in the future. Natural gas from gas wells contains contaminants such as carbon dioxide, sulphur dioxide, nitrogen and heavier hydrocarbons. Sour gas reserves contain a high percentage of carbon dioxide and/or sulphur. CO_2-rich gas reserves are distributed worldwide. The LaBarge field (USA) has up to 65% CO_2, Natuna (Indonesia) has up to 71% CO_2 and the Ying-Qiong basin (China) contains up to 71.5% CO_2 (Fenter & Hadiatno, 1996; Dai et al., 2009; Burgers et al., 2011). Transportation of natural gas depends on several factors including the distance, geographical area and economics of the process. Transporting natural gas via pipelines is more economical at shorter distances while liquefied natural gas is more cost-effective at longer distances.

The removal of CO_2 from natural gas is vital as CO_2 content may reduce the quality of the natural gas product by reducing its calorific value and causing corrosion in equipment (De Guido & Spatolisano, 2021). Removal of CO_2 also reduces the amount of CO_2 released on combustion. Also, natural gas requires a liquefaction temperature of -161°C where the presence of CO_2 may lead to CO_2 freezing in process equipment. Therefore, it is necessary to remove CO_2 to meet the liquefied natural gas specification of 50 ppm. The CO_2-rich gas reserves contain a significant amount of CO_2 which needs to be properly managed. It is imperative that CO_2 removed from natural gas is sequestrated to minimise the impact of CO_2 emission on the environment. Low-temperature distillation is explored in this study as it is applicable for a high concentration of CO_2 and could produce high-pressure liquid CO_2 which may reduce operating costs for CO_2 storage purposes. However, low-temperature distillation can cause formation of solid CO_2 which may affect the operation of a distillation column. ExxonMobil developed a controlled-freeze zone process to separate acid gases from methane that allows CO_2 solids to form deliberately in a controlled section. Berstad et al. (2012) developed a low-temperature process to reduce CO_2 concentration in a natural gas feed from 52.6 mol% to 50 ppm. In this scheme, pentane and hexane are recycled from the first column and added to the second and third columns to avoid CO_2 freezing. Maqsood et al. (2014) proposed a cryogenic process with the addition of butane to its second and third distillation column to purify feeds containing 50 mol% and 72 mol% CO_2 to 338 ppm CO_2. This process consists of three CO_2 removal distillation columns which was able to avoid the CO_2 solid formation region. Langè et al. (2015) proposed a low-temperature distillation process with two columns at 50 and 40 bar and implemented a ‘feed-splitting

technique' in the second column. This study also explored the thermodynamic behaviour of CH_4-CO_2 binary mixture at the two pressures to understand the behaviour of CO_2 solid formation.

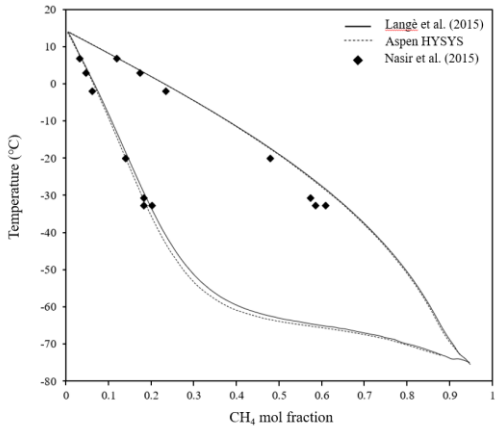
As discussed in the literature, low-temperature distillation can avoid CO_2 freezing by recycling and adding heavier hydrocarbons to the column and splitting the stream to be heated up and cooled down the feed before it undergoes distillation. From the thermodynamic studies, binary mixture CH_4-CO_2 has been studied extensively but studies exploring the multicomponent natural gas are limited. In this work, the operating range for distillation to purify CO_2 is explored and the phase equilibrium models for CO_2-CH_4 binary mixture accounting for CO_2 freezing were applied and validated against the data by Langè et al. (2015). Hence, proposing a conceptual distillation design to purify natural gas is the first step towards an energy-efficient and compact design suitable for offshore implementation.

