

# Slurry Phase Synthesis and Utilization of Dimethyl Ether

Yotaro Ohno\*, Norio Inoue\*\*, Takashi Ogawa\*\*\*,  
Masami Ono\*\*\*, Tsutomu Shikada\*\*\*\* and Hiromasa Hayashi\*\*\*\*\*

\* Chief Engineer, Dr, Environmental Solution Center  
\*\* Manager, Environmental Solution Center  
\*\*\* Senior Research Engineer, Engineering Research Center  
\*\*\*\* Chief Researcher, Dr, Applied Technology Research Center  
\*\*\*\*\* Senior Research Engineer, Applied Technology Research Center

*DME (dimethyl ether) has been attracting the attention of industry as a clean fuel for the 21st century. NKK has been conducting original DME synthesis research since 1989. Operational research was performed in a 5 tons-DME production/day pilot plant, which operated continuously under very stable conditions for periods up to two months. These studies led to the successful synthesis of DME from methane directly from coal layers. Combustion tests of DME in a commercial type household cooking gas stove and diesel truck driving tests confirmed that DME has high potential as an alternative fuel.*

## 1. Introduction

DME (Dimethyl ether) is a new, easily handled fuel that is currently the subject of considerable interest. NKK began basic research and development on a new synthesizing catalyst in 1989. Following completion of this work in 1995, NKK established a small-scale bench plant capable of producing DME at a rate of 50 kg per day. In 1997 a large-scale bench plant capable of producing approximately five tons per day was constructed to develop a new, high-efficiency, DME synthesis process<sup>1)</sup>.

DME is currently manufactured at a rate of approximately 10000 tons annually for such applications as cosmetics and aerosol paint propellants. This DME is produced using methanol as the raw material and involves a dehydration reaction to remove a single water molecule from two methanol molecules.

NKK developed new production technology that uses carbon monoxide (CO) and hydrogen (H<sub>2</sub>) gases as the raw material for synthesizing DME in a highly-efficient, single-step reaction process. The conversion efficiency for the raw material gases for the synthesis reaction and the selectivity level to the DME product are extremely high. Thus, the synthesis process is more compact and simple than that for the production of methanol from CO and H<sub>2</sub>.

The large-scale bench plant introduced in 1997 was a technology development program supported by the Resources and Energy Agency within the Ministry of International Trade and Industry (now the Ministry of Trade,

Economics and Industry). The technology was implemented jointly by the CCUJ (Center for Coal Utilization, Japan), Taiheiyo Coal Mining Co., Ltd., and Sumitomo Metal Industries, Ltd. at a plant constructed at the Taiheiyo Coal Mining site in Kushiro City. Construction began in the summer of 1999, and operation and research commenced approximately 18 months later. A total of six continuous trials have been conducted, and operation of the plant has proven to be extremely stable, with the longest continuous period of operation being two months. A total of approximately 400 tons of high-purity DME has been produced during these trials.

## 2. Characteristics of DME as a fuel

DME has similar properties to LPG in that it is a gas at ambient temperature and atmospheric pressure. It becomes a colorless clear liquid under six atmospheres at ambient temperature or at atmospheric pressure and a temperature of  $-25^{\circ}\text{C}^1)$ . Thus, DME can be transported and stored as a liquid at low temperature in a similar manner to LPG.

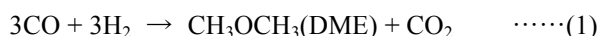
DME is a clean fuel that contains no sulfur or nitrogen compounds, has extremely low toxicity for humans, and has no corrosive effect on metals. Its calorific value is approximately 65% that of methane (natural gas) and approximately 40% that of methanol. Although DME has a lower calorific value than LPG because of differences in the chemical structure, the density of liquid DME is greater, so the total calorific value of a tank of DME is approximately 90% of that of a similar tank of LPG.

When used as a replacement for diesel fuel, DME has a high cetane value, contains oxygen, and has a chemical structure that forms carbon-carbon bonds, so that its combustion is not accompanied by black smoke or soot. This property has attracted considerable interest in DME as a clean fuel.

