

Identification and Quantification of CO₂ Solidification in Cryogenic CO₂ Capture from Natural Gas

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ABSTRACT

The composition of natural gas strongly depends on the geological conditions and depth of the gas well. Presently, CO₂ content in the discovered natural gas reservoirs is up to 90%. Prior to customer use, the amount of CO₂ needs to be reduced. Cryogenic CO₂ capture is one of the emerging technology for CO₂ capture from natural gas. Comprehensive knowledge of vapor-liquid, vapor-solid, and solid-liquid equilibria for the gaseous mixture is required for designing cryogenic separation processes for CO₂ capture from its gaseous mixtures. No thermodynamic phase data is available for the highest CO₂ content N.G mixture. The present work is an effort to generate the thermodynamic data for CO₂ capture at low temperatures. CO₂ solid phase identification and quantification need to be studied for the CO₂-CH₄ binary mixture. In this work, four samples of natural gas having CO₂ content 40%, 60%, 75% and 90% were selected for simulation through Aspen HYSYS. Pressure-temperature data and temperature-composition data for the binary mixtures were predicted using PR EoS for CO₂ phase identification and quantification respectively. Simulation for temperature-composition phase envelope was carried out at different pressures i.e. 10, 20, 30, and 40 bar. The operating region selected from the P-T phase envelop was from 1 to 40 bars. From the temperature composition graphs, it was concluded that temperature for the maximum CO₂ capture in S-V region at 10, 20, 30, and 40 bar is -95, -90, -75, and -70 °C respectively.

Keywords: Natural gas; carbon dioxide; cryogenic process; Aspen HYSYS; Peng Robinson.

INTRODUCTION

Due to the alarming situations of the energy crisis, scientists focused on exploring the undiscovered natural gas reservoirs having high CO₂ content [1]. Although natural gas is considered as a clean fuel, still the quality of natural gas strongly depends upon the geological conditions of the gas well [2]. Natural gas may have many impurities among which CO₂ is the major greenhouse gas. CO₂ content in natural gas may vary from 20% to 90% [3]. High CO₂ content in natural gas decreases its calorific value and also causes corrosion problems in the processing equipment. Using raw natural gas with high CO₂ content is a threat to the environment. Due to the increasing global warming decline of anthropogenic CO₂ emissions becomes a primary issue. So, it must be processed for

purification before the customers use. Many technologies have been used for CO₂ capture. Figure 1 shows the technologies used for CO₂ capture.

As by the perception that energy demand for the cryogenic process is very high, at the start of 20th century cryogenic separation technology was not given any significant attention. The use of some better technologies has made cryogenic CO₂ capture process economical and energy efficient [4]. Therefore, in the mid of 20th century cryogenic processes has gained considerable importance. Cryogenic CO₂ capture technology is now considered dominant over the other technologies. because there is no chemical reaction involved in it, it is applicable for high CO₂ contents, applicable at any pressure, due to the possible offshore application, and low hydrocarbons losses [5].

In the cryogenic process, the high triple point of CO₂ makes the CO₂ solid formation possible under any operating conditions. Blockage of process equipment, plant shutdowns, and safety hazards are related to these unexpected CO₂ solid formation in natural gas cryogenic processing [6]. Due to both liquid and solid CO₂ formation throughout the process, the detailed thermodynamic study is very crucial for the cryogenic CO₂ capture from natural gas. Achieving more efficient and economical results in CO₂ capture than any other conventional methods compelled the scientists to have proper phase equilibrium data of CO₂ binary and multicomponent mixtures [7]. At the end of 20th century with the rapid increase in cryogenic processing of hydrocarbons, a high increase in demand for an accurate thermodynamics data for binary and multicomponent mixtures of natural gas was observed. This demand becomes a basis for the design of the experimental equipment and process for a specific separation process [8].

Researchers examined V-S and V-L equilibrium data for different mixtures of CO₂ with other hydrocarbons, which is useful for the separation of CO₂ from any gaseous mixture by desublimation or liquefaction [9]. Proper prediction of CO₂ phase is crucial for the enhancement of CO₂ capture efficiency by the solid and liquid quantification in the cryogenic process. Precise application of phase envelop also reduces the operational difficulties in cryogenic beds, hence making the phase equilibria crucial in designing the separation process.