Thermodynamic validation for CH_4-CO_2 binary mixtures

The thermodynamic framework needs to be developed as it will be the basis to find the operating conditions which are able to separate the high CO_2 content in natural gas to be purified to the liquefied natural gas specification of 50 ppm. Due to the extremely low CO_2 content to meet liquefied natural gas specifications, accurate thermodynamic models are needed to identify freezing. In this work, the experimental data and themodynamic model by Langè et al. (2015) is used to predict the accuracy of thermodynamic data in Aspen HYSYS software package and CO_2 freeze-out tool in Aspen HYSYS. The model is selected as a comparison in this study as they have developed a CO_2 removal process using low-temperature distillation and avoided CO_2 freezing in the distillation operations with pressures of 50 and 40 bar. The thermodynamic model and phase prediction using Aspen HYSYS are compared against published experimental data of Nasir et al. (2015), Davis et al. (1962) and Kurata and Im (1971). Pressures of approximately 40 bar and 50 bar with a temperature range of -110°C to 9.85°C are considered in the validation process.

The first validation has been made considering vapour-liquid equilibrium of the binary mixture at 50 bar as shown in Figure 1. The values calculated using Aspen HYSYS are very close to the thermodynamic model by Langè et al. (2015) but the bubble point curve calculated from Aspen HYSYS is slightly lower than the model. The average temperature difference between the model and Aspen HYSYS is approximately 2°C. The experimental data has good agreement with the model and Aspen HYSYS but data points at temperatures between -30.75°C and -32.8°C from experiments of Nasir et al. (2015) are below the predicted dew point curve. The solid-liquid region at 50 bar shows a slight deviation from 0.1 to 0.4 mol fraction. Meanwhile, the calculated CO_2 freeze-out temperature is slightly below the equilibrium curve of Langè et al. (2015) and the highest temperature difference is 2.33°C. The overall trend of CO_2 freeze-out temperatures using Aspen HYSYS follows the decreasing pattern of the model, indicating an excellent agreement. The results obtained from Aspen HYSYS are also close to the experimental data of the solid region which are available at high CH_4 mol fraction. It is also apparent from Figure 1 that the solid region and vapour-liquid region do not overlap which means that the vapour-liquid phase can exist without the presence of solid above the solid region.

a)



b)

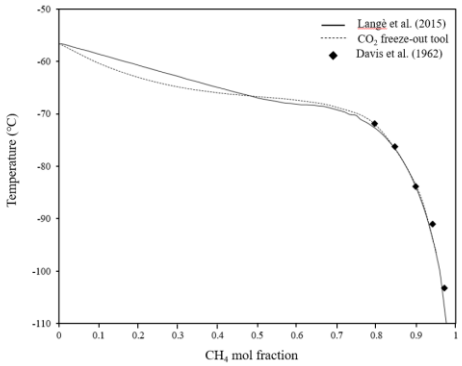


Figure 1. Phase equilibrium for binary mixture CH_4-CO_2 at 50 bar (a) Vapour-liquid equilibrium (b) Solid-liquid equilibrium

The vapour-liquid equilibrium of Aspen HYSYS calculation and thermodynamic model are close to the experimental data of Nasir et al. (2015). At 40 bar, the solid-liquid-vapour equilibrium lies between the vapour and liquid equilibrium curves. The solid line of the thermodynamic model also shows good agreement with experimental data of Kurata and Im (1971). The calculation of the solid region using the CO_2 freeze-out tool has excellent agreement with the model as shown in Figure 2.