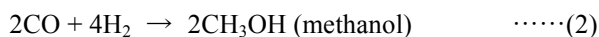
DME may be used in the same domestic applications as LPG, as well in an extremely wide range of industrial applications, such as a replacement for diesel fuel and for high-efficiency power generation fuels (e.g. for gas turbine powered generators). DME is also easily stored and transported.

### 3. Features of DME direct synthesis technology

The technology for direct synthesis of DME developed by NKK employs a single-step reaction to synthesize DME from CO and H<sub>2</sub> as shown in (1) below.



This formula summarizes the DME direct synthesis reaction. In practice, the reactions shown in the formulae (2), (3), and (4) below occur simultaneously.



The two molecules of methanol synthesized from CO and H<sub>2</sub> in formula (2) are dehydrated in formula (3) to produce DME. The water produced in formula (3) is recycled as hydrogen in formula (4).

It is important to note that the hydrogen produced at the completion of the direct synthesis reaction becomes raw material for the reaction in step (2). In this way, a reaction cycle is formed in which the three reactions consume the by-products in each step. The by-products of the reactions therefore accumulate only to a minimal extent, allowing an extremely high conversion efficiency for the total reaction formula (1).

Formula (1) becomes increasingly favorable with increasing pressure, so the reaction is conducted at a pressure of 3 to 7MPa and temperature of 250 to 280°C (basic reaction conditions are 5MPa and 260°C).

Formula (1) is a highly exothermic reaction that produces 58.8 kcal per mole of DME (approximately 1280

kcal per kilogram of DME). This reaction heat must be removed efficiently from the reactor to maintain a stable temperature and to allow stable control of the DME direct synthesis reaction. NKK therefore developed a high-pressure DME slurry bed reactor that has excellent mixing characteristics and easy control of the reaction temperature. This slurry bed reactor contains a high boiling point solvent (reaction medium) in which fine catalyst particles are mixed. The gases that form the raw materials of the reaction provide strong mixing of the catalyst. This ensures good flow of the gases within the reactor, a very even temperature distribution, and ready control of the DME direct synthesis in the presence of the highly exothermic reaction.

The DME direct synthesis reaction is characterized by NKK's proprietary highly active catalyst and the DME slurry bed reactor technology, which controls the reaction to extract the maximum performance from this catalyst.

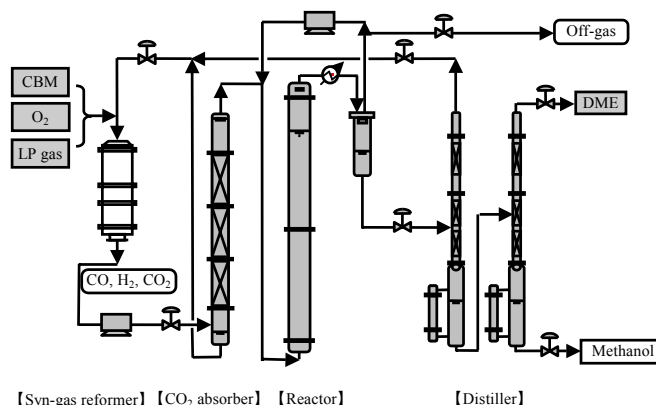
## 4. Five tons per day large-scale bench plant

### 4.1 Process flow

The large-scale bench plant is shown in **Photo 1**. Process flow is shown in **Fig.1**.



**Photo 1** Five ton per day DME test plant



**Fig.1** Process flow for five ton per day DME test plant

This plant employs refined methane from coal layers or simulated coal gas (produced from LPG in this plant) as a raw material to efficiently produce DME in a single-step reaction using a slurry bed reactor.

The process components are described below.

