



CO₂ Frost Phenomenon for Binary System of Methane-Carbon Dioxide Mixtures

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Abstract. In the present study, the CO₂ frost phenomenon of CH₄-CO₂ mixtures has been observed for the rational design of CO₂ removal from natural gas using a controlled freeze out area. The CO₂ frost conditions were estimated using the ZNE method and process simulation software (Aspen HYSYS® v7.3). The experiment was carried out using a double pipe heat exchanger (DPHE) with the concentration of CO₂ in the gas mixture at 5 and 10% and pressure of the gas mixture from 1 to 20 bar. The equilibrium temperature predictions of the ZNE method and the process simulation software only had a slight difference, with a magnitude deviation of less than 1% for pressures below 20 bar and 3% for pressures in the range of 20-30 bar, respectively. In the experimental study, CO₂ frost formation was detected at pressures of 1, 5, 10 and 20 bar. The locations of the initial CO₂ frost formation were determined using a pressure drop indicator associated with the predicted frost temperatures obtained from the ZNE method and the process simulation software. For all studied variables, the locations of initial CO₂ frost formation were found at 0.887-1.531 m from the inlet.

Keywords: CO₂ removal; controlled freeze out area; cryogenic technology; equation of state; natural gas.

1 Introduction

Indonesia's natural gas resources are very large and scattered in various areas. Active natural gas wells are located in several places, such as Natuna, South Sumatra, West Java, East Java, East Kalimantan, Central Sulawesi, and Papua. Many technologies are available for transmitting natural gas, such as compressed natural gas (CNG), liquefied natural gas (LNG) and piping. Recent energy demands in Indonesia are getting more diverse with locations in remote areas that cannot be serviced by conventional pipes. Based on this, the transmission of gas in the form of LNG is still the most economical method for natural gas. In addition, there has been increasing demand for the use of natural gas as more efficient and cleaner fuel. Natural gas is also considered as the principal feedstock for the chemical industry [1]. Raw natural gas is collected at

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the wellhead as a gaseous mixture containing a wide range of compounds, mainly methane, ethane, other alkanes, and impurities such as water and carbon dioxide (CO₂) [2]. The CO₂ content in natural gas should be removed from the feed gas to meet the operation standards of the plant and the product specifications since the liquefaction process usually takes place at temperatures below 200 K and CO₂ content in natural gas will freeze and cause blockage in the system at this temperature. A number of gas separation methods are available to remove CO₂ from natural gas, including membrane, physical and chemical scrubbing, temperature swing adsorption (TSA), pressure swing adsorption (PSA), and distillation [3].

Chang and Smith Jr. [4] have observed frost formation of supersaturated contaminants in a cryogenic helium heat exchanger. Using this concept, Chang, *et al.* [3] proposed a new method to remove CO₂ from natural gas using a cryogenic heat exchanger. This method was integrated between the process of removing CO₂ and that of liquefying CH₄ to become LNG. Using this method, the CO₂ contaminant can be removed as frost on the surface wall of the heat exchanger operated at a below triple point temperature of CO₂, using nitrogen as cooling medium.

A new LNG concept—called Cluster LNG—using a pressure of around 20 bar and a temperature of -110°C has been proposed [5]. With this concept, the tolerance of CO₂ content in the LNG is 2% mole maximum compared to conventional LNG, with a maximum of 50 ppm. Optimization of the design concept for a floating LNG facility, specifically for stranded gas resources, has been done [6]. The results showed that the design of the floating LNG facility should be considered carefully from an economical point of view. Also, a study of the cost-effectiveness of CO₂ removal technologies in the floating LNG facility has been done [5]. This study pointed out that the controlled freeze out area method was the most cost-effective technology for small-capacity LNG plants. Since this technology has not yet been applied commercially, finding out detailed information regarding the phase behavior of CH₄-CO₂ mixtures is necessary. Phase equilibrium data of the CH₄-CO₂ system and the CO₂ frost point in light hydrocarbon systems have been generated by some researchers [7-9] and a semi-empirical liquid freezup correlation has been suggested for the CH₄-CO₂ system based on data published by Mraw, *et al.* [8]. Prediction of CO₂ freezing points for mixtures of CO₂-CH₄ under cryogenic conditions using the standard Peng-Robinson equation of state [10] was done by ZareNezhad [11] and ZareNezhad and Eggeman [12]. In our previous work [13], we investigated the performance of the Peng-Robinson equation of state in the prediction of the solid-vapor and the solid-liquid equilibrium of the CH₄-CO₂ system and we proposed an interaction parameter for a CO₂ concentration of 1% to improve the accuracy. However, for CO₂ concentrations of more than 1%, ZareNezhad and