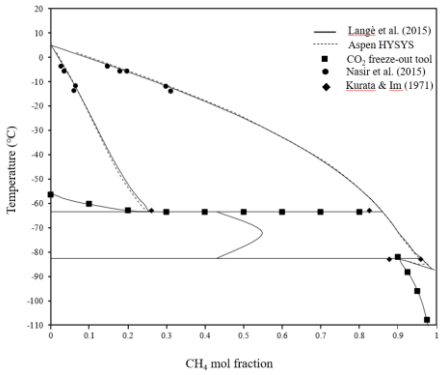


Figure 2. Solid-liquid-vapour phase equilibrium for binary mixture CH_4-CO_2 at 40 bar

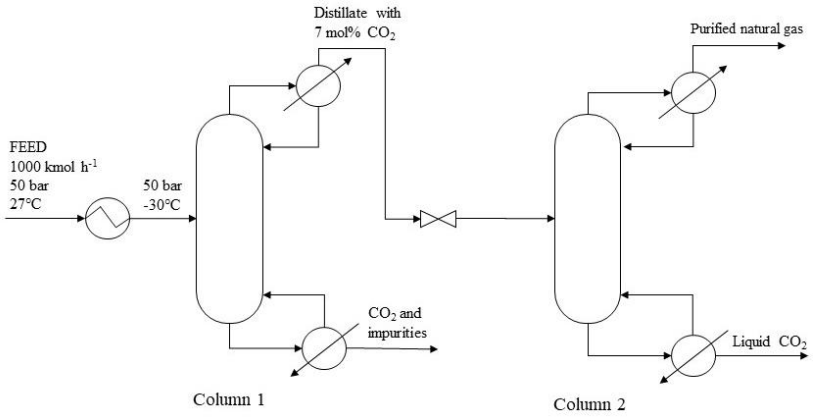
Note that vapour-liquid equilibrium at 50 bar is limited by the critical point of the mixture at about 0.935 CH_4 while at 40 bar the equilibrium is limited at a higher CH_4 mol fraction. The validation does not represent a real gas system as only CH_4 and CO_2 are considered. The thermodynamic equilibrium when impurities such as N_2 and heavier hydrocarbons are present needs to be further explored at high pressures and with a significant amount of CO_2. The results from the thermodynamic validation suggest that the Aspen HYSYS gives realistic predictions of phase equilibrium to be applied in the process development studies. The CO_2 freeze-out tool in Aspen HYSYS has not been widely explored and there are limited studies using the tool in literature. The validation against experimental data and thermodynamic model by Langè et al. (2015) gives confidence for it to be used in the process simulation.

Development of low-temperature distillation

This work simulates natural gas and impurities as three different mixtures to investigate the feasibility of the low-temperature distillation to purify natural gas to contain 50 ppm CO_2. The natural gas mixtures considered in this study are a binary mixture (30 mol% CH_4, 70 mol% CO_2), a ternary mixture (30 mol% CH_4, 65 mol% CO_2, 5 mol% N_2) and a multicomponent mixture (30 mol% CH_4, 60 mol% CO_2, 5 mol% N_2, 1.9 mol% C_2H_6, 1.3 mol% C_3H_8, 0.5 mol% i-C_4H_{10}, 0.5 mol% n-C_4H_{10}, 0.33 mol% i-C_5H_{12}, 0.33 mol% n-C_5H_{12}, 0.1 mol% n-C_6H_{14}). The CO_2 composition of the binary mixture is the highest to simulate the distillation process to represent a CO_2-rich gas reserve. The range of the

natural gas included N_2 and heavier hydrocarbons to investigate the effect of impurities in natural gas on CO_2 freezing. Process simulations of the mixtures were performed in a steady state using Aspen HYSYS v11 with the Peng-Robinson equation of state. In order to detect freezing, Aspen HYSYS has a CO_2 freeze-out analysis tool which could report the CO_2 freeze temperature, the phase it freezes from and indicates CO_2 solid presence in a stream. Peng-Robinson equation of state was chosen as it is compatible with the CO_2 freeze-out analysis tool.

