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COMPARATIVE STUDY OF VARIOUS CHEMICAL REFRIGERANTS FOR NATURAL GAS HYDRATES PRODUCTION AS ALTERNATIVE MEDIA FOR NATURAL GAS TRANSPORTATION

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ABSTRACT

COMPARATIVE STUDY OF VARIOUS CHEMICAL REFRIGERANTS FOR NATURAL GAS HYDRATES PRODUCTION AS ALTERNATIVE MEDIA FOR NATURAL GAS TRANSPORTATION. Indonesia has been facing natural gas declining problem since 2003, and one of the alternative solutions which can be proposed is by producing gas from the stranded area. Stranded gas is not much developed due to its remote location and a small number of gas reserves. Natural Gas Hydrates or NGH is one of promising alternative medium for natural gas transportation, but it is not much developed yet. Transportation of NGH requires neither cryogenic temperature as LNG does nor high pressure as CNG does. This theoretical study will suggest a simulation scheme to produce synthetic NGH. Production of synthetic NGH utilizes a refrigeration cycle as a cooling source. Based on proposed proses for converting natural gas to NGH, various design parameters for a refrigeration cycle have been investigated. Results obtained suggested that propane as a refrigerant with a specific operating parameter can be a good alternative for the production of NGH.

Keywords : Natural Gas Hydrates, Natural gas transportation, Refrigeration cycle

ABSTRAK

***STUDI KOMPARASI BERBAGAI JENIS REFRIGERAN BERBASIS BAHAN KIMIA PADA PRODUKSI* NATURAL GAS HYDRATES *SEBAGAI MEDIA ALTERNATIF TRANSPORTASI GAS ALAM*.** *Indonesia saat ini mengalami masalah penurunan produksi gas alam sejak 2003 dan salah satu solusi yang dapat dilakukan adalah memproduksi gas dari lapangan* stranded*. Gas dari lapangan* stranded *tidak banyak diproduksi karena lokasinya yang jauh dan cadangan produksi yang tidak terlalu besar.* Natural Gas Hydrates *atau* NGH *merupakan salah satu media alternatif transportasi gas alam yang menjanjikan, namun belum banyak dikembangkan. Transportasi menggunakan* NGH *tidak memerlukan suhu kriogenik sebagaimana* LNG *atau tekanan operasi yang tinggi sebagaimana* CNG*. Studi ini membahas skema simulasi untuk memproduksi* NGH *sintetis. Proses produksi* NGH *sintetis menggunakan* refrigeration cycle *sebagai sumber pendingin. Berdasarkan proses produksi gas menjadi NGH yang diajukan, berbagai parameter untuk* refrigeration cycle *telah diteliti. Hasil yang didapatkan menyarankan penggunaan propana sebagai refrigeran yang dapat menjadi alternatif untuk produksi NGH.*

Kata kunci : Natural Gas Hydrates, Transportasi gas alam, Refrigeration cycle

INTRODUCTION

Indonesia has been known as one of oil and gas exporting country since the 1970s. However, since 2003 Indonesia became an oil exporting country (Ministry of Energy and Mineral Resources 2014), and similar condition may happen to a natural gas commodity in Indonesia. Indonesia's natural gas supply shows declining from 2004 to 2013, while its demand shows increasing for the same period (Purwanto *et al.* 2016). Natural gas holds the vital role for industrial development in Indonesia. Indonesian gas utilization data in 2016 shows 23.26% of natural gas was used as raw material or utility gas for industries, for example, glass and cement industries, while 14.61% and 9.58% were used for electrical supply and fertilizer industry (Satuan Kerja Khusus Pelaksana Kegiatan Usaha Hulu Minyak dan Gas Bumi 2016). Decreasing of natural gas supply will affect the development of industry in Indonesia.