Eggemen's parameters [12] were adequate. For commercial applications, the predicted results are not reliable enough. Further clarification supported by experimental data should be elaborated. In this work, the CO₂ frost phenomenon in CH₄-CO₂ mixtures was evaluated in a double pipe heat exchanger at pressures ranging from 1-20 bar and CO₂ concentrations of 5-10% in the mixtures. Frost performance was evaluated based on experimental work and phase equilibrium predictions using the Peng-Robinson equation of state.

2 Experiment and Method

2.1 Materials

Gas mixtures containing CH₄ and CO₂, with CO₂ concentrations of 5 and 10%, and liquid nitrogen were purchased from PT. Samator, Indonesia. Ultra high purity grade nitrogen gas was purchased from PT. Trigas, Indonesia. All materials were used directly without pretreatment.

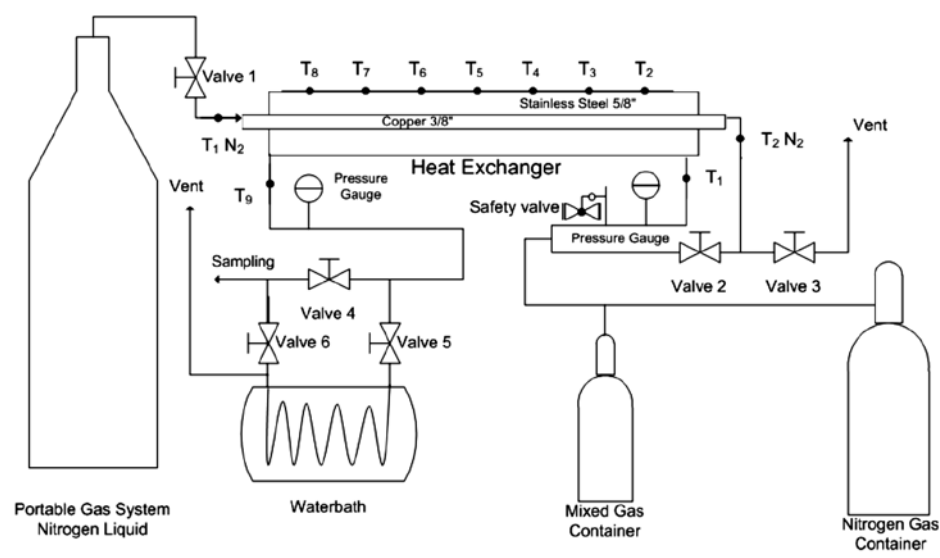


Figure 1 A schematic diagram of the experimental apparatus.

2.2 Apparatus and Procedure

A schematic diagram of the experimental apparatus is shown in Figure 1. The apparatus consists of four main parts, i.e. double pipe heat exchanger (3/8 x 5/8 inch diameter and 1.9 m length) with insulation, mixed gas container, portable liquid nitrogen and nitrogen gas container.

