

SCALE UP STUDY OF DME DIRECT SYNTHESIS TECHNOLOGY

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Keywords: 1. dimethyl ether; 2. scale up; 3. tri-reforming; 4. syngas; 5. synthesis.

1 Introduction

Dimethyl ether (DME) is the simplest ether and is considered a leading alternative to petroleum-base fuels and liquefied natural gas. Its physical properties are similar to liquefied petroleum gas (LPG) and can be stored and delivered using existing land and sea based infrastructures with minor modifications. DME can be prepared from various energy sources including natural gas or coal, as well as biomass. We call the DME is multi source, multipurpose.

The largest market for DME is Asia, where the capacity has steadily increased and will continue to grow with new plants constructed for the domestic fuel market. This has been especially true in China, due to the rapid growth of the economy and aggressive investment in methanol and DME plants. Annual production capacity and production were only 31.8 and 20 TPA, respectively, in 2002, but increased to 480 and 320 MTPA by 2006, with annual increases of around 96 to 97%. A 3 million TPA DME plant in Inner Mongolia has been approved by the government and will be put into production by 2010, with a gross investment of 21 billion RMB. In the next 3 years, China will continue to construct large DME plants. By 2010, it is estimated that annual production capacity will be 15 million TPA. DME production is ready for mass utilization and large-scale market operation in China [1].

Japan DME, Ltd. announced plans in February 2007 to establish a Joint Venture Company for DME production, and to construct an 80,000 TPA DME production plant within Mitsubishi Gas Chemical Company's Niigata Factory. The plant is scheduled to start operation in June 2008, with production capacity expandable to 100,000 TPA. JGC is in charge of the construction of this new production plant, and Mitsubishi Gas Chemical will be operator.

The potential market for DME imports as a LPG substitute in Asia is expected to grow from 18 MMTPA in 2012 to 27 MMTPA by 2030. This amount is well above the planned capacity for DME in the region Korea, China, Japan and India are expected to have the largest markets.

Table 1. DME imports to various countries, in million TPA. [2]

	China	Japan	Taiwan	Korea	India	Indonesia	Vietnam	Philippines	Total
2012	7.0	4.7	0.5	1.5	3.7	0.0	0.3	0.3	18.1
2020	7.6	4.7	0.5	1.6	5.3	1.7	0.1	0.4	21.9
2030	8.3	4.7	0.5	1.6	7.6	2.8	0.8	0.5	26.8

Table 2 shows the plans for construction of new plants in Japan, Iran, and New Guinea and Korea were currently under consideration.

Up to now, commercial DME plants have been constructed based on conventional 2 step process. Technology providers of 2 step process include Haldor Topsøe, Lurgi, Toyo, and MGC. On the other hand, KOGAS and JFE Holdings have developed 1 step process which produces DME directly from the synthesis gas. KOGAS and JFE have adopted fixed bed and slurry bed technology respectively [3].

In Korea, KOGAS has been developing the DME project using 10 TPD demonstration (Demo) plant since 2005. In this project three companies and four research institutes are involved. In May 2008, test run of Demo plant was started and operation for 9 month was finished successfully. KOGAS performed the test operation three times and validate the technology of 1 step DME synthetic process for a 1 MMTPA commercial plant.

KOGAS has developed a process in which syngas is produced from natural gas in a proprietary auto-thermal reformer (the Tri-Reformer) and then converted to DME in a single-step reactor. This study contains the technical discussion of the 3,000 TPD KOGAS DME process design.

Table 2. International DME Projects [4]

Company	Location	Capacity	Start Up Date	Use
Zagros Petrochemical	Assaluyeh	800,000 MTPA	Will come on stream in 2008	Domestic Fuel
Japan DME ^{*)}	Niigata	80,000 MTPA	Onstream June 2008	Aerosol, Domestic Fuel
Japan DME ^{*)}	Papua New Guinea	1,000,000 MTPA	Feasibility Study announced March 1, 2007. If commercialized, projected onstream in 2011	Domestic Fuel
KOGAS	SEA	1,000,000 MTPA	Preliminary Feasibility Study finished April 2008. If commercialized, projected onstream in 2013	Domestic Fuel

2 Objectives

Energy problems are no longer future problems. There is an increase in energy consumption, and carbon dioxide emission is also a serious problem, so we need to develop the clean energy technology. KOGAS is developing technology for future energy security..