The process developed in this study is illustrated in Figure 3. The feed streams containing CH_4 and other impurities are assumed to be available at 27°C, a high pressure of 50 bar and a molar flow rate of 1000 kmol h^{-1}. The feed gas is pre-treated to remove H_2O prior to the CO_2 removal process to avoid hydrate formation as the process involves low-temperature conditions. The pre-treated feed gas is pre-cooled before entering the first distillation column. In the first column, which is a bulk removal column, the concentration of CO_2 was reduced from as high as 70 mol% to 7 mol%. The vapour distillate is then throttled to 40 bar and CO_2 is further purified to obtain 50 ppm CO_2 in the distillate of the second distillation column. The bottom stream of both distillation columns contains CO_2 and other impurities at high pressure which product can be utilized for sequestration. The CO_2 content of the intermediate CO_2 distillate presents a degree of freedom and was determined based on the vapour-liquid phase equilibrium at 50 bar. Vapour-liquid equilibrium of binary mixture CH_4-CO_2 at 50 bar is limited by the critical point of the mixture and was taken as the basis for the intermediate CO_2 mol fraction. The distillate of the second column is specified to be at a maximum of 50 ppm. The CH_4 recovery in the natural gas stream is specified as 99.9% in both columns. Ten stages were specified for the first column and twenty stages for the second column. Since a higher degree of separation was required in the second column to achieve the higher purity requirement, an increased number of stages is necessary to improve the separation.



	Column 1	Column 2
Pressure	50	40
Distillate phase	Vapour	Vapour
Number of stages	10	20
Feed stage	5	10
Column Specification		
CO_2 mole fraction in top product	0.07	5×10^{-5}
CH_4 recovery in top product	0.999	0.999

Figure 3. Distillation sequence to purify CO_2-rich feed to 50 ppm

Results and discussion

The simulations were able to remove CO_2 down to 50 ppm in two distillation columns The processing feasibility of CO_2-rich gas to achieve 50 ppm CO_2 in the product was demonstrated at 50 and 40 bar. While the process is feasible, N_2 and heavier hydrocarbons in the feed stream changes the freezing behaviour inside the distillation column. The summary of the simulation results of the low-temperature distillation process is illustrated in Table 1, which shows that the presence of N_2 and heavier hydrocarbons lowers the condenser temperature.

The simulation of a binary mixture is well predicted by the thermodynamic validation and no CO_2 freezing occurred in the first column, but CO_2 freeze-out is expected based on the thermodynamic validation and occurred in the second column. As shown in Figure 4, the stage temperature at stage 1 did not cross freeze temperature but the difference is very close with a ΔT of only 1.4°C. Moving down the column, the temperature difference increases as a higher concentration of CO_2 is present throughout the column. In the second column, CO_2 freezing occurs in the stripping section specifically on stages 18 and 19. Based on the temperature profile of the second column in Figure 5, the top section of the second column has a large temperature difference between the stage temperature and freeze temperature, but it gets smaller in the stripping section. On stage 17, the temperature difference is 7.8°C but decreased to -17°C at stage 18 and -3.2°C at stage 19.

Table 1. Distillation simulation results for binary, ternary and multicomponent mixtures

	Binary mixture		Ternary mixture		Multicomponent mixture	
	Column 1	Column 2	Column 1	Column 2	Column 1	Column 2
Reflux ratio	13.2	8.4	5.1	4.7	6.8	4.8
Distillate flow rate (kmol h^{-1})	322.3	299.4	376.0	349.4	381.4	349.4
Condenser temperature (°C)	-73.8	-87.3	-78.9	-94.3	-75.5	-94.3
Reboiler temperature (°C)	14.3	2.2	14.3	2.7	15.6	-0.38
Condenser duty (MW)	2.880	1.802	2.690	1.352	3.850	1.379
Reboiler duty (MW)	3.241	1.792	2.800	1.297	4.137	1.298
CO_2 freezing (stage)	None	18 and 19	Condenser	18	Condenser	None