Phase equilibria are the detailed graphical study of different phases of a material with respect to some thermodynamic properties [10]. Temperature, pressure, specific volume, specific enthalpy, or specific entropy may be graphed in phase diagrams. Phase equilibria diagrams are of two types, two-dimensional graph, and three-dimensional graph. The two-dimensional graph has one thermodynamic quantity on the horizontal and other on vertical axes while 3-dimensional graphs show three thermodynamic quantities on its three axes.

Figure 2 shows the qualitative phase diagram for a binary gaseous mixture. In Figure 2 lines BDF, FH, and FG represent the 3-phase locus. But in FH and FG methane freezes as a separate solid phase. The frost line is represented by line AB. Line BC shows the dew point curve which is the boundary between the vapor phase and two-phase V-L region. Line CD is the bubble point line or the boundary between liquid and V-L region. The critical point of the mixture is Point C. Line DE shows the freezing line.

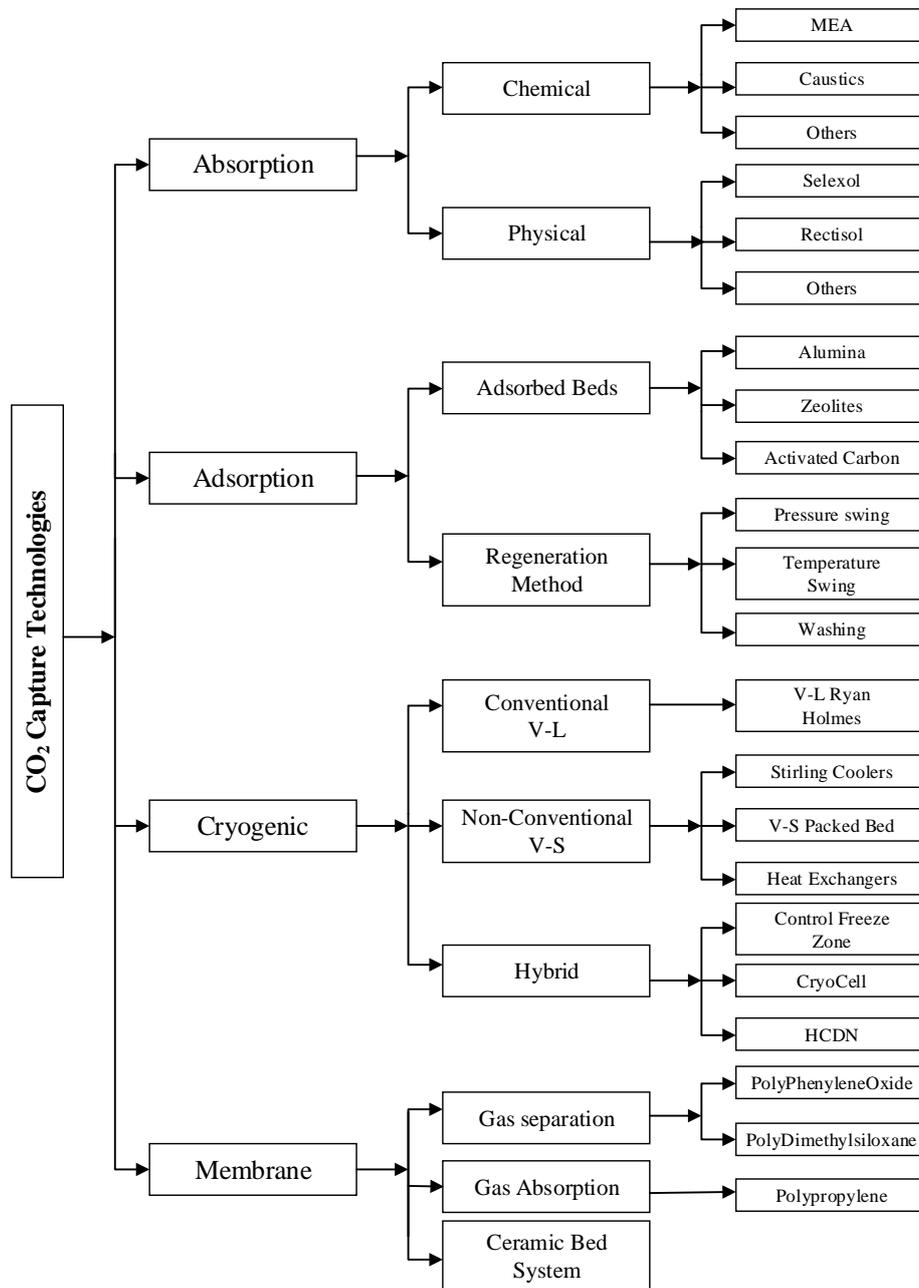


Figure 1. CO₂ capture technologies.

