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KOGAS DME 공정을 이용한 CBM으로부터 DME 생산

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Production of DME from CBM by KOGAS DME Process

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ABSTRACT

The traditional feedstock for dimethyl ether (DME) has been natural gas obtained by pipeline from a nearby natural gas or oil field. This report focuses on other feedstock: Coal bed methane (CBM). The resource availability and suitability of CBM for DME manufacturing have been investigated. CBM in a short time has become an important industry, providing an abundant clean-burning fuel and also suggesting as a feedstock for gas industry. The use of CBM will have very little impact on the KOGAS' DME process design and economics up to 50 vol% of CO_2 in the CBM source. Many of the CBM sources in Asia are high in CO_2, but pose no difficulties for the KOGAS' DME plant. Since tri-reformer requires substantial CO_2 in its feed, no CO_2 removal from the CBM feed is needed. The CO_2 in the CBM means that less CO_2 needs to be recycled from the downstream in the process.

KEY WORDS : DME(디메틸에테르), KOGAS DME process(KOGAS DME 공정), CBM(석탄층가스), Synthesis gas(합성가스), Tri-reforming process(삼중개질공정), CO_2(이산화탄소)

1. Introduction

The characteristics of DME are similar to those of liquefied petroleum gas (LPG)[1-3]. It is widely used as solvent and propellant in various aerosol products[4,5]. DME is a cleanly burning, easily stored and transported hydrocarbon that can be used in diesel engines, can be a substitute for LPG, and can be mixed with natural gas for pipeline use[2,6,7]. The physical properties of DME are similar to those of LPG, and Marchionna et al. researched for fundamental investigations on DME as LPG substitute[8]. DME is volatile organic compound which is non-toxic, non-mutagenic and non-car-

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cinogenic. Good et al. have been researched for the lifetimes and global warming potential of DME[9]. Their results indicate a lifetime of DME to be 5.1 days, and concluded that it is environmentally benign.

Korea Gas Corporation (KOGAS) is one of the major energy companies to pursue development and commercialization of DME production. KOGAS' research effort in the past decade produced novel technologies such as the tri-reformer reactor that produces syngas with a good control of H_2/CO ratio, a key operating variable in DME production and with a minimum coke formation[10-13]; and one-step synthesis of DME reactor[14]. KOGAS has developed a complete DME process incorporating these technologies and has successfully been operating 10 tons per year demonstration plant since 2008. KOGAS plans to bring its research and demonstration effort into commercialization starting with 300,000 tons per year commercial plant in Saudi Arabia starting in 2014. Future development by KOGAS includes designing a DME plant on a mobile platform such as on a floating production and storage and offloading (FPSO) unit.

The flexibility to utilize various feedstocks is a key strength in DME production. KOGAS' recent DME development effort investigated utilizing different types of feedstock in its process focusing on renewable sources such as biomass, CBM and underutilized sources such as natural gas from small to medium fields.

In this paper, we describe the adaptation of DME process to utilize CBM: we review the availability and quality of the CBM for DME use; and discuss process design and product economic considerations in utilizing them.

2. Description of KOGAS DME process

KOGAS DME process design using natural gas as the feedstock will be used as a basis for considering process design and economics using alternative feedstocks. As shown in Fig. 1, the natural gas-based KOGAS DME Process was consisted of four major steps: reforming to produce synthesis gas, removal of CO_2 and liquid condensate by absorption and stripping, synthesis of DME, and purification of DME and conversion of methanol to DME if needed.

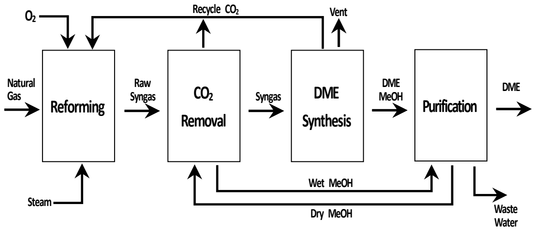

Fig. 1 Schematic diagram of direct DME process of KOGAS

The Reforming Section creates syngas (H_2 and CO) by preheating natural gas, steam, oxygen, and CO_2 before reacting them in KOGAS' proprietary tri-reformer (Fig. 2)[13]. The natural gas, steam, and oxygen are the only feed streams to the process. The CO_2 is recycled from downstream. The KOGAS tri-reformer is a proprietary auto thermal reformer design and it can handle natural gas feeds with