The first step was flushing the apparatus to remove gas and water impurities. The second step was starting up the apparatus by using cold nitrogen gas flowed through the heat exchanger tube and flowing the nitrogen gas (UHP) into the annulus at the same time. In this step, an appropriate operating temperature condition of the apparatus was expected to be achieved. The third step was the measurement of CO₂ frost by flowing the gas mixture of CH₄ and CO₂ with a CO₂ concentration of 5% at 1 bar in the annulus of the heat exchanger. In this step, cold nitrogen gas was flowed through the inner tube of the heat exchanger in the opposite direction as a cooling medium. The heat transfer was allowed to achieve steady state condition and CO₂ frost formation was revealed by the increase of the pressure drop on the annulus side, detected by pressure gauges installed in the influent and effluent of the annulus side. At steady state condition, the temperatures along the double pipe heat exchanger were recorded. Samples of the gas mixture going out of the exchanger were taken using a sampling tube in order to analyze its composition using gas chromatography.

The last step was the determination of the CH₄ concentration trapped in the CO₂ frost to investigate the possibility of the existence of CH₄ in the CO₂ frost. In this step, all valves must be closed before starting. After the third step was completed, cold nitrogen gas with a temperature below the frost temperature was flowed into the annular heat exchanger at atmospheric pressure to release the remaining gas mix from the annulus by opening valve 5 for around 5 minutes. Then, valve 5 was closed again and the annulus temperature was allowed to return to room temperature in order to vaporize the trapped CO₂. When the wall temperature of the annulus reached room temperature, the CO₂ gas was obtained from the outlet of the heat exchanger by opening valve 4. Its composition was analyzed using gas chromatography (Techcomp GC D7900, Guangdong, China) equipped with a flame ionization detector. Separations were carried out on a TM 5 column. The experiments were repeated for pressures of the influent gas mixtures at 5, 10 and 20 bar and for a CO₂ concentration of 10% as well.

3 Results and Discussion

3.1 Prediction of CO₂ Frost Formation

The CO₂ frost condition was necessary in order to investigate whether CO₂ frost occurred on the annulus side. In this work, CO₂ frost formation was predicted with the Peng-Robinson equation of state [10] using the ZNE method proposed by ZareNeshad and Eggeman [12] and the process simulation software (Aspen HYSYS® v7.3). The calculations were made at various pressures (1-40 bar) and various CO₂ concentrations (2-20%). The calculation results using the ZNE method and the process simulation software showed that there was no

significant difference in the pressure range of 1-20 bar, with a magnitude of difference less than 1%, and only slight differences were shown between both methods, with a magnitude of difference between 2 and 3% at pressures of 30-40 bar. An illustration of the comparison between both methods is presented in Figure 2. The predicted CO₂ frost phenomenon was used as a reference in analyzing the CO₂ frost condition data obtained from the experiment using a double pipe heat exchanger in order to approach the experimental temperature of CO₂ frost in the annulus to that obtained from the calculations.

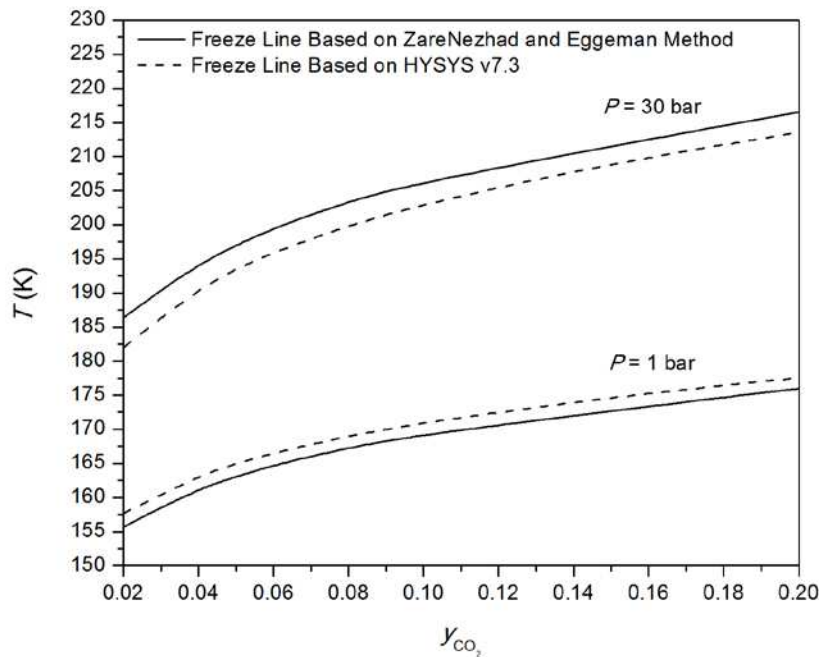


Figure 2 Comparison of CO₂ frost temperatures calculated by ZNE method and process simulation software (Aspen HYSYS® v7.3) at 1 and 30 bar.