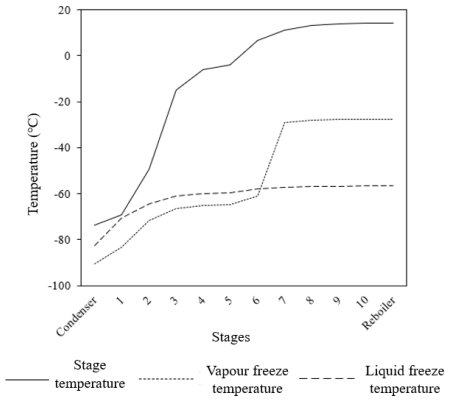


Figure 4. Temperature profile for binary mixture of first column at 50 bar

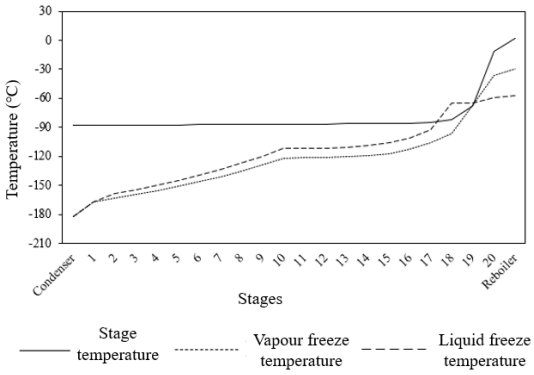


Figure 5. Temperature profile binary mixture of the second column at 40 bar

Further simulation of the ternary mixture and the multicomponent mixture was investigated. The simulation revealed that the presence of N_2 increases the CO_2 freeze-out temperature. For example, in the binary mixture, the CO_2 freeze temperature from the vapour phase is -90.43°C, while in the ternary mixture with the presence of 5 mol% N_2, the CO_2 freeze temperature from the vapour phase increases to -74.66°C. The increasing CO_2 freeze-out temperature causes the column to be more susceptible to CO_2 freezing, especially in the low-temperature stages such as in the. Due to the

presence of N_2, the formation of CO_2 solids occurs at the condenser stage of the first column and the stripping section of the second column. For multicomponent mixtures, CO_2 freeze-out occurs in the condenser of the first column while the second column indicates no temperature crossover. The presence of hydrocarbons depresses the freezing point which allows the column to operate at low temperatures safely and widens the temperature gap between stage temperature and freeze temperature.

The condenser and first stage of the first column and a few stages towards the reboiler of the second column have a high possibility of CO_2 solid formation, indicated by the low-temperature difference between stage temperature and freeze-out temperature. Although freezing does not occur in the second column in the presence of hydrocarbons, the minimum temperature difference is very narrow at less than 1℃. The small temperature gap suggests that future process development should also be aware of the vulnerability of the stages in the stripping section of the second column toward CO_2 freezing.

Conclusions

This study sets out to explore the operating conditions of distillation for CO_2 removal from CO_2-rich natural gas and validate the phase equilibrium models for CH_4-CO_2 binary mixture at 40 and 50 bar. The thermodynamic model of Langè et al. (2015) and that from Aspen HYSYS are validated against experimental data. The CO_2 freeze-out tool in Aspen HYSYS was used to predict the solid boundary of the phase equilibriums. The results indicated that the thermodynamic model and Aspen HYSYS showed excellent agreement with experimental data. This validation indicated the reliability of using Aspen HYSYS for the low-temperature distillation process.

Simulation of the low-temperature distillation was conducted in Aspen HYSYS for a binary mixture, a ternary mixture and a multicomponent mixture. The simulation showed that obtaining 50 ppm CO_2 is feasible using a sequence of two distillation columns at 50 and 40 bar. One of the significant findings to emerge from the simulation is the understanding of CO_2 freezing in the columns. CO_2 freezing is identified in both columns, in which the condenser and first stage of the first column and stripping section of the second column are the most vulnerable to CO_2 freezing. The present study lays the groundwork which will be useful for future research to develop a CO_2 removal process which can purify to 50 ppm CO_2 and avoid CO_2 freezing in the distillation. Future work will study the pressure range to avoid CO_2 freezing in both distillation columns by varying the specifications and the addition of heavier hydrocarbons into the column following Berstad et al. (2012). Subsequently, further studies will need to develop a process with the aim of energy efficiency and investigate the intensification of columns to be implemented in offshore operations.

Acknowledgements
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