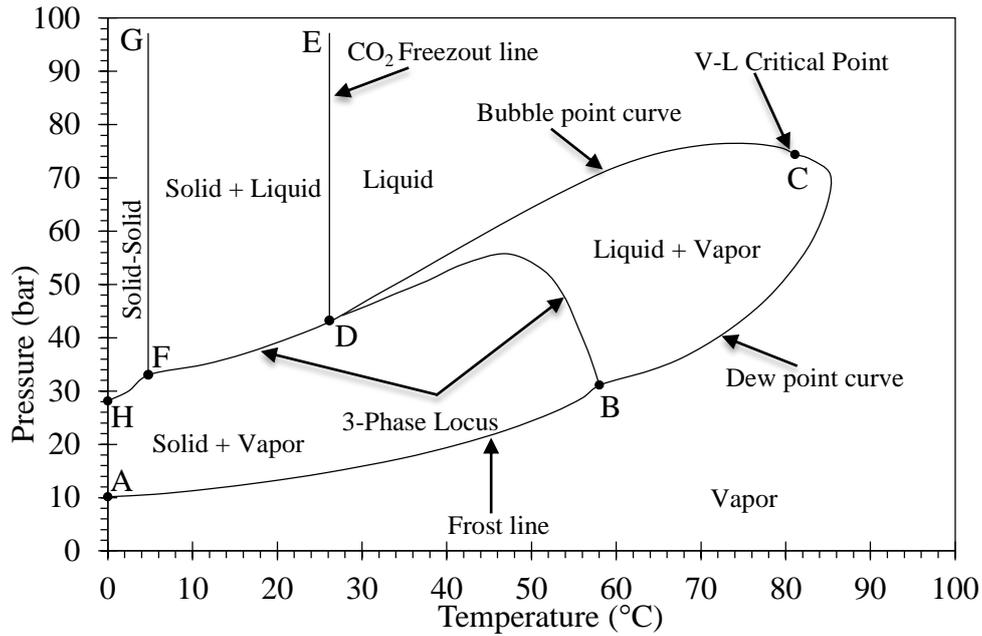


Figure 2. Qualitative P-T phase envelop [11].

Donnelly and Katz [12] obtained experimental data for the CH₄-CO₂ binary mixture. They analyzed the critical locus of the mixture by finding the phase diagram of four different composition mixtures in the vicinity of the critical point temperature. For each of the four mixture volume percent and pressure of the liquid was observed at equilibrium. The critical temperature and pressure for the four mixtures are given in Table 1. V-L phase equilibria was also studied for seven isotherms at different temperatures i.e. -1.67, -13.33, -31.67, -49.44, -53.89, -63.89, and -73.33 °C, and pressure ranges from 6.8 to 68 atm. The author also reported three phase loci at which all the three phases of CO₂ are in equilibrium and investigated the liquid composition at the triple point at all pressures.

Table 1. Critical conditions for CH₄-CO₂ system [12].

Mole fraction CH ₄	Critical Temp[°C]	Critical Pressure [atm]
0.00	31.11	73.01
0.12	13.33	82.67
0.295	0.56	85.06
0.457	-16.67	83.36
0.82	-51.11	67.02
1.00	-82.22	45.79

The phase composition at lower temperature was observed by linking down the data to -101.11 °C. Donnelly and Katz pointed out a eutectic point after extrapolating the system down to -98.33 °C, thus there will be no solid formation below 4% CO₂ at any pressure.

Pikaar [13] in 1959 used two different apparatus to examine the CH₄-CO₂ binary system. He used isochoric apparatus and non-sampling approach for gaseous mixtures having 1% to 20% CO₂ content. V-L, V-S, and L-S equilibria of CO₂ were determined by measuring boiling, dew and frost points. A saturation cell apparatus with a sampling

technique was used for determining the vapor and liquid composition in equilibrium with the solid CO₂ at a pressure up to 100atm and a temperature range of -63 to -160 °C. V-S equilibria were shown analytically by an equation involving three temperature-dependent parameters. By comparison with Donnelly and Katz data at low temperature he found a disagreement at -67 and -73 °C. Furthermore, he observed that at the lower temperatures the divergence with Donnelly and Katz data is about 4 atm. He also showed that the triple-point locus determined by Donnelly and Katz must be incorrect below -67 °C.