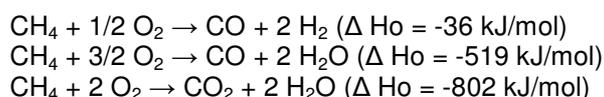
The Korea Institute of Science and Technology, the Korea Institute of Energy Research and the Korea Research Institute of Chemical Technology as well as Korea Gas Corporation conducted the study of the synthesizing methanol and DME from carbon dioxide by hydrogenation, as the program of carbon dioxide treatment, and are currently under operation of the experiment in the DME plant scale enlarged from the pilot scale.

In 1997 KOGAS has conducted "the project study of the preparation of liquid fuels from natural gas" with the support of the Ministry of Commerce, Industry and Energy, and then proposed that DME preparation according to Gas to Liquid (GTL) procedures for liquefying natural gas is the optimum process in connection with the program for removal of carbon dioxide. Meanwhile, from the year 2000 the study of "the development of technology for preparing DME from natural gas and carbon dioxide" was conducted. In the year 2001 they started the study of development of the 50 kg/day DME process with the support of the Ministry of Science & Technology, and then established the pilot plant in the year 2002, successfully operated the plant in 2003. At present, this process is in the 10 TPD demonstration stage. The Demo plant had constructed in 2008.

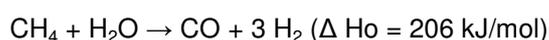
3 KOGAS DME process

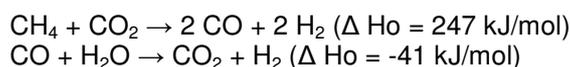
The 10 TPD Demo plant can be divided into two parts. Firstly, reforming reaction section wherein carbon dioxide, oxygen and steam are reacted with natural gas in the reforming reactor. Other section is the carbon dioxide recovering section wherein carbon dioxide is recovered and treated for re-use as the raw material. Second part is the DME synthesizing part wherein DME is prepared from syngas. Figure 1 schematically and briefly represents a series of processes for producing DME from natural gas [5].

To produce C1 and hydrogen from C2, C3 components occupying 8~10% of natural gas, the natural gas and steam were treated by pre-reforming reactor and then went into the tri-reformer. Oxygen and carbon dioxide were went into the upper part of the tri-reformer and then raised an intense oxidation reaction (combustion reaction) from oxygen and methane gas according to the following reaction to elevate the temperature of the reformer:



Subsequently, the steam reforming reaction, CO₂ reforming reaction and water-gas shift reaction occurred according to the following reactions:





The tri-reforming reaction of methane with CO_2 , O_2 and H_2O has the advantage in that the ratio of H_2/CO can be controlled, although it has a very complicated mechanism.

The syngas and un-reacted methane are used as the raw materials for DME synthesis. CO_2 is separated by adsorbing onto methanol, recovered in the CO_2 stripper and used as the raw material feed. The syngas is compressed up to 5 MPa and then goes into DME reactor wherein the reaction temperature is 200~300°C. The reaction is quite exothermic so the vertical tubes containing the catalyst are surrounded by a jacket containing boiling water to remove heat. The pressure of the boiling water is set to keep a constant temperature in the jacket. Sufficient heat is removed into the boiling water to maintain the reacting gas at 260 C. The resulting DME is collected in a DME tank wherein the test samples are taken from each sampling port at the top and bottom and then analyzed with gas chromatography.