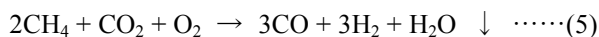
- (1) Synthesis gas production system incorporating a reformer to produce CO and hydrogen from the coal bed methane (or LPG)
- (2) Reaction system for direct synthesis of DME
- (3) Distillation system for refining the DME produced, and separating and recovering the by-product CO<sub>2</sub>
- (4) Product storage and utility equipment system.

Each unit is controlled from a central computer in the control room.

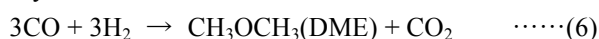
The coal bed methane or LPG is burned in the auto-thermal reformer in an atmosphere of pure oxygen to produce CO and H<sub>2</sub> in a ratio of 1:1 (H<sub>2</sub>/CO=1). The CO<sub>2</sub> produced in the reformer and the CO<sub>2</sub> produced as a by-product of direct synthesis of DME are separated and partially recycled back to the reformer for use as a raw material for gas synthesis.

If an efficiency of 100% was possible for the reforming and DME direct synthesis reactions, natural gas (methane) could be used in the ideal synthesis process described in formula (7).

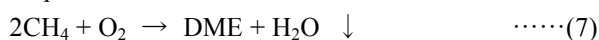
Reformer



DME synthesis



Overall process



## 4.2 Operation and research

Operation and research of the large-scale bench plant commenced in September 1999 and continued until December 2000. The objective of the work was to establish technology for a high-performance DME synthesis process under the long-term and stable operation of a large-scale plant, to obtain detailed data for use in scaling-up the process, and to produce large volumes of DME. The plant was run continuously six times (Run Nos. 100 to 600). Details are shown in **Table 1**.

Run 100 was conducted solely to test the gas synthesis system. The reaction and distillation systems were tested without producing DME.

**Table 1** Continuous plant operation details

Run.	Test period	Plant operation [h]	Syn-gas production [h]	DME production [h]
100	1999/Sep.9–Sep.23	270	207	—
200	Oct.9–Nov.2	466	460	408
300	Nov.11–Dec.2	492	488	457
400	2000/Jun.12–Jul.9	700	652	464
500	Jul.18–Aug.6	495	484	458
600	Sep.18–Dec.6	1870	1780	1650
Sum.		4293	4071	3437

Run 200 was the first in which DME was produced. The entire plant was started, and various tests were conducted on all systems.

Run 600 involved continuous and stable operation of the plant for a period of two months. Approximately 400 tons of DME was produced during Run 200 through Run 600.

## 4.3 Results of operation and research

### 4.3.1 Outline of results

All systems in the plant operated in a stable manner during Run 200 through Run 600, and a detailed process mass-balance data was recorded for further analysis. The primary operation and research results are as follows.

- (1) A per-pass synthesis gas conversion of higher than 50% and a product DME selectivity of higher than 90% were achieved in the direct synthesis of DME.
- (2) A total synthesis gas conversion of at least 95% was achieved.
- (3) The purity of the DME produced was at least 99.5%.
- (4) The successful direct synthesis of DME from 100% coal bed methane was a world first.
- (5) The daily production was attained up to 5.7 tons while the plant was designed for a daily production of 5 tons.
- (6) A stable operation of the reaction system was maintained for 1650 hours (the plant operated for 1870 hours in total).
- (7) Data was recorded for use in scaling-up the DME slurry bed reactor.

### 4.3.2 Plant material balance and product selectivity

The mass-balance data (materials used, product) for a representative plant producing 5.7 tons of DME per day is shown in **Table 2**. The process consists of partial oxidation with pure oxygen to synthesize gas at a ratio of H<sub>2</sub>/CO=1 using LPG as the primary raw material and CO<sub>2</sub> and steam as the secondary raw materials. Production was approximately 5.7 tons of DME per day and 0.6 tons of methanol per day from the synthesis gas. The CO and H<sub>2</sub> in **Table 2** are un-reacted gases included in the gas purged

from the reactor system as off gas. The total CO conversion was 94%.