3.2 Validation of CO₂ Frost Formation

The occurrence of CO₂ frost on the annulus side was characterized by the presence of a pressure drop between upstream and downstream indicated by two pressure gauges installed on the annulus side of the double pipe heat exchanger, as shown schematically in Figure 3. The increase of the pressure drop gave an indication that blockage had occurred on the annulus side, which was allowed until total blockage. The effect of pressure on time required to reach total blockage is shown in Table 1. The results showed that the higher the pressure in the mixed gas, the less time was required to reach total blockage because the frost temperature obtained from the calculations indicated that a greater pressure

and CO₂ content leads to an increase in the frost temperature, as shown in Figure 2. The gas chromatography analysis of the frozen CO₂ revealed that it contained only CO₂ or no methane was found. This analysis result agreed with the assumption of the frost temperature calculations using the Peng-Robinson equation of state.

Table 1 The Effect of Pressure on the CO₂ Frost Growth Rate for Mixed Gas with 10% CO₂ Concentration.

<i>P</i> (bar)	<i>t</i> (min)	Pressure drop (bar)
5	12	5
10	6.5	10
20	5	20

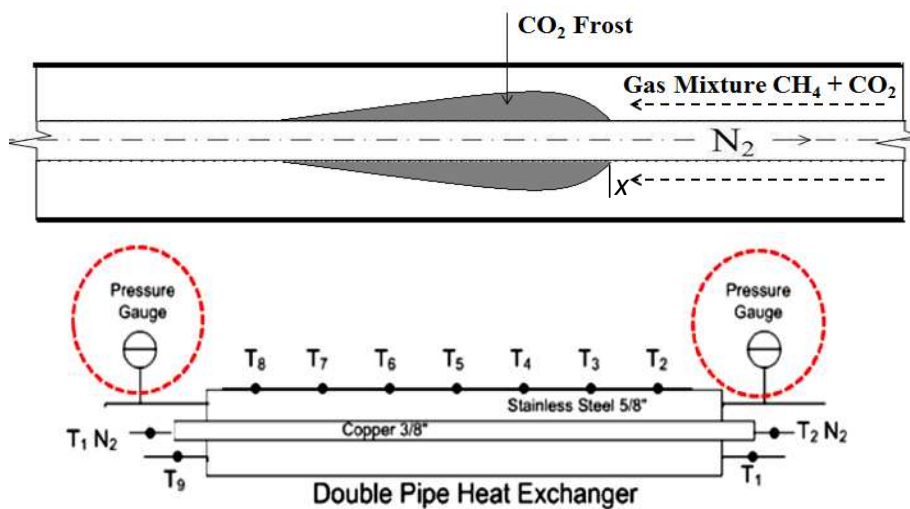


Figure 3 Schematic diagram of validation section of CO₂ frost formation in the experimental apparatus.

3.3 Initial Point Location of CO₂ Frost Formation in the Double Pipe Heat Exchanger

Figure 3 also shows an illustration of the CO₂ frost formation on the annulus side of the double pipe heat exchanger. Initial formation of CO₂ frost in the annulus was indicated by a pressure drop in the annular flow. Experiments were carried out at various pressures (1, 5, 10 and 20 bar) and CO₂ concentrations in the mixed gas (5 and 10%). The temperature distributions along the annulus side are presented in Tables 2 and 3 for CO₂ concentrations of 5 and 10%, respectively.