One of the efforts to enhance national gas production is by developing the stranded gas field. The stranded gas field in Indonesia is reported with a potential of 10 TCF at onshore and 44 TCF at offshore (Attanasi and Freeman 2013). Recently, stranded gas fields are not much developed yet due to their geographical location, distance with consumer and supporting infrastructure, and limited hydrocarbon reserves. Widely known gas transportation modes as Pipeline Natural Gas (PNG), Liquefied Natural Gas (LNG), or Compressed Natural Gas (CNG) become uneconomic with these conditions. For example, development of LNG's infrastructure needs enormous gas reserves (>3 TCF) and an extended period of the contract (>20 years) with a large capacity of production (500 MMSCFD) (Thomas and Dawe 2003).

One of promising alternative media for natural gas transportation but not much developed yet, neither in Indonesia nor the world, is using Natural Gas Hydrates (NGH). Currently, NGH is widely known as one of unconventional gas reserve or threat for natural gas transportation by using PNG. 1 m^3 of NGH contains ~165 m^3 of gas and 0.8 m^3 of water. Operating parameter for NGH is in milder condition due to needing neither cryogenic temperature (-162 °C) as LNG nor high pressure (2,500 psig until 3,600 psig) as CNG does (Makogon 2010). Several papers have reported the feasibility of NGH as an alternative medium for natural gas transportation besides of widely known method as LNG, CNG, and PNG (Javanmardi *et al.* 2005; Kanda 2006; Najibi *et al.* 2015; Taheri *et al.* 2014; Shin *et al.* 2016).

Characteristic of NGH which support utilization of NGH as an alternative medium for natural gas transportation is self preservation phenomenon. This phenomenon is only found in gas hydrate under freezing point of water. Gas hydrate shows an anomaly of low dissociation rate, even though there is an increase in temperature (Mel'nikov *et al.* 2016). This phenomenon causes gas hydrate to be able to entrap gas in atmospheric condition. Methane and carbon dioxide hydrate show self preservation phenomenon, while ethane and propane hydrate does not. The presence of ethane and propane at methane hydrate was reported to decrease the preservation ability of methane hydrate (Stern *et al.* 2003; Takeya and Ripmeester 2008; Mimachi *et al.* 2014).

This paper intends to compare the operating parameters of several refrigerants needed for the production process of synthetic NGH, e.g., compressor power and coefficient of performance for each of refrigerants. Operating parameters for the refrigeration system will be evaluated to determine the most technically feasible and economically beneficial ways to produce synthetic NGH with the assistance of chemical refrigerant. Thereby, it is expected to bring an alternative medium for natural gas transportation, which able to enhance national gas production and increase the development of industries in Indonesia.

MATERIALS & METHODS

NGH Production System

The proposed process for NGH production is shown in Fig. 1. This process was modified based on the method explained by Javanmardi (Javanmardi *et al.* 2005). Operational parameters for the NGH production process are given in Table 1. Feed natural gas as hydrate former and fresh water was fed to the reactor with a known operational parameter. The heat of hydrate formation was removed inside of the reactor, and an external refrigeration system was used. The temperature of the reactor was assumed to be 2 °C below the equilibrium temperature. NGH was formed inside of the reactor, and hydrate free water mixture was separated after leaving the reactor.

The hydrate formation process could be represented by the following Equation 1 :

$$(1 \text{ mole) NG} + (R \text{ moles) } H_2O \rightarrow (R - 1/F \text{ moles) } H_2O + (1 \text{ mole) hydrate crystal} \quad (1)$$

Previous equation could be simplified to the following Equation 2 :

$$(1 \text{ mole) } H_2O + (F \text{ moles) hydrate former} \rightarrow (F \text{ moles) hydrate crystal} \quad (2)$$

Table 1. Operational parameters for NGH production process

Composition of feed natural gas	CH_4 94% C_2H_6 4% C_3H_8 2%
Temperature of feed natural gas	300 K
Temperature of feed fresh water	300 K
Temperature of reactor	285.4 K
Temperature of stored hydrate	258.15 K
Pressure of feed natural gas	6 MPa
Pressure of feed fresh water	0.10125 MPa
Pressure of reactor	6 MPa
Pressure of stored hydrate	0.10125 MPa
Number of train (parallel)	10
Volumetric flow rate of feed natural gas	25 MMSCFD