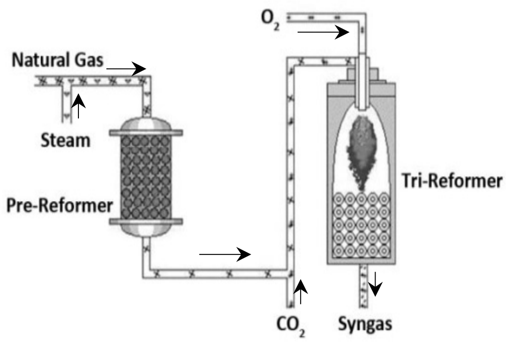

Fig. 2 Tri-reforming process of KOGAS

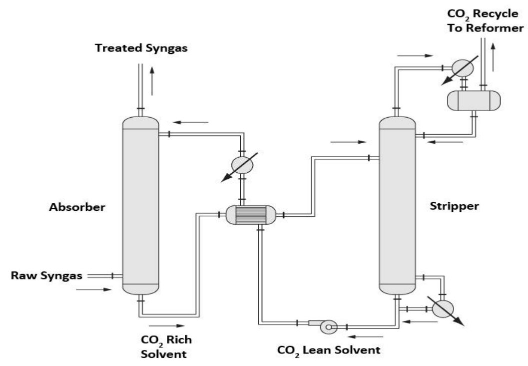

Fig. 3 Typical CO_2 absorber/stripper system

very high CO_2 content. The output of this section is synthesis gas ("syngas", mixture of H_2, CO and CO_2) with a particular H_2:CO ratio. As will be discussed in more detail below, this section can be replaced with the equipment needed to convert other feedstocks (e.g. CBM, coal, waste plastic, etc.) to syngas.

The CO_2 absorption and stripping section cools the raw syngas, removes aqueous condensate, and compresses the syngas to high pressure before removing the CO_2 using a physical absorbent. Conceptually, all physical absorption processes have the same equipment and layout (see Fig. 3). The raw syngas would enter the bottom of an absorber column where it would be contacted with a solvent which has a high solubility for CO_2. The CO_2 is removed into the liquid phase while the CO_2 free syngas leaves the top of the absorber. The CO_2-rich solvent leaves the bottom of the column and undergoes a pressure drop and is heated before it enters the top of the stripper column. At the higher temperature and lower pressure in the stripper, the CO_2 is less soluble in the solvent and is transferred into the vapor phase. The CO_2 stripped out of the solvent leaves the top of the stripper column (and is recycled to the upstream reforming section) while the CO_2-lean solvent leaves the bottom of the column. The CO_2-lean solvent is pumped back up to correct pressure for the top of the absorber and is cooled to increase its ability to absorb CO_2. Two CO_2 removal technologies have been examined: Rectisol which uses chilled methanol as the absorbent[15] and Selexol which uses a proprietary DME of polyethylene glycol mixture as the solvent[15]. In both technologies, the CO_2-free synthesis gas is sent to the DME synthesis section and the CO_2-rich solvent is sent to a stripper where the CO_2 is removed and recycled to the Reforming section. The CO_2 that is not needed by the reforming section is vented.

The processed syngas is sent to the DME synthesis section where it is mixed with recycled unreacted syngas, and then reacted in KOGAS' proprietary DME reactor. In the reactor, the syngas is converted to DME, which was explained in detail our previous work[16]; methanol is also produced but is a minor product. The exit stream from the DME reactor is cooled and unreacted syngas is separated from the DME, methanol, CO_2 and water co-products. Unreacted syngas is recompressed and sent back to the DME reactor feed. CO_2 mixing with DME, methanol and waster is stripped and recycled to reforming section. The mixture of DME, methanol and water stream is then sent to the DME and methanol purification section.

KOGAS DME synthesis reactor (Fig. 4) is a multi-tubular type reactor, which use KOGAS' proprietary bifunctional catalyst[14]. Overall reactions are quite exothermic so the vertical tubes containing the catalyst are surrounded by a jacket containing water to remove the heat as shown in Fig. 4 shows that the exit stream from the DME reactor is sent to the DME and Methanol Purification section. In the DME and methanol purification section, the co-products from the DME reactor exit (primarily DME, methanol, and water)

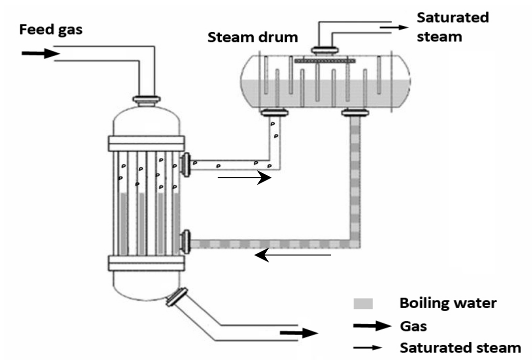

Fig. 4 KOGAS reactor converting syngas directly to DME

are separated in the DME column (DME from methanol and water) and the methanol dehydration column (separating methanol from water). DME product stream is sent to the battery limits. The dried methanol is sent to a methanol dehydration reactor where it is converted to additional DME. It is also possible to design this section to purify the byproduct methanol and produce it as a commercial product.