Based on the temperature distributions shown in Tables 2 and 3 and the first occurrence of a pressure drop on the annulus side, the location of initial CO₂ frost formation on the annulus side of the double pipe heat exchanger can be observed by comparing the experimental temperature distributions with the calculated values using the ZNE method and the process simulation software. The initial locations of CO₂ frost formation at pressures of 1 and 5 bar both followed the same pattern, as can be seen in Figure 4.

Table 2 Temperature Distribution along the Annulus Side of Double Pipe Heat Exchanger for Gas Mixture with 5% CO₂.

x (m)	$P = 1$ bar ($\Delta P = 1$ bar)	$P = 5$ bar ($\Delta P = 2$ bar)	$P = 10$ bar ($\Delta P = 8.5$ bar)	$P = 20$ bar ($\Delta P = 15$ bar)
	T_{mix} (K)	T_{mix} (K)	T_{mix} (K)	T_{mix} (K)
0.000	298.15	298.15	293.15	289.15
0.238	249.15	260.15	251.15	229.15
0.475	212.15	227.15	227.15	199.15
0.713	194.15	204.15	205.15	192.15
0.950	176.15	187.15	203.15	197.15
1.188	163.15	179.15	197.15	200.15
1.425	146.15	165.15	190.15	185.15
1.663	135.15	148.15	177.15	207.15
1.900	131.15	140.15	207.15	247.15

Table 3 Temperature Distribution along the Annulus Side of Double Pipe Heat Exchanger for Gas Mixture with 10% CO₂.

x (m)	$P = 1$ bar ($\Delta P = 0.5$ bar)	$P = 5$ bar ($\Delta P = 5$ bar)	$P = 10$ bar ($\Delta P = 5$ bar)	$P = 20$ bar ($\Delta P = 16$ bar)
	T_{mix} (K)	T_{mix} (K)	T_{mix} (K)	T_{mix} (K)
0.000	294.15	294.15	295.15	293.15
0.238	235.15	233.15	236.15	252.15
0.475	199.15	195.15	202.15	225.15
0.713	186.15	186.15	196.15	212.15
0.950	179.15	187.15	197.15	206.15
1.188	185.15	192.15	202.15	203.15
1.425	171.15	175.15	185.15	198.15
1.663	189.15	195.15	203.15	195.15
1.900	214.15	137.15	241.15	226.15

For the gas mixtures at 1 bar with 5% CO₂, the initial location of CO₂ frost formation was detected at 1.187 and 1.154 m from the inlet based on the ZNE method and the process simulation software, respectively. Meanwhile, at a pressure of 5 bar, the initial location of CO₂ frost formation was detected at 1.210 and 1.171 m from the inlet based on the ZNE method and process simulation software, respectively. In the region extending beyond the initial location of frost formation, the temperature tended to decrease, as shown in Figure 4. This illustrates that the CO₂ concentration in the mixed gas decreased.