**Table 2 Materials balance in LPG plant operation**

Raw material	Flow rate [Nm <sup>3</sup> /h]	Product	Flow rate [kg/h]	Production [t/d]
LP gas	124.1	DME	238.2	5.72
CO <sub>2</sub>	66.8	MeOH	26.3	0.63
Steam	241.9	water	3.7	0.09
O <sub>2</sub>	85.9	CO <sub>2</sub>	111.4	
		CO	22.9	
		H <sub>2</sub>	15.9	
		Total CO conversion		94.0 [%]

The ratio of hydrogen atoms to carbon atoms in propane (C<sub>3</sub>H<sub>8</sub>), which is the primary component of the LPG raw material, is less than that for methane (CH<sub>4</sub>), so all of the CO<sub>2</sub> produced as a by-product of DME synthesis cannot be reconverted in the reformer. However, approximately 60% of the 111Nm<sup>3</sup>/hr of CO<sub>2</sub> generated is reused as a secondary raw material in the production of synthesis gas.

The product selectivity is shown in **Table 3**. A feature of this DME direct synthesis method is that it has a very high once-through conversion synthesis gas, along with a DME product selectivity of higher than 90%. In addition to the CO<sub>2</sub> and methanol produced, the only other by-product of the process is a very small amount of methane.

The process produces no by-products such as heavy oils and not even trace quantities of toxic materials. These characteristics eliminate the need for complex separation and refining of generated products and guarantee a simple synthesis process, leading to reduced plant costs and operating expenses.

The CO<sub>2</sub> produced as a by-product when natural gas (methane) is used as the primary raw material is recirculated to the reformer. The methanol produced has value as a product, but it is recycled to the reactor and may be finally converted to DME because it is an intermediate product of the DME synthesis reaction. The DME product selectivity shown in **Table 3** is the carbon selectivity to DME without CO<sub>2</sub> and DME contained in recovered methanol.

**Table 3 Product selectivity (once-through basis)**

Raw material	Selectivity [C-mol%]			DME product selectivity [C-mol%]
	DME	CO <sub>2</sub>	MeOH	
LPG100%	64.7	33.8	1.6	97.6
CBM85% + LPG15%	64.8	32.4	2.8	95.8
CBM100%	63.4	30.9	5.7	91.8

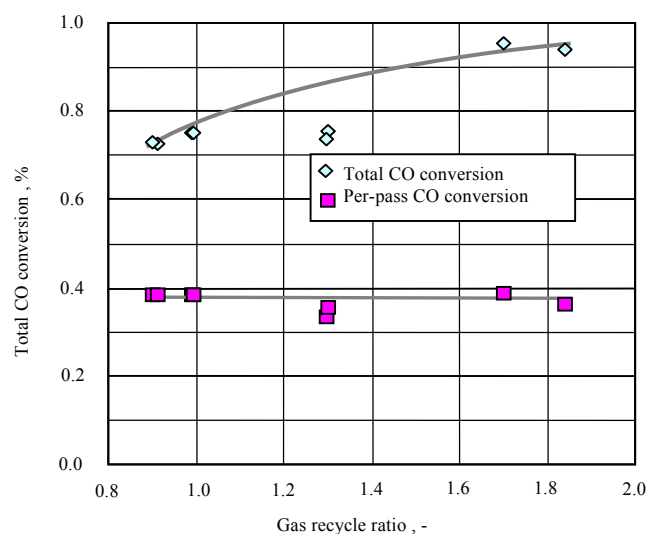
(CBM = Coal bed methane)

### 4.3.3 Total conversion of synthesis gas

Between 40 and 50% of the raw material gas is converted to DME after passing through the reactor (the once-through conversion varies with the operating conditions). As shown in the process flow diagram, the un-reacted raw material gas discharged from the reactor passes through the recycling compressor before being recirculated to the reactor. The amount of this un-reacted gas that is recycled depends upon the conversion efficiency of the reaction process and affects such factors as the scale of the equipment (e.g., the compressor size), the operating costs of the equipment, and the final cost of production.