KOGAS DME plant requires an Air Separation Unit (ASU) and a number of utilities sections. The ASU produces the pure oxygen required by the reforming section. The utility sections required would typically include as followings:

· Steam & boiler feedwater
· Cooling water
· Refrigeration
· Process water
· Waste water treatment
· Electricity
· Product and byproduct storage & handling

The complexity and cost of the utilities sections will be a function of the site location. The more remote and less developed the site, the more self-sufficient the plant will need to be. In a more developed environment, some utilities (particularly electricity) may be available for purchase from outside the plant boundary. A special case would be DME FPSO, which would have to be entirely self sufficient.

3. DME synthesis

3.1 Physical and thermo-physical properties of DME

DME is the simplest ether which has a chemical formula of CH_3OCH_3. It has high oxygen content of 34.8% by mass and the absence of C-C bonds

Table 1 Comparison of DME's physical and thermo-physical properties to commonly used fuels

		Methane	Methanol	DME	Propane	Ethanol	Gasoline	Diesel
Formula		CH_4	CH_3OH	CH_3OCH_3	C_3H_8	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
Molecular weight (g/mol)		16.04	32.04	46.07	44.10	46.07	100.2	198.4
Density (kg/m^3)		0.72	792	661	582	785	737	856
Vapor garavity		-	-	1.59	1.52	-	-	-
Cetane number		-	-	>55	-	-	-	40-50
Normal B.P (℃)		-162	64	-24.9	-42.15	78	38-204	125-400
CHO content (mass%)	Carbon (C)	74	37	52.2	81.8	52.2	84	87
	Hydrogen (H)	26	12.5	13	18.2	13.0	16	13
	Oxygen (O)	0	50	34.8	0	34.5	0	0
LHV (MJ/L)		0.037	17.8	20.63		23.1	47.46	46.94
LHV (MJ/kg)		51.76	22.36	30.75	49.97	52.2	85.5	87
Sulfur content (ppm)		7-12	0	0		0	~200	~250

in the molecular structure.

Table 1 shows the physical properties of DME in details compared to commonly used fuels[2,3]. The physical properties of DME are similar to those of propane. DME has such high cetane number of 55~60 that it can be used as diesel engine fuel.

3.2 Feedstock description for DME synthesis

Natural gas from large gas fields is the assumed feedstock in most DME process development and commercialization studies. However, several other feedstocks offer potentially attractive alternatives for economic, environmental and/or strategic reasons at the national level. Attractive factors in the alternative feedstock are the sources that have a close proximity to the potential market such as CBM in China and Central Asia; renewable sources such as biomass in Southeast Asia; and source of potentially low-cost gas sources such as stranded gas. This section gives a brief overview of these alternative feedstocks summarizing the availability and key characteristics for use in DME production.

CBM is a form of natural gas that is extracted from coal beds. Traditionally most natural gas has been obtained as a byproduct from oil fields (i.e. associated natural gas) or from isolated natural gas fields (i.e. non-associated natural gas). CBM was viewed in the past as an unwanted and dangerous byproduct of coal mining but is now viewed as a resource in its own right. In addition, because methane is a more potent greenhouse gas than carbon dioxide, fugitive methane from coal mining activity is being viewed as a significant factor in global warming. Nearly 10 percent of atmospheric methane resulting from human activity is derived from coal mining[17]. Since CBM has only recently become viewed as a resource and the technology to estimate the amount is not yet

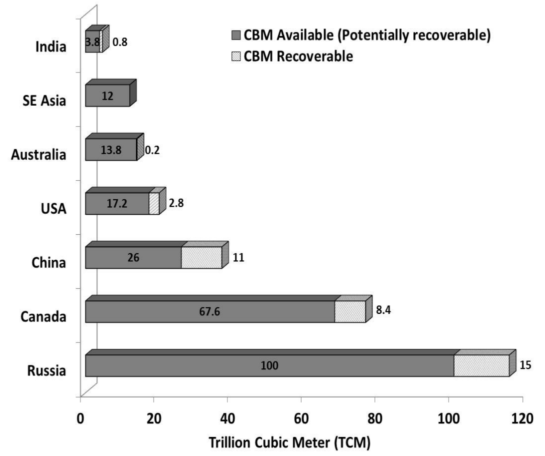

Fig. 5 Available CBM resources; the values in the above figure are estimated from all information collected in this study, not based on a specific study on the range for each site

well established, the information regarding the size or location of CBM resources is scarce. Reported here are estimations based on compilations and analysis of available information mostly from literature sources.