Using free water content of hydrate free water mixture leaving the reactor, i.e., 12 wt.%, the parameter F could be obtained by the following Equation 3 (Abdalla and Abdullatef 2005) :

$$R - \frac{1}{F} = 0{,}12\left(\frac{M_w NG}{M_w H_2O} + R\right)$$
$$F = \frac{1}{0{,}88.R - 0{,}12\left(\frac{M_w NG}{M_w H_2O}\right)} \qquad (3)$$

The heat of formation for one mole of hydrate crystal could be calculated by the following Equation 4 :

$$\Delta H = H|_{\text{hydrate crystal}} - H|_{\text{hydrate former}} - (1/F).H|_{H2O} \qquad (4)$$

NGH formation reaction is exothermic, and reactor duty for one mole of feed natural gas fed to the reactor can be evaluated by the following Equation 5 :

$$\text{Reactor duty} = -H_{\text{hydrate,PC}} + H_{\text{hydrate,R}} + R.C_{p,\text{water}}.(T_{\text{reactor}} - T_{\text{feed water}}) + \Delta H \qquad (5)$$

Free water from the separator was then recycled as feed water to the reactor, while hydrate crystal leaving from separator was fed to the heat exchanger. Hydrate crystal should be lowered to 242 K to 271 K before entering storage tanks. This range of temperature would help to activate the self preservation phenomenon at atmospheric pressure, and this temperature would be kept during the transportation process of NGH. In this paper, a temperature of 258 K was chosen as a temperature of stored hydrate. Heat exchanger duty for one mole of hydrate could be evaluated by the following Equation 6 :

$$\text{HE duty} = (R - 1/F)[C_{p,\text{water}}.(273.15 - T_{\text{pre-cooler}}) + C_{p,\text{ice}}.(T_{\text{stored hydrate}} - 273.15)] + (R - 1/F)(H_{\text{ice}} - H_{\text{water}}) + C_{p,\text{hydrate}}(T_{\text{stored hydrate}} - T_{\text{pre-cooler}}) \qquad (6)$$

Before being stored, NGH should be pelletized. Takaoki reported that pelletized NGH had lower dissociation rate than powdered NGH (Takaoki 2006).

Refrigeration Cycle

External refrigeration system was used to transfer the heat released during the NGH production process. The method of refrigeration consisted of evaporation, compression, condensation, and expansion process. Several refrigerants which widely used in industry will be examined at various operating parameters. The flow rate of refrigerant was set a range of 1 MMSCFD to 150 MMSCFD for simulation or with refrigerant/feed natural gas molar ratio of 0.04 to 6 for train capacity of 25 MMSCFD of feed natural gas. The total duty of refrigeration cycle could be calculated by the following Equation 7 :

$$\textit{Refrigeration duty} = \textit{Reactor duty} + \textit{HE duty} \qquad (7)$$