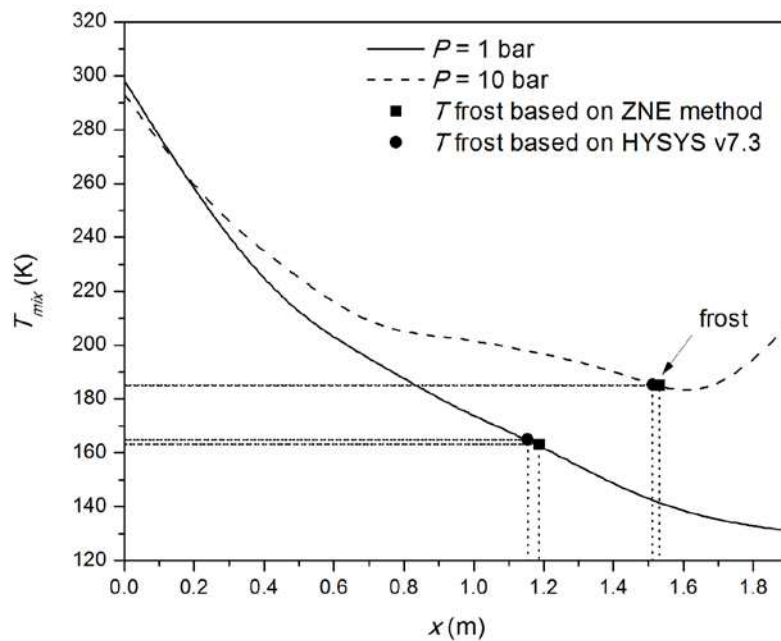


Figure 4 Initial CO₂ frost location on annulus side of double pipe heat exchanger at 5% CO₂ in gas mixtures.

However, when the pressure of the mixed gas was 10 and 20 bar, different temperature distribution patterns were found. After the frost location was detected, the temperatures in the region extending beyond the initial location of CO₂ frost formation increased, as can be seen in Figure 4. This figure shows that at the location prior to the initial CO₂ frost formation, the pressure in the system was 10 bar and in the location after the initial frost formation, the pressure decreased to 1.5 bar due to blockage of the CO₂ frost. The measurements were performed at a pressure drop of 8.5 bar. In accordance with the equilibrium phase at pressures below 10 bar, the mixed gas conditions should move to a new equilibrium condition. Another possibility to explain this phenomenon is the solubility of CO₂ in liquid methane. Methane in high-

pressure condition tends to become liquid. In this case, the liquid methane was sufficiently condensed, so the solubility of the CO₂ in the methane increased. This phenomenon releases energy from the CO₂ solubility process in liquid CH₄ and causes a rise of temperature. A more detailed study is needed to explain this phenomenon. At a pressure of 10 bar, the initial frost location was detected at 1.531 and 1.511 m from the inlet based on the ZNE method and the process simulation software, respectively. At higher pressures of the mixed gas, a longer length of the heat exchanger was needed to allow CO₂ frost formation. However, the distance between the initial frost formation location and the inlet at a pressure of 20 bar was shorter than that at a pressure of 10 bar. Details of the initial CO₂ frost formation obtained in this work are presented in Tables 4 and 5. As presented in these tables, significant differences in initial frost location were shown by both calculation methods, even though no significant differences were shown in the predicted frost temperatures.

Table 4 Initial Point of CO₂ Frost Formation Prediction Results Based On ZNE Method and Process Simulation Software at 5% CO₂ in Gas Mixtures.

<i>P</i> (bar)	<i>x</i> (m)	
	ZNE Method	Process Simulation
1	1.187	1.154
5	1.210	1.171
10	1.531	1.511
20	1.322	1.368

Table 5 Initial point of CO₂ frost formation prediction results based on ZNE method and process simulation software at 10% CO₂ in gas mixtures.

<i>P</i> (bar)	<i>x</i> (m)	
	ZNE Method	Process Simulation
1	0.911	0.887
5	1.121	1.035
10	1.328	1.302
20	1.272	1.345

The mole fractions of the CO₂ in the product for various values of pressure and CO₂ mole fraction at the inlet are shown in Table 6. It was found that the CO₂ mole fraction in the product fraction increased along with the increase of pressure.

Table 6 CO₂ Mole Fraction in the Product for Various Values of Pressure and CO₂ Mole Fraction at Inlet

<i>P</i> (bar)	CO ₂ mole fraction in the product (%)	
	5% CO ₂ mole fraction at inlet	10% CO ₂ mole fraction at inlet
1	0.12	0.22
5	0.00	0.20
10	1.28	0.50
20	1.18	0.00

4 Conclusion

The CO₂ frost phenomenon for binary system of CH₄-CO₂ mixtures was studied for the applicability of the controlled freeze out area as CO₂ removal method in natural gas. Even though no significant differences were found between the temperature estimation of CO₂ frost formation using the ZNE method and the process simulation software (Aspen HYSYS® v7.3), it may have a significant effect on the location of CO₂ frost formation in the heat exchanger. The CO₂ frost formation could be detected well at pressures of 1, 5, 10 and 20 bar. The locations of the initial CO₂ frost formation may be determined well using a pressure drop indicator associated with the frost temperatures obtained from the ZNE method and the process simulation software, and were found at distances between 0.887-1.531 m from the inlet of the gas mixtures.