Davis et al. [14] in 1962 presented experimentally the phase behavior of a binary mixture of CH₄-CO₂ at three phase locus. Kohn and Kurata [15] in his research presented the equipment used by Davis et al. He further revealed P-T phase diagram along the three-phase locus. The temperature range in his study was from CO₂ triple point to -176.05 °C. Davis compared his three-phase data with Donnelley's data and found dissimilarity in the two data below -67.78 °C. Davis also refused the presence of eutectic in the CH₄-CO₂ binary system as shown by Donnelly and Katz. Davis found a good comparison with the Sterner's data excluding the highest temperature of Sterner's data.

Ali et al. [5] experimentally studied cryogenic CO₂ capture from the binary mixture of CO₂-CH₄ in cryogenic packed beds. They explored energy consumption minimization for countercurrent flow of feed gas and refrigerant. They investigated the effect of different operating factors like the initial temperature of the cryogenic bed, feed composition, and feed flow rate on energy requirement. The amount of energy required per kilogram of CO₂ recovery for conventional distillation was 1,472 kJ which was reduced to 810 kJ in cryogenic packed bed for the same feed composition.

Limited data is available for the validation of the Aspen HYSYS simulator. Thermodynamic phase behavior of natural gas with high CO₂ content need to be studied. Also, research work needs to be done for solid identification and quantification of the natural gas mixture. This is purely simulation work based on the binary CO₂-CH₄ mixture. Validation of Aspen HYSYS simulator with Peng Robinson property package is also done to investigate its reliability for the data prediction. Thermodynamic phase data for four natural gas samples are generated. Phase envelope for the natural gas with highest CO₂ content is also discussed.

METHODOLOGY

As natural gas from different gas wells has different CO₂ concentrations and may vary up to 90%. Four natural gas compositions with different CO₂ concentration were selected for this work. The composition of the gas samples that were used in this research work are shown in Table 2.

Table 2. Natural gas composition

N.G sample	Mol% CO ₂	Mol% CH ₄
1	40	60
2	60	40
3	75	25
4	90	10

To find out the different phase conditions for CO₂ capture from natural gas of the above-mentioned compositions, it was simulated in Aspen HYSYS version 8.0 licensed by Universiti Teknologi Petronas, Tronoh, Perak Malaysia. Peng Robinson property package was used. For P-T phase envelop the three-phase locus data was taken from Davis et al. [14] research. A gaseous stream containing CO₂ and CH₄ was selected in Aspen HYSYS. The composition of the stream was varied according to the compositions given in Table 2. The utility “stream analysis” was used to find out the dew point bubble point conditions. The pressure was then plotted against temperature to obtain the required V-L phase envelope. For finding the CO₂ freeze-outline the CO₂ freeze-out utility was used. For each natural gas sample, the CO₂ freeze-out temperature was observed at different pressures. By plotting the pressure against temperature CO₂ freeze-out line was obtained. The available experimental S-L-V data obtained by Davis et al. was used in this research work.

For the T-xy phase diagram, the dew and bubble point temperatures were generated through Aspen HYSYS at different pressures and different compositions. At a specific temperature a unique T-xy graph is obtained. For example, to predict the T-xy data for 10 bar pressure, the composition of the gas stream was changed from 0% CO₂ to up to 100% CO₂ at a gap of 10% CO₂. At each concentration the temperature at total vapor and total liquid is noted. The obtained temperatures were then plotted against CO₂ concentration to get the T-xy plot. From the T-xy plot, we can quantify the amount of CO₂ in the top and bottom streams. This study is about thermodynamic data generation for maximum CO₂ capture.

Validation of Aspen Hysys

Before extracting data through Aspen HYSYS, its use for the binary system was validated by comparing the data generated through HYSYS with Donnelly’s experimental data. Figure 3 shows the comparison of the experimental data obtained by Donnelly and Katz with the three-phase data generated by Aspen HYSYS. An excellent agreement was found between the HYSYS generated data and the experimental data of Donnelly. The maximum percentage deviation was found only $\pm 3\%$.