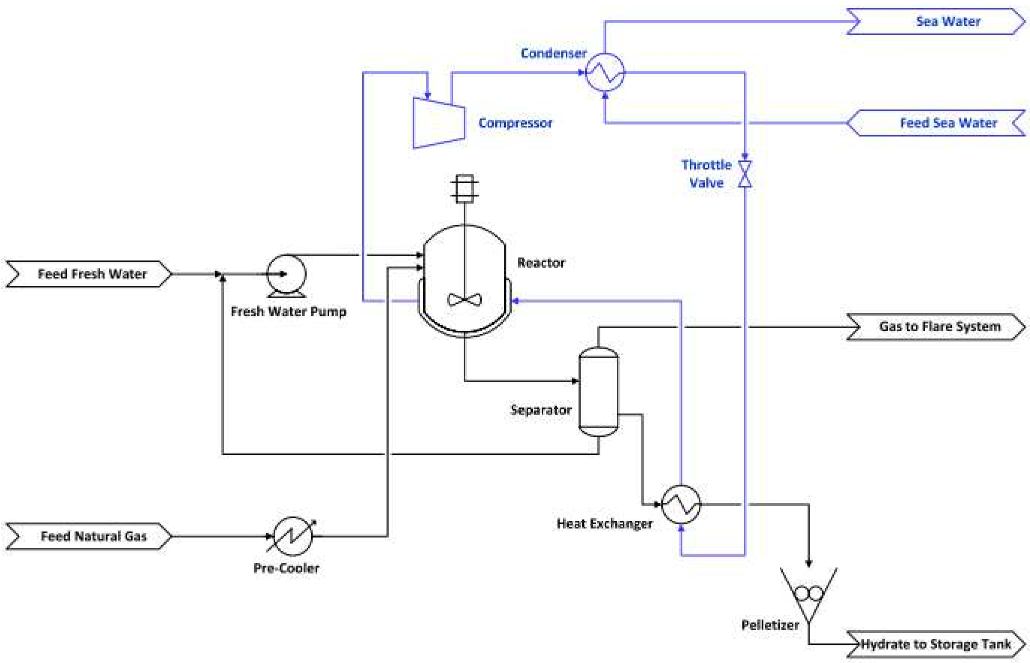

Figure 1. Proposed process of NGH production process

A computer aided program had been prepared for simulation of refrigeration cycle used at the production process of NGH. Performance of refrigeration cycle was expressed regarding coefficient of performance (COP_R) which could be calculated by the following Equation 8 :

$$COP_R = Q_L / W_{net,in} \quad (8)$$

The isentropic efficiency of 0.8 was used to simulate the compressor in this refrigeration cycle. The operational temperature of the refrigerant was set under their auto ignition temperature to ensure safety during operation. Auto ignition temperature for working fluid was given in Table 2. Refrigerants used for the production of synthetic NGH may grant permission based on Significant New Alternatives Policy released by the United States Environmental Protection Agency.

RESULTS AND DISCUSSION

For the case studied, calculation result for the specification of equipment for NGH production process is reported in Table 3. Hydrate crystal production for 1 train with 25 MMSCFD capacity of feed natural gas was obtained around 3,866 m^3/day. Based on the result described in Table 3, refrigeration duty for NGH production was calculated with the total of 22.06 MW. The results of reactor and heat exchanger duties obtained from calculation agreed with a report of Javanmardi as described in Table 4 (Javanmardi *et al.* 2005).

Seven types of refrigerant as working fluid of refrigeration system for NGH production process have been analyzed. A ratio of refrigerant/feed natural gas was set from 0.04 MMSCFD to 6 MMSCFD or 1 MMSCFD to 150 MMSCFD of refrigerant for every 25 MMSCFD of feed natural gas. A compression ratio of the compressor was set at 3, and other parameters were kept constant. Fig. 2 showed an effect of molar ratio of refrigerant/feed natural gas on a coefficient of performance. Performance of refrigerants can be examined by the COP_R value which demonstrates heat exchange performance of refrigerants.

Based on Fig. 3, propane, butane, R-134a, and R-142b have a higher coefficient of performance around 7 to 9 compared with other refrigerants at a lower molar ratio of refrigerant/feed natural gas. Propane, butane, R-134a, and R-142b have passed the technical assessment. Therefore based on Fig. 4, heat sink for propane, butane, R-134a, and R-142b were less than other refrigerants. Less heat sink from a refrigeration system leads to less seawater used as cooling fluid for a refrigeration system.

Table 2. Auto ignition temperature for component of refrigerant

Component		Auto-ignition temperature (K)
Propane	(R-290)	728.15
n-Butane	(R-600)	678.15
$C_2F_4H_2$	(R-134a)	1,023.15
Ammonia	(R-717)	923.15
$C_2H_3ClF_2$	(R-142b)	898.15
CO_2	(R-744)	-

Table 3. Specification of different equipment for synthetic NGH production process per train

Equipment	Specification
Pre-cooler	Duty: 0.025 MW
Feed water pumps	No. of pumps: 2
	Total power: 0.53 MW
Reactor	Duty: 19.34 MW
Heat exchanger	Duty: 2.72 MW
Pelletizer	Duty: 3 MW

Table 4. Comparison of reactor and heat exchanger duties

	Reactor duty (MW)	HE duty (MW)
Calculation	19.34	2.72
Javanmardi (2005)	21.20	2.70
Deviation (%)	8.75	0.60