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References

- [1] Yeo, Z.Y., Chew, T.L., Zhu, P.W., Mohamed, A.R. & Chai, S.-P., *Conventional Processes and Membrane Technology for Carbon Dioxide Removal from Natural Gas: A Review*, Journal of Natural Gas Chemistry, **21**(3), pp. 282-298, 2012.
- [2] Bellussi, G., Broccia, P., Carati, A., Millini, R., Pollesel, P., Rizzo, C. & Tagliabue, M., *Silica-Aluminas for Carbon Dioxide Bulk Removal from*

- Sour Natural Gas*, Micropor. Mesopor. Mater., **146**(1-3), pp. 134-140, 2011.
- [3] Chang, H.-M., Chung, M.J. & Park, S.B., *Cryogenic Heat-Exchanger Design for Freeze-out Removal of Carbon Dioxide from Landfill Gas*, Journal of Thermal Science and Technology, **4**(3), pp. 362-371, 2009.
- [4] Chang, H.-M. & Smith Jr., J.L., *Mass Transfer of Supersaturated Contaminants in Cryogenic Helium Heat Exchangers*, Int. J. Heat Mass Transfer, **33**(6), pp. 1299-1306, 1990.
- [5] Wibawa, G., Sumarno, S. & Gunawan, S., *Optimum Utilization of Natural Gas in Indonesia and Cryogenic Technology for LNG Processing*, 19th Regional Symposium of Chemical Engineering (RSCE), Bali, Indonesia, 2012.
- [6] Lee, S., Long, N.V.D. & Lee, M., *Design and Optimization of Natural Gas Liquefaction and Recovery Processes for Offshore Floating Liquefied Natural Gas Plants*, Ind. Eng. Chem. Res., **51**(30), pp. 10021-10030, 2012.
- [7] Le, T.T. & Trebble, M.A., *Measurement of Carbon Dioxide Freezing in Mixtures of Methane, Ethane, and Nitrogen in the Solid-Vapor Equilibrium Region*, J. Chem. Eng. Data, **52**(3), pp. 683-686, 2007.
- [8] Mraw, S.C., Hwang, S.-C. & Kobayashi, R., *Vapor-Liquid Equilibrium of the Methane-Carbon Dioxide System at Low Temperatures*, J. Chem. Eng. Data, **23**(2), pp. 135-139, 1978.
- [9] Shen, T., Gao, T., Lin, W. & Gu, A., *Determination of CO₂ Solubility in Saturated Liquid CH₄ + N₂ and CH₄ + C₂H₆ Mixtures above Atmospheric Pressure*, J. Chem. Eng. Data, **57**(8), pp. 2296-2303, 2012.
- [10] Peng, D.-Y. & Robinson, D.B., *A New Two-Constant Equation of State*, Ind. Eng. Chem. Fund., **15**(1), pp. 59-64, 1976.
- [11] ZareNezhad, B., *Prediction of CO₂ Freezing Points For the Mixtures of CO₂-CH₄ at Cryogenic Conditions of NGL Extraction Plants*, Korean J. Chem. Eng., **23**(5), pp. 827-831, 2006.
- [12] ZareNezhad, B. & Eggeman, T., *Application of Peng-Robinson Equation of State for CO₂ Freezing Prediction of Hydrocarbon Mixtures at Cryogenic Conditions of Gas Plants*, Cryogenics, **46**(12), pp. 840-845, 2006.
- [13] Wibawa, G., Nafi, M.F.A., Permatasari, A. & Mustain, A., *Application of Peng-Robinson Equation of State for Calculating Solid-Vapor and Solid-Liquid Equilibrium of CH₄-CO₂ System*, Modern Applied Science, **9**(7), pp. 177-182, 2015.