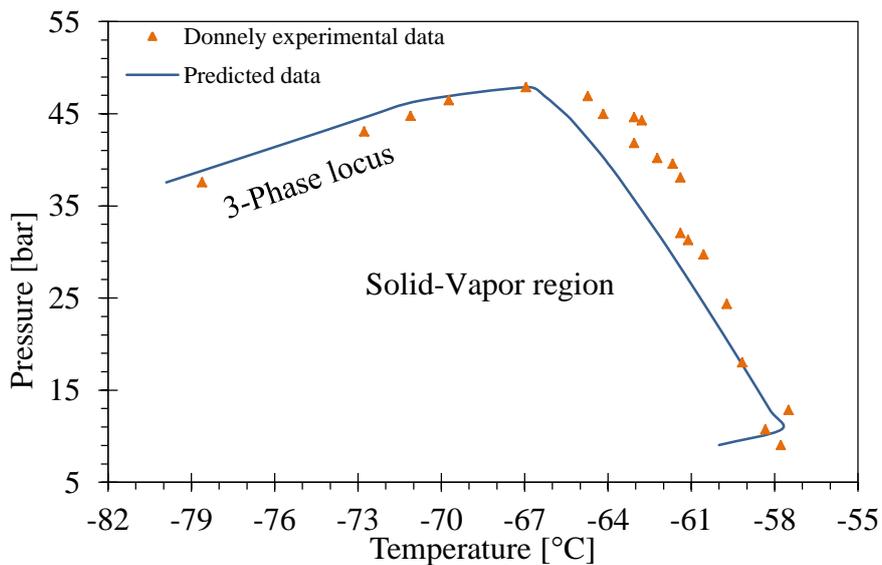


Figure 3. Validation of Aspen HYSYS with Donnelly's data [12].

Table 3 shows the T-xy validation of Aspen Hysys simulator. Experimental T-xy data from Donnelley's research at 68.9476 bar was regenerated using the simulator. Simulation data was obtained at five different temperatures including 15.56, -6.67, -15.56, -17.78, -28.89, and -40 °C. CO₂ and CH₄ composition in the liquid phase were obtained and then compared with the experimental data as shown in Table 3. An excellent agreement was obtained between the two set of data showing the reliability of the simulator.

Table 3. T-xy validation of Aspen Hysys with Donnelley's data.

P (bar)	T (°C)	Experimental		Predicted	
		x_{CO_2}	x_{CH_4}	x_{CO_2}	x_{CH_4}
68.9476	-28.89	0.700	0.300	0.675	0.325
68.9476	15.56	0.830	0.170	0.801	0.199
68.9476	-40.00	0.250	0.750	0.268	0.732
68.9476	-6.67	0.570	0.430	0.586	0.414
68.9476	-17.78	0.450	0.550	0.423	0.577

RESULTS AND DISCUSSION

Solid Identification

Process temperature and pressure conditions have a great influence on the phase diagram of the CH₄-CO₂ mixture. In this research, phase equilibria were studied for observing this influence. Simulation for obtaining temperature composition (T-xy) data for CO₂ quantification was done at four set of pressures starting from 10 bar to 40 bar with a gap of 10 bar. The vapor-liquid composition at each temperature was compared to each other to find out the optimum composition. Our desired composition is to get maximum CH₄ and minimum CO₂ in vapors, and maximum CO₂ and minimum CH₄ in bottom products.

Using the P-T diagram obtained through HYSYS the optimum conditions of pressure and temperature for the experimental works can be selected. Figure 5 shows the results of the P-T phase envelop for the four samples of gases having shown in Table 2.

It can be seen from Figure 4 that S-V-region for the binary CO₂-CH₄ starts from about -180 °C and exists up to -58 °C. On the right side of the S-V region is vapor region at low pressures, while by increasing the pressure the vapor will enter the two-phase L-V region. Above the two-phase L-V region is single Liquid region. Decreasing temperature of the liquid phase it will cross the CO₂ freeze out and enters the solid region. Figure 4 helps in identifying the solid formation in the cryogenic CO₂ capture process from natural gas.