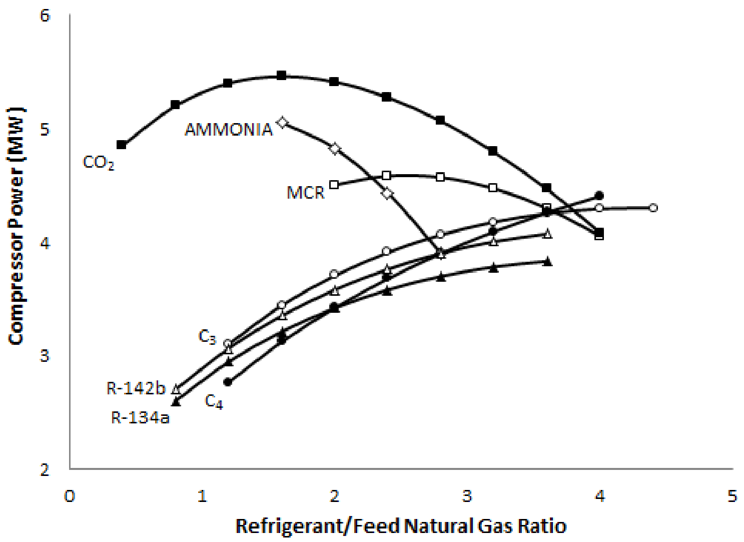

Figure 2. Effect of molar ratio of refrigerant/feed natural gas on compressor power

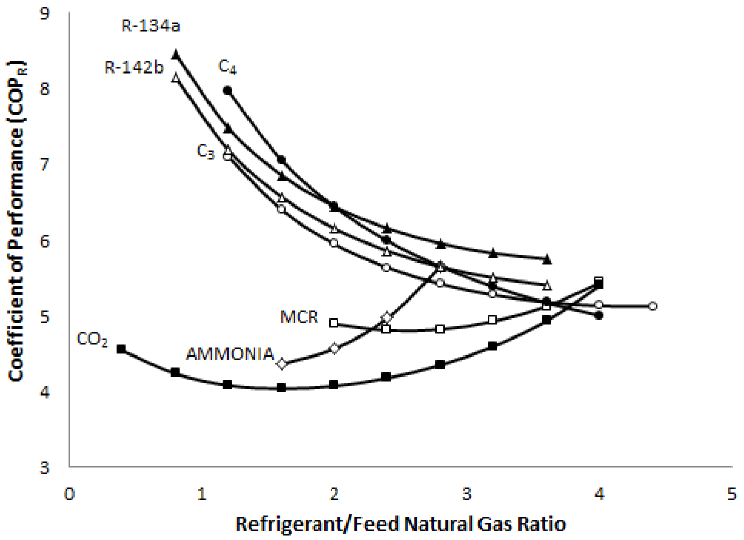

Figure 3. Effect of molar ratio of refrigerant/feed natural gas on coefficient of performance

The economical assessment was performed to appraise the feasibility of utilization for each working fluid for a refrigeration system. Table 5 delivers amortized CAPEX and OPEX for every working fluid. Fig. 5 shows depreciated CAPEX and OPEX for a refrigeration system with propane, butane, R-134a, and R-142b as working fluid. This comparison intends to analyze and determine total product cost of synthetic NGH based on refrigeration system only. Based on the given result, R-134a with the highest value of COP_R gives total product cost 315 times higher than butane. This condition is not preferred at actual situation due to increasing of OPEX leads to the project do not pass the economic assessment. Thereby, butane was chosen as working fluid of refrigeration system at synthetic NGH production process with the lowest total product cost of US$ 1.06/MMBTU.