As DME direct synthesis has a very high once-through conversion level in comparison to methanol synthesis, the volume of un-reacted, recycled gas is small, permitting a plant of compact design. **Fig.2** shows the effect of the recycling ratio, i.e., the ratio of the un-reacted, recycled gas volume to the volume of synthesized gas introduced into the reactor system (make-up gas). The total conversion of CO in the make-up synthesized gas as calculated from measured data is also shown. **Fig.2** indicates that the total CO conversion exceeds 95% at a recycling ratio of approximately 1.7, and that the once-through CO conversion maintains a relatively constant value.

The process is commercially viable provided the gas recycling system is designed to handle recycling of a volume of gas approximately twice the volume of the synthesized make-up gas. Under the same reaction conditions, the process is considerably more compact than the methanol synthesis process.



**Fig.2 Total CO conversion as a function of recycling ratio**

## 5. DME utilization technology

### 5.1 Use as an LPG alternative

DME is already used as an aerosol propellant, and it is expected that, in the future, it will also be used in such applications as fuel for power generation, diesel vehicles, and consumer applications, as a raw material for chemical processes, and as a cooling medium<sup>2-4</sup>). The prospect of DME as an alternative fuel to LPG in consumer applications stimulated experiments to investigate DME combustion in existing mass-produced combustion equipment in order to gain an understanding of its combustion characteristics.

DME has a WI (Wobbe Index, which is the higher calorific value/(specific gravity)<sup>1/2</sup> and is used as a basic measure of heat input for gas appliances) of 51.91 MJ/Nm<sup>3</sup> and an MCP (an index of the rate of gas combustion) of 48 to 50. The WI for DME is close to that of 13A and 12A municipal gases, but its MCP is outside the corresponding range. DME is equivalent to a gas classification of 12C, a type not currently used.

Combustion tests of DME were conducted using standard domestic cooking stoves designed for LPG or municipal gas 13A. Combustion of DME using the LPG stove shown in **Photo 2(a)** is clearly unsatisfactory. No significant improvement in combustion was observed, even when the air adjustment damper, which is normally fixed, was closed down to approximately 80%. This lack of improvement is due to the fact that the diameter of the main nozzle on the LPG stove is very small (0.9 mm), thus preventing a sufficient supply of DME and resulting in insufficient heat of combustion.

Combustion of DME with the municipal gas 13A stove is shown in **Photo 2 (b)**. Combustion was relatively satisfactory, but the flame tended to be shorter than is the case when 13A is burned. Changing the opening of the variable air adjustment damper from 8/10 to 5/10 reduced the primary air supply and resulted in good combustion, as shown in **Photo 2(c)**. Changing the gas pressure from 1 to 3.3 kPa did not result in any significant difference in combustion.

JIS combustion testing (JIS S 2093) to determine the suitability of the gas combustion equipment for DME resulted in passes in all items on the test schedule, from tests in no-wind conditions to tests with large pots, and certification was granted (see **Table 4**). JIS thermal efficiency testing (JIS S 2093) to determine the performance of gas combustion equipment in use showed a thermal efficiency



(a) LPG specification, damper opening : fixed



(b) 13A specification, damper opening : 8/10



(c) 13A specification, damper opening : 5/10

**Photo 2 Combustibility of DME**

of 47.9% with DME, approximately 2% less than with municipal gas 13A. DME is well within the JIS standards, which require a thermal efficiency of at least 40%.

**Table 4 DME combustion test results**

Item	JIS standard	Result	
Test under windless condition	Ignition	No explosive ignition	None
	Flame stability	Steady flame	Passed the standard
	Back fire	No back fire	None
	Combustion noise	60 dB or less	Within the standard
	Fire extinguish	No explosive noise	Within the standard
	CO concentration	0.14% or less	0.05%
	Soot emission	No emission of soot	Within the standard
Oversized pot test	Steady flame / no odor	Passed the standard	
Total evaluation		Passed the standard	

Conditions : Japanese municipal gas 13A specifications. damper opening 5/10

### 5.2 Use as a diesel fuel alternative

DME has the same or higher cetane value as diesel fuel and is therefore ideal for use in diesel engines. However, modifications to the fuel supply system are required because both the boiling point and viscosity of DME are less than those of diesel fuel.