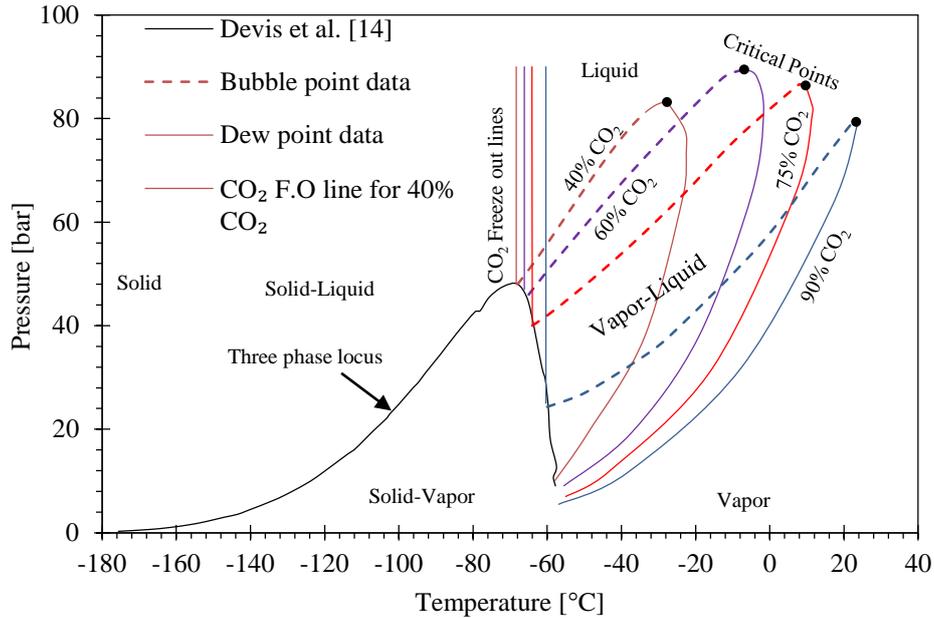


Figure 4. P-T diagram for CO₂-CH₄ binary mixtures

Solid Quantification

T-xy diagram obtained through Aspen HYSYS was used for the quantification of solidification in the cryogenic process. At reduced pressures, the S-V section is large and hence supports CO₂ capture at reduced temperature. Figure 5 (a) - (d) describes the effect of pressure on temperature-composition phase envelop for the natural gas mixtures shown in Table 2. The curve in these figures represents the bubble point data while the bottom curve represents the dew point data. Vapor and liquid regions in the system exist above the dew point line and below the bubble point curve. The area in between the two horizontal lines A and B in the T-xy diagram represents the S-V region.

Figure 5 (a) shows the T-xy diagram for 10 bar pressure. The graph shows the Solid-Vapor (S-V) band along with its initial and final temperatures. The initial and final temperatures for S-V region at 10 bar are -58 °C to -128 °C respectively, which indicates that for a high range of temperature the system can be in S-V region. It shows that low pressure supports CO₂ solidification. Figure 5 (b) shows the T-xy diagram for 20 bar pressure. From the graph, it is observed that the S-V band width is decreased as compared to the T-xy at 10 bar. The graph shows that at 20 bar pressure the vapor-solid region will start at -60 °C and this region exists until the temperature reaches almost -108 °C.

Figure 5 (c) shows the T-xy diagram for 30 bar pressure. Increasing the pressure of the system increases the solidification temperature, but the band width for solidification has been decreased. Compared to 10, and 20 bar, it is obvious that in case of 30 bar pressure S-V region lies in between -90 °C and -60 °C. From the graph, it can be seen that the S-V band width is decreased as compared to the T-xy at 10 bar. Figure 5 (d) shows the T-xy diagram for 40 bar pressure. Further increase in the pipeline pressure further decreases the vapor-solid bandwidth, while the vapor-liquid region is increased. While decreasing the temperature vapor-solid region will start at -62 °C and ending temperature for this region is -75 °C Compared to 10, and 20 bar graph it is

obvious that in case of 30 bar pressure S-V region lies in between -90 °C and -60 °C. From the graph, it can be seen that the S-V band width is decreased as compared to the T-xy at 10 bar.

In Figure 5 the temperature ranges for S-V region is taken from the P-T data of Davis et al. [14] plotted in Figure 4 which shows that by increasing pressure the temperature range for the vapor-solid region decreases.