Fig. 5 shows the estimated available CBM resources for the top five countries[18] Russia, Canada, China, U.S. and Australia. Of the total 279 TCM (Trillion Cubic Meters) available CBM, approximately 14% is reported to be recoverable with the greatest amount of recoverable CBM residing in Russia, China and Canada; the 14% of the available CBM that is viewed as recoverable amounts to 39.06 TCM. To put this in perspective, 39.06 TCM is equivalent to about 67% of the proven conventional gas reserves for the same 5 countries[19].

The composition of CBM is an important consideration in determining the suitability for use as a feedstock for DME. Table 2 shows the composition of CBM from various locations in the world[20-23]. The CBM from Southeast Asia shows particularly high content of CO_2. The CO_2 content is an important variable in determining the per-

Table 2 Gas composition of CBM within United States

Basin	CH_4 (%)	CO_2 (%)	C_2+ (%)
Piceance, Colorado, USA	56.8 to 99.9	0 to 25.4	0.1 to 17.8
San Juan, Colorado and New Mexico, USA	77.1 to 99.9	0.1 to 9.4	0 to 13.5
Deep, Alberta, Canada	90.9 to 92.9	Not Given	7.1 to 9.1
Galilee, Queensland, Australia	98	1	1
Eastern China	60.9 to 99.9	0.1 to 5.1	0 to 34
South Sumatra, Indonesia	80 to 95	5 to 20	N/A
Northeastern Vietnam	60 to 80	20 to 40	N/A

formance of the DME plant and some CO_2 removal steps may be needed in these regions. The use of CBM will have very little impact on the KOGAS' process design and economics up to 50 vol% of CO_2 in the CBM source. Many of the CBM sources in Asia are high in CO_2, but pose no difficulties for the KOGAS' DME plant. Since the tri-reformer requires substantial CO_2 in its feed, no CO_2 removal from the CBM feed is needed. The CO_2 in the CBM means that less CO_2 needs to be recycled from the downstream in the process. In addition to the amount and composition, factors that affect extraction of CBM are also important considerations. Properties such as permeability, porosity, adsorption capacity and fracture permeability are key properties that determine the extractability. These factors are highly specific to each site and are beyond the scope of this article.

3.3 DME process variations for alternative feedstock

DME process can accommodate essentially any feedstock that can be converted to a syngas; in some cases some upgrading of the syngas may be needed to produce the a desired H_2:CO ratio for DME synthesis. In the overall plant design, the only section that might require a substantial modification is the reforming section. The downstream sections of the process in which CO_2 is removed and recycled, the syngas is reacted to DME, and the DME is recovered and purified will only require minor modifications to accommodate different feedstocks.

As discussed in Section 3 above, CBM is very similar in its range of composition to conventional natural gas with the exception that CBM sources are typically lower in sulfur compounds (e.g. H_2S) than conventional natural gas and some CBM sources have quite high CO_2. The low H_2S composition makes CBM attractive but high CO_2 makes it unattractive since it would have to be removed at some cost before the gas could be transported by pipeline or as LNG.

The KOGAS tri-reformer and DME reactor technology is able to accept CBM resources with CO_2 content between 0 and 50 vol% with virtually no changes to the reforming section or any of the downstream sections. Most conventional reforming technologies cannot tolerate high CO_2 content and will require costly CO_2 removal step. Hence, in regions of feedstock with high CO_2 content such as in Southeast Asia, the KOGAS process offers some competitive advantage.

As are the case with CBM, there are, essentially, no changes required in the process side of the design to utilize the natural gas from small to medium scale fields. The high CO_2 content prevalent in the fields of Southeast Asia can also be readily used in the KOGAS process as mentioned earlier. However, since these fields tend to be in remote locations, the plant may require a completely self-sufficient utilities plant. To address the situation where the small to medium scale gas fields is under the sea and far from land, KOGAS has begun