NKK employed its diesel engine test bench, which has been in use since 1997, to investigate both the characteristics of DME when used in diesel engines and the fuel supply system required for this application. In 1998, a light truck was operated on DME, which was a world first<sup>4)</sup>.

A description of the modifications of diesel engines to use DME and the associated combustion characteristics are presented below.

The use of DME, with its low boiling point and low viscosity, does not require modifications to the diesel engine itself. Nevertheless, in contrast to diesel fuel, DME must be supplied to the fuel injection pump under pressure. In initial experiments, gas pressure from a nitrogen bottle was used for pressurization, but this installation resulted in supply equipment of considerable size, and nitrogen gas dissolved into the liquid DME. A small fuel supply pump was therefore developed<sup>5)</sup> to overcome these problems. The DME diesel truck employed in the experiment is shown in **Photo 3**. The original diesel fuel tank was used to contain the DME.

As shown in **Fig.3**, the combustion characteristics of the DME diesel engine include a thermal efficiency that is similar to that of diesel, but without soot emission and with greatly reduced NOx emissions and noise levels. This is due to the fact that DME is an oxygenated fuel without carbon bonding and to the greater ignitability in comparison to diesel.

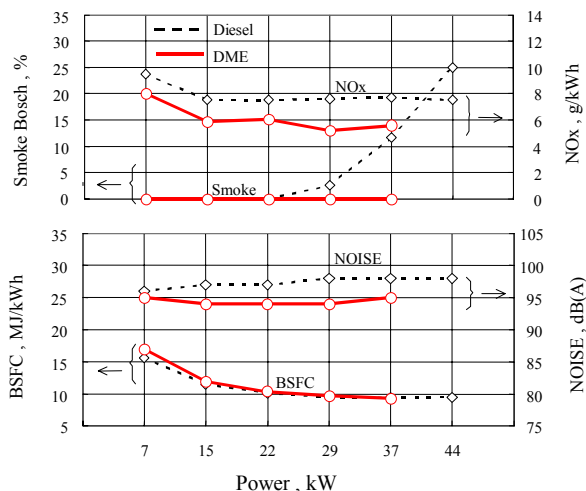


**Photo 3 DME diesel truck**

An oxidation catalyst is sufficient for purifying the exhaust gas because the engine does not emit black exhaust smoke, and the CO and HC emissions are greatly reduced.

The modifications to a diesel engine to permit the use of DME are minimal, consisting only of changes to the fuel supply system. With these minimal changes, the highly energy-efficient diesel engine may be converted to a relatively clean-burning engine, providing an effective method to resolve the environmental problems posed by diesel ve-

hicles. It is therefore hoped that the use of such vehicles will become widespread in the near future.



**Fig.3 DME and diesel fuel performance comparison (at 2000rpm)**

**References**

- 1) Ogawa, T. et al. NKK Technical Review, No.81, pp.13-17(1999).
- 2) Fleisch, T. et al. SAE Paper, 950061 (1995).
- 3) Sorenson, S. C. et al. SAE Paper 950064 (1995).
- 4) Ikizawa, et al. Motor Vehicle Technology Conference, Autumn Lectures, 13 (1998).
- 5) Jidousha Kougaku, July 2001, pp.60-73.

<Please refer to>

Yotaro Ohno  
 Environmental Solution Center  
 Tel. 03 (3217) 3266  
 E-mail address : Yotaro\_Ohno@ntsgw.Tokyo.nkk.co.jp

Takashi Ogawa  
 Engineering Research Center  
 Tel. 044 (322) 6241  
 E-mail address : Takashi\_Ogawa@ntsgw.Tokyo.nkk.co.jp