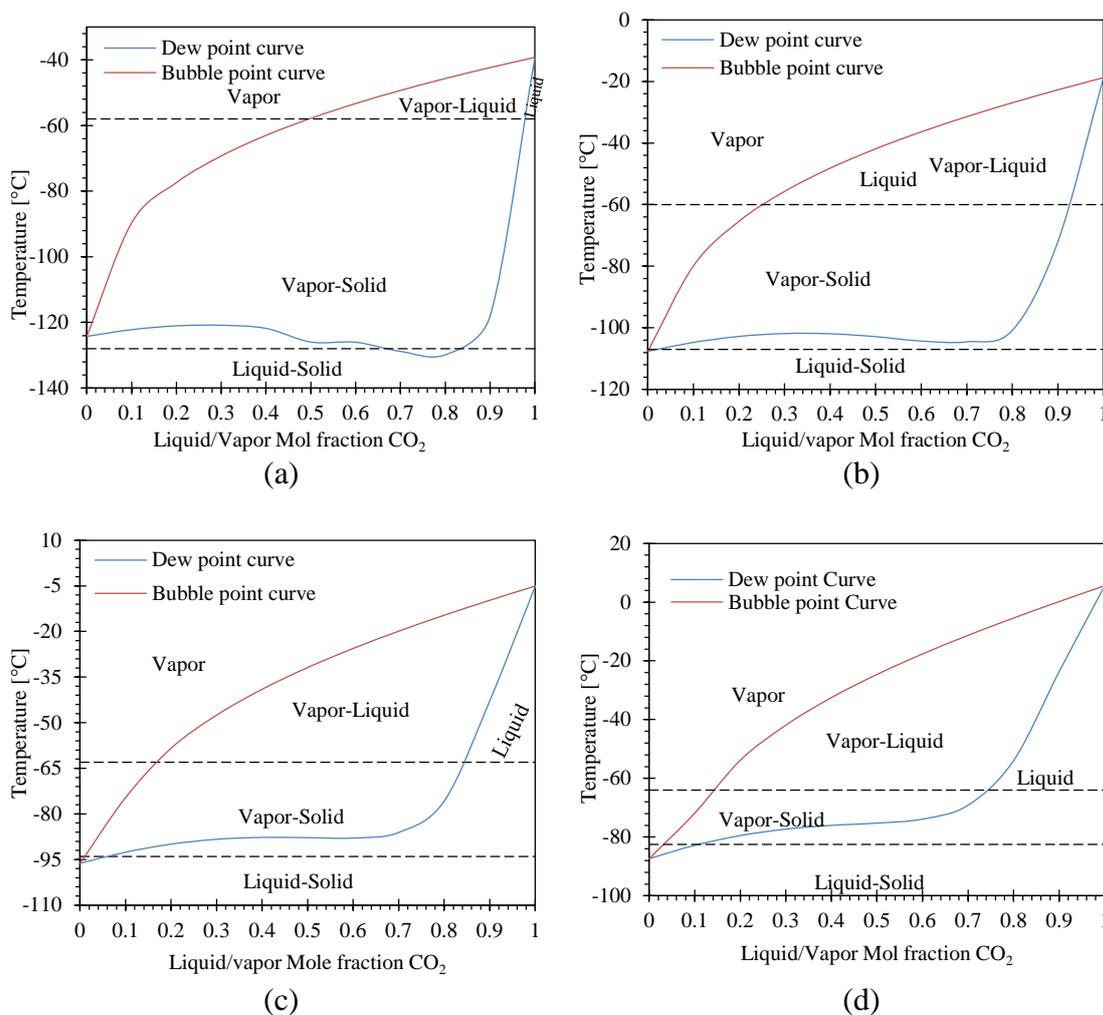


Figure 5. T-xy diagram for a binary CO₂-CH₄ mixture at (a) P=10 bar, (b) P=20 bar, (c) P=30 bar and; (d) P=40 bar.

CONCLUSION

From the simulation work discussed above Aspen Hysys simulator with PR property package was validated and different phase conditions for cryogenic purification of natural gas are obtained. It will help the researchers in the designing of a cryogenic process for CO₂ capture from natural gas. This research work provides data for CO₂ capture hence it will also be helpful in reducing the global warming.

It is recommended to study the phase equilibria for multicomponent CO₂ mixtures with hydrocarbons. The effect of the addition of higher hydrocarbons on CO₂-CH₄ phase envelope also needs to be studied.

ACKNOWLEDGMENT

We are thankful to the CO₂ Research center [CO₂RES], department of chemical engineering, Universiti Teknologi PETRONAS for providing the necessary support in the research.

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