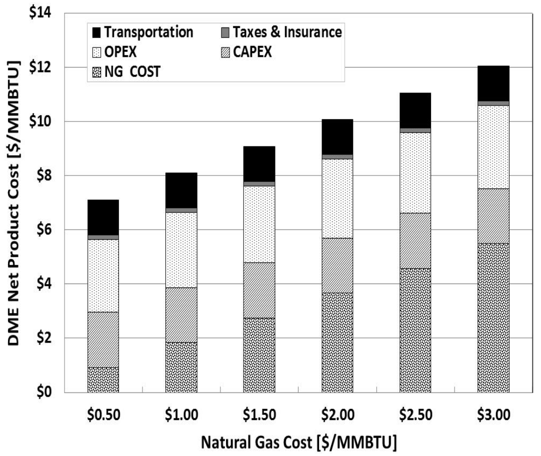

Fig. 6 Net product cost vs. natural gas cost (CAPEX fixed at $2.03)

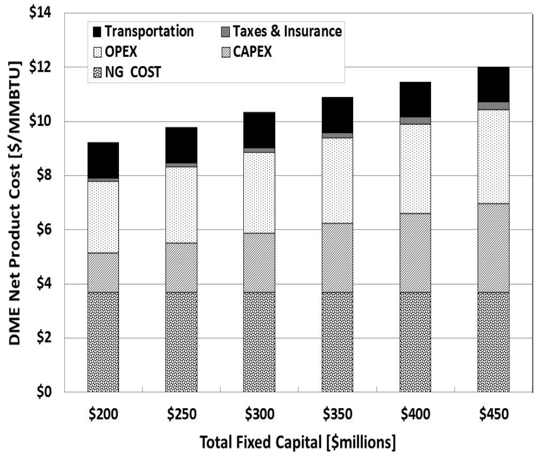

Fig. 7 Net product costs vs. total fixed capital (Natural gas cost is fixed at $2/MMBTU)

a research program of designing a shipboard DME plant (DME FPSO) that could be floated to any remote gas fields that is accessible from the sea. The gas would be converted to DME which would then be shipped to market by shuttle tankers. Numerous process designs, operation and safety issues will need to be investigated to meet the requirements that are unique to FPSO. Some of these requirements include entirely self-sufficient process including utilities; introduction of compact process equipment to overcome limited topside space, weight distribution and maximum height; and process technologies that can operate properly under the influence of the ship's motion.

4. Net Product Cost Estimation

The major cost factors that determine the Net Product Cost of DME are: the capital cost (CAPEX) to build the plant; operating cost (OPEX) involved in operating the plant; cost of the feedstock; cost of transportation from the DME plant to the market; and other expenses such as taxes and insurance. To illustrate the impact of these cost factors,

Fig. 6 and Fig. 7 shows net product cost as a function of natural gas price and capital cost respectively. The individual cost factors were obtained utilizing the cost data for 300,000 metric ton per year plant in the Middle East.

Table 3 Summary of the major cost factors that impact the DME net product cost for each of the alternative feedstock

	CBM	Small to Medium Gas Fields
CAPEX	Expected to be almost identical to conventional natural gas	Expected to be somewhat higher due to higher remote site construction costs and the need to be entirely self-sufficient in utilities
OPEX	Expected to be almost identical to conventional natural gas	Expected to have identical process efficiency to conventional natural gas for a land-base plant
Transportation Cost	Will depend on whether the resource is accessible by sea and what the distance is to end-use market.	Will depend highly on the site and whether transport by ship is feasible since it is far less costly than by rail.

A reliable estimation of the DME net product cost for the cases of the alternative feedstock is currently difficult due to the high uncertainty in the price of the feedstock and/or cost of adapting the existing DME process to use the alternate feedstock. Table 3 gives a summary of the major cost issues posed by each alternative feedstock on the net product cost. For CBM, the key determinant of the overall economic merit will depend on the CBM cost and distance of the resource from the end-use market. The economic merit will improve in areas where the CO_2 credit becomes reality.

5. Conclusions

The KOGAS DME process can accept a variety of alternative feedstocks[24] that are currently underutilized and convert them to a desirable, clean burning fuel with a wide range of application.

The alternative fuels are of interest since they might be available for use in the DME process at lower net cost than conventional natural gas.

CBM can be accepted by the KOGAS DME process with virtually no change in process design. CBM frequently has high CO_2 which makes pipeline or LNG transportation uneconomic but can accepted by the KOGAS DME process without pre-treatment. KOGAS DME process will convert a harmful greenhouse gas to a more clean fuel; may be eligible for CO_2 Credits which will positively impact process economics.

The KOGAS DME process has an advantage in that it will be able to exploit alternative feedstock but it will be essential that the alternate resource be available at a cost that allows the process to operate economically given the efficiency of conversion of the feedstock to DME, the capital and operating costs for the process operating with that feedstock, any tax benefits or subsidies associated with the feedstock, transportation costs from the plant site to market, and the expected range of DME market prices

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