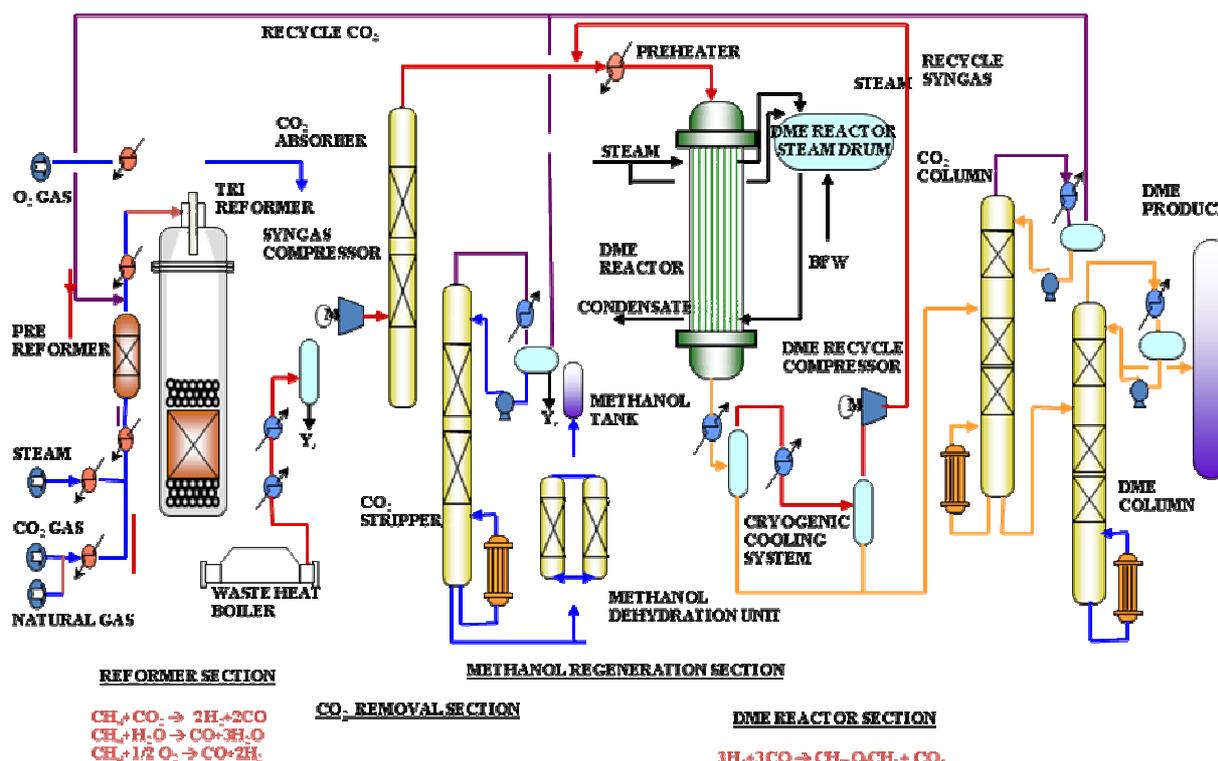


Figure 1. Schematic diagram of the process of 10 TPD DME production Demo plant

4 Results

a. Operation results of 10 ton/day demonstration plant

The temperature in the tri-reformer was stably maintained between 950 and 1000 C. Figure 2 show the methane conversion results. The averaged methane conversion was about 99.7 %. After all the conditions got stable, the methane conversion was 99.9%. Figure 3 describe the H_2/CO ratio. Syngas ratio was between 3 and 5 during autothermal reforming reaction. While, the ratio was between 1.0 and 1.2 during tri-reforming reaction.

Figure 4 show the CO conversion results. We could get 82 % conversion of CO in operation. DME production graph is described in the figure 5. DME selectivity was higher than 67 %, DME yields were about 55%. These results are relatively high and very satisfactory.

In OPR100 the maximum production rate was 10.6 ton per day, and 8.1 was the averaged value.

Table 3 shows the test operation results. We carried out three test operation from 2008 to 2009 to demonstrate the validity of the direct DME synthesis technology and collect engineering data for commercial scale plant.

In view of the result from the operation of 10 TPD DME Demo plant, it is considered that the syngas ratio and the DME selectivity according to the gas phase direct synthesis (GPDS) show the result arriving at the advanced technological level.

