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 19 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 [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_2 as shown in (1) below.

$$3CO + 3H_2 \rightarrow CH_3OCH_3(DME) + CO_2 \quad \dots\dots (1)$$

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

$$2CO + 4H_2 \rightarrow 2CH_3OH \text{ (methanol)} \quad \dots\dots (2)$$

$$2CH_3OH \rightarrow CH_3OCH_3 \text{ (DME)} + H_2O \quad \dots\dots (3)$$

$$H_2O + CO \rightarrow H_2 + CO_2 \quad \dots\dots (4)$$

The two molecules of methanol synthesized from CO and H_2 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 (basic reaction conditions are 5MPa and 260).

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

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_2

(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_2 in a ratio of 1:1 (H_2/CO=1). The CO_2 produced in the reformer and the CO_2 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

$$2CH_4 + CO_2 + O_2 \rightarrow 3CO + 3H_2 + H_2O \downarrow \quad \cdots\cdots (5)$$

DME synthesis

$$3CO + 3H_2 \rightarrow CH_3OCH_3(DME) + CO_2 \quad \cdots\cdots (6)$$

Overall process

$$2CH_4 + O_2 \rightarrow DME + H_2O \downarrow \quad \cdots\cdots (7)$$

4.2 Operation and research

Operation and research of the large-scale bench plant from the reactor system as off gas. The total CO conversion was 94%.

Table 2 Materials balance in LPG plant operation

The ratio of hydrogen atoms to carbon atoms in propane (C_3H_8), which is the primary component of the LPG raw material, is less than that for methane (CH_4), so all of the CO_2 produced as a by-product of DME synthesis cannot be reconverted in the reformer. However, approximately 60% of the 111Nm^3/hr of CO_2 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_2 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_2 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_2 and DME contained in recovered methanol.

Table 3 Product selectivity (once-through basis)

(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 syn-

5.

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[4].

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[5] 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