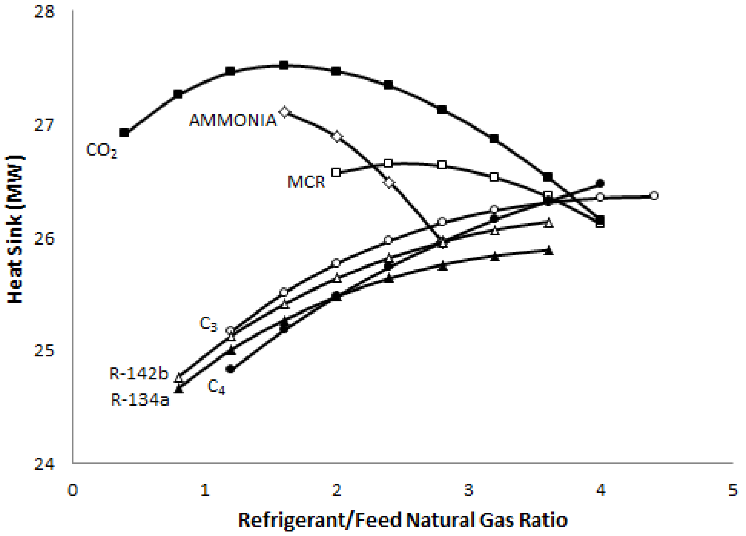

Figure 4. Effect of molar ratio of refrigerant/feed natural gas on heat sink

Table 5. Specification of different equipment for synthetic NGH production process per train

Refrigerant	CAPEX (US$)	OPEX (US$)	Amortized CAPEX (US$/MMBTU)	Amortized OPEX (US$/MMBTU)	Total Product Cost (US$/MMBTU)
Propane	48,168,704	3,443,936	0.77	0.39	1.16
Butane	44,140,336	3,101,904	0.71	0.35	1.06
R-134a	15,410,209,202	767,515,530	246.58	86.90	333.48
R-142b	4,213,545,801	210,508,751	67.42	23.84	91.26

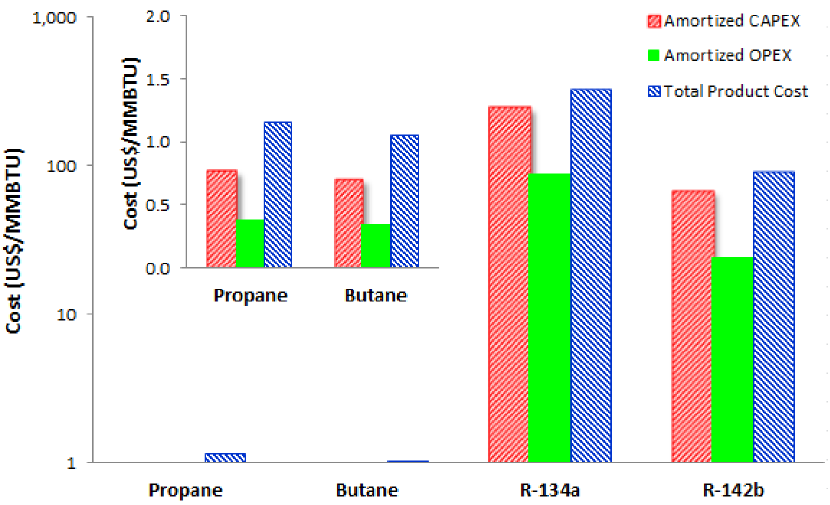

Figure 5. Amortized CAPEX and OPEX for various refrigerants

CONCLUSIONS

Natural Gas Hydrates have excellent prospects as an alternative medium for natural gas transportation besides LNG or CNG. NGH leads than other alternatives for the stranded gas field, located away from supporting infrastructure with a small number of reserves. Therefore, it is important to evaluate the NGH production process to determine a profitable way to produce NGH. Based on this study, it is concluded that producing NGH with the assistance of butane as working fluid for a refrigeration system with operating pressure of 0.2 MPa and compression ratio of 3 will give adequate power consumption and high efficiency of NGH production. 30 MMSCFD of butane is used as a refrigerant for 1 train of NGH with a capacity of 25 MMSCFD natural gas. Utilization of butane as working fluid yields on additional of US$ 1.06/MMBTU to total product cost of NGH production process. Based on the result obtained, NGH is feasible to perform as alternative media for natural gas transportation.

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