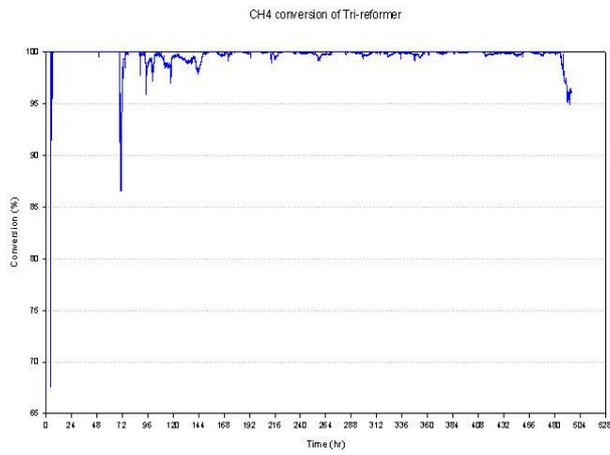


Figure 2. CH4 conversion of tri-reformer

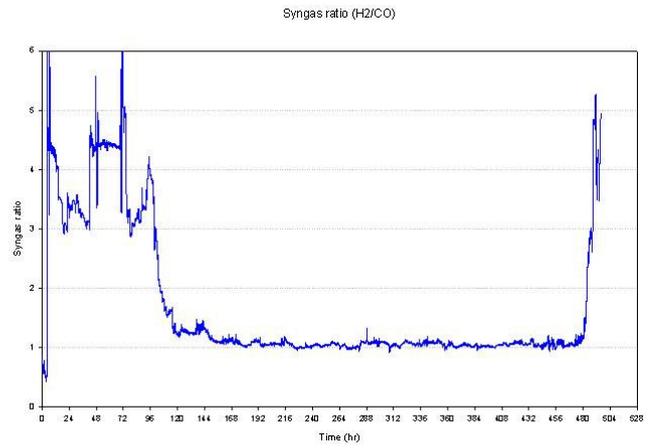


Figure 3. Syngas ratio at the reformer outlet

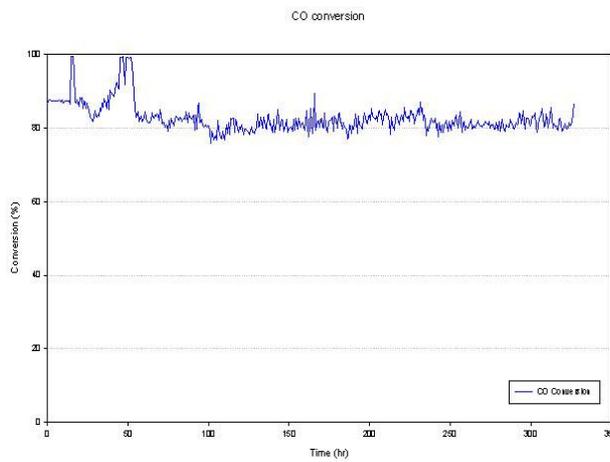


Figure 4. CO conversion in DME reactor

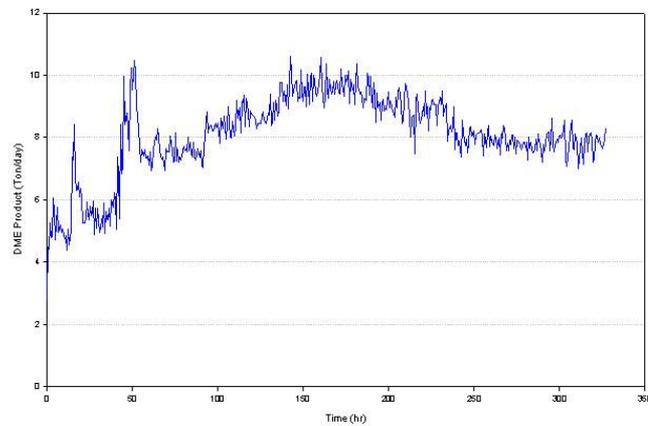


Figure 5. DME production on 10 TPD Demo plant

Table 3. Results of Test Operation

Operation No.	Period	Duration (day)	DME production (t)
OPR 100	2008/09/29 - 2008/10/31	33	25
OPR 200	2009/03/09 - 2009/04/03	25	116
OPR 300	2009/05/13 - 2009/06/03	20	60
Total		78	201

b. Concept engineering of commercial DME plant [6]

The design bases of KOGAS DME process are as follows. This plant is designed with a stream factor of 8,000 hr/yr to produce 3,000 TPD DME. The natural gas feedstock is also used to provide all the energy requirements (direct heat, steam, and electricity) for the process. The natural gas cost at the battery limit is assumed to be: \$2.00 \$/MMBTU (HHV). The DME product is to be 99.6 wt% pure. The storage facilities are consist of intermediate DME storage (2 x 1 day tanks, 1 x 1 day off-spec tank) and 2 x 65,000 cubic meter storage tanks (~28 days).

We designed the natural gas reforming, syngas processing, DME reaction, and DME separation system. Also we defined utility site data, battery limit condition, codes, and standards.

In the Reforming section, natural gas is reacted with steam, oxygen, and recycled CO₂ to produce synthesis gas. The key pieces of equipment in this section are the pre-reformer and the tri-reformer. The pre-reformer is an adiabatic fixed-bed catalytic reactor that cracks these heavier hydrocarbons to form methane and byproducts. The Tri-Reformer is an adiabatic auto-thermal reformer that is based on KOGAS' own technology. It has a homogeneous section and a fixed bed catalyst section (using KOGAS' proprietary catalyst) and react the pre-reformed natural gas (primarily methane), steam, oxygen, and carbon dioxide to produce synthesis gas containing the correct amount and ratio of carbon monoxide and hydrogen. As an auto-thermal reactor, the Tri-Reformer uses exothermic combustion reactions to offset the endothermic reforming reactions. The resulting exit temperature is around 1000 C and the pressure is 3.101 MPa. The ratio of hydrogen to carbon monoxide in the Tri-Reformer outlet is set to be 1.3 to provide the correct H₂:CO ratio in the mixed feed into the DME reactor. The current assumption is that the 3,000 metric ton per day plant will require three Pre-Reformers/Tri-Reformer reactor set in parallel.

Syngas processing section serves to remove recover heat from the raw syngas and to condense most of the water vapor. The syngas is used to preheat the natural gas feed, the feed to the pre-reformer, and the feed to the Tri-Reformer before being is used to raise process steam which results in the syngas being cooled to 331 C. The syngas is then cooled in stages to 158 C. This heat is available for use in the OSBL utility section.

The DME synthesis reactors are jacketed, tubular reactors using KOGAS' proprietary catalyst. The mixed recycle/makeup syngas stream is then heated to 230 C before entering the DME reactor and being partially reacted to form DME, methanol, and byproducts. The inlet to the reactor is set to 230 C and 6.101 MPa. The CO₂ in reactor feed is currently maintained at less than 10 vol% and the H₂:CO ratio is maintained between 1.4 and 1.5 molar. The DME reactors are expected to achieve a 68% conversion of CO. The 3,000 metric ton per day process is expected to require 4 of these tubular, jacketed reactors

DME separation and purification section will be a single train that takes the combined output streams from the four DME synthesis reactors, removes CO₂, recycles unreacted syngas to the DME reactor feeds, separates DME from the byproduct methanol and provides a DME product stream with the specified purity. The DME outlet stream is at 260 C and about 6 MPa and is cooled in stages against boiler feed water, air cooling, and cooling water. Condensate is removed in knockout drum and the overhead vapor is cooled to -40 C. We also design the utility section, but do not manipulate in this paper.

The energy efficiency for a green field plant is defined as the energy content (LHV) of the product (DME) divided by the energy content of the natural gas process feed and the natural gas needed to provide all of the plant utilities.

Process Energy Efficiency		
Energy Consumed	kg/hr	GJ/hr
NG Process Feed	115,841	5,086
OSBL Boiler		199
Section 400 Purge		-168
	Total	5,117
Product Energy	kg/hr	GJ/hr
DME	125,000	3,590
	Total	3,590
Overall Energy efficiency		70.1%
Electricity Consumption		934
Modified energy efficiency		59%

The imported electricity is assigned a generation efficiency of 35% to remain equivalent to green field plant operation.

c. Cost estimation of commercial DME plant

A conceptual design of 3,000 TPD KOGAS DME process was completed and the cost of this design was estimated to be as follows:

Case	17	100
Equipment	\$311 million	\$249 million
ISBL	\$733 million	\$477 million
OSBL	\$367 million	\$238 million
TFC	\$1.1 billion	\$715 million

The Case 17 represents an intermediate process design which served to identify areas of potential cost savings. A series of design changes were made to lower the cost using simulation, resulting in the Case 100 which represents the lowest cost design we have produced to date.

The Equipment and ISBL costs were based on Stone & Webster's in-house cost estimation data and vendor-assisted estimates. Factored Cost estimation method was used which typically has an accuracy of +/- 20 to 30%. The OSBL was factored off the ISBL that is commensurate with the competitor's processes.

This study suggests that the KOGAS process is economically competitive and could potentially surpass them.

5 Summary

Due to environmentally friendly properties, DME is considered as one of the most promising candidates for the substitute of LPG and diesel fuel. In this work, we describe the one-step synthesis of DME process and operation results of 10 TPD scale Demo plant. KOGAS DME Demo plant shows the good data on methane and carbon monoxide conversion as well as DME selectivity and productivity. From the operation result we can design the commercial scale DME plant. Also, we can estimate the cost of the 3,000 TPD DME plant. KOGAS completed the preliminary feasibility study on commercial scale DME project in 2008. A plan has been prepared to implement the DME project with a target of end-year 2012 for the start-up of the plant.

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