

New Direct Synthesis Technology for DME (Dimethyl Ether) and Its Application Technology[†]

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Abstract:

Dimethyl ether (DME) is a clean fuel that does not produce toxic gases or particulate matter (PM) at burning. JFE Group develops a direct synthesis process of DME which has advantages in economics. Construction of a demonstration plant with 100 t/d capacity was finished in Nov. 2003. The first demonstrating operation (Run 100) through Dec. 2003 to Jan. 2004 and the second operation (Run 200) through June 2004 to Aug. 2004 were completed successfully. The conversion of synthesis gas, the selectivity to DME and the purity of DME reached to 96% (Target: more than 95%), 93% (Target: more than 90%) and 99.6% (Target: more than 99%), respectively. As an application technology of DME, a DME diesel generation system is now under development. Its demonstration test facility has 1 250 kW capacity and a Nox reduction system using DME as a reducing agent.

1. Introduction

Over the mid-to-long term, energy consumption in the Asian region is expected to increase substantially

during the 21st century. In realizing sustained growth in this region in the future, energy supply and environmental problems associated with mass energy consumption will be major problems. High expectations are placed on dimethyl ether (DME) as a new fuel which can be synthesized from diverse hydrocarbon sources, including natural gas, can be handled as easily as liquefied petroleum gas (LPG), and causes a small load on the environment. Thus, if DME can be produced and distributed at low cost and in large quantities, this fuel can make an important contribution to solving the energy supply problems and environmental problems resulting from expanded energy consumption expected in Asia in the future.

At the beginning of the 1990s, the JFE Group began development of a direct synthesis process for DME to realize low-cost mass production of DME. Work advanced through the steps of catalyst development, 50 kg/d bench plant test research, and 5 t/d large-scale bench plant test research, and demonstration tests with a 100 t/d demonstration plant have been in progress since 2002¹⁻⁴⁾. The JFE Group is also engaged in research and development related to the use of DME, and in 1997,

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conducted a series of road tests using DME fuel with a small diesel truck improved by the company's researchers, thereby demonstrating the superiority of DME as a diesel fuel^{3,5)}. Demonstration test with large-scale DME diesel power generation have been conducted since 2002.

2. Properties and Features of DME

2.1 Chemical Properties and Applications

Dimethyl ether is the simplest ether expressed by the chemical formula CH_3OCH_3 . Under ambient conditions, it is a colorless, transparent gas. Its boiling point at normal pressure is -25.1°C and its saturated vapor pressure at 25°C is 0.6 MPa. It is therefore easily liquefied and can be handled as easily as LPG. Current production is 10 000 t/y in Japan and 150 000 t/y worldwide. The largest part of this is used as a fluorocarbon-substitute spray propellant in cosmetics, paints, and similar applications. Its human toxicity is lower than that of methanol and similar to that of LPG. It does not cause corrosion in metals, but it causes expands of rubber.

2.2 Features of DME as Fuel

As an oxygenated compound, DME has excellent combustion characteristics, and because it has no carbon-carbon bonds in its chemical structure, it does not generate particulate matter (PM) in the combustion process. Furthermore, as it contains no sulfur, it does not generate SOx. Because it has a high cetane value of 55–60, it can be used as a diesel fuel. In a liquid state, its low heating value per unit of weight is 6 900 kcal/kg, which is lower than that of propane and methane, but in a gaseous state, its low heating value is higher than that of methane, at 14 200 kcal/m³-nomm. A wide range of applications is considered possible, including (1) alternative fuel for LPG in the general private sector, taking advantage of DME's easy liquefaction and excellent handling properties, (2) fuel for transportation, enabling diesel engine drive without generation of PM, and (3) low environmental load fuel for power generation, etc.

3. DME Direct Synthesis Process

3.1 DME Direct Synthesis Process and Conventional Process (Indirect Synthesis)

The existing DME manufacturing process is a double step (indirect) synthesis process in which natural gas or other feedstocks are reformed and the obtained synthesis gas is converted to methanol using methanol synthesis technology, followed by conversion to DME by dehydra-

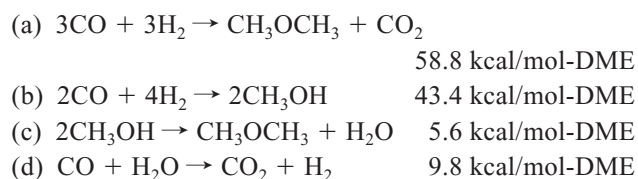
tion. In the direct synthesis process, DME is synthesized directly from the synthesis gas. Research and development on technologies capable of mass-producing DME at low cost are being carried out by the JFE Group, Hal-dor Topsoe A/S (Denmark)^{6–8)}, Air Products and Chemicals, Inc. (United States)^{9–11)}, and others.

3.2 Features of JFE Process

The process developed by the JFE Group (hereinafter referred to as the JFE Process) has reached a high degree of completion, and consists of the element technical development described below.

3.2.1 Development of synthesis reaction catalyst

The equations and reaction heat in DME synthesis in the JFE Process are expressed as follows.



Equation (a) is the overall equation, and is materialized from three step reactions: the methanol synthesis reaction in Eq. (b), the methanol dehydration reaction in Eq. (c), and the water-gas shift reaction in Eq. (d).

The synthesis catalyst developed by the JFE Group promotes the three step reactions shown by Eqs. (b)–(d) under conditions of a reaction temperature of 260°C and pressure of 5 MPa, and as shown by the overall equation, Eq. (a), has activity which synthesizes DME at a high conversion from a synthesis gas with a 1:1 molar ratio of CO and H_2 .

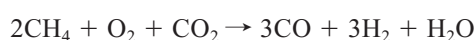
3.2.2 Application of slurry bed reactor and development of optimum reaction heat control technology

Because the reaction heat in the DME synthesis reaction is large, it is necessary to remove reaction heat and perform reaction temperature control properly in order to prevent a reduction of equilibrium conversion and catalyst deactivation due to temperature rise. The JFE Process uses a slurry bed reactor in which the reaction is promoted by placing the synthesis gas in contact with the catalyst in a slurry in which the catalyst is suspended in a reaction medium. Because the heat capacity and thermal conductivity of the reaction medium are both large, the reaction heat is absorbed by the reaction medium and leveling of the temperature in the reactor is easy. In the 100 t/d demonstration plant, efficient reaction temperature control is performed by changing the pressure of steam generated by a heat exchanger installed in the reactor. With the slurry bed reactor, it is

also possible to exchange the catalyst during operation when necessary.

3.2.3 Establishment of formation technology for synthesis gas suitable for JFE Process

When synthesis gas is obtained by reforming gas, even when an autothermal reformer (hereinafter, ATR) using oxygen is employed, the molar ratio of H_2/CO in the synthesis gas being formed is ordinarily 1.8–2.8. With the JFE Process, gas with a ratio of $H_2/CO = 1$, which is the optimum for the JFE Process, can be obtained by recycling the byproduct CO_2 from DME synthesis in Eq. (a) to the ATR.



4. History of Technical Development of JFE Process

At the beginning of the 1990s, the former NKK before the merger creating the JFE Group, with the cooperation of the Prof. Fujimoto's Laboratory in the Department of Synthetic Chemistry (of the time), Faculty of Engineering, University of Tokyo, developed a DME direct synthesis catalyst with the aim of effectively utilizing by-produced gas in the steel works. This was the first step in this development. Thereafter, beginning in 1994, research and development were carried out using a small-scale 50 kg/d bench plant installed in the technology research center of former NKK, and the basic technology of the DME direct synthesis process was established. Then, over a 5 year period from 1997, a 5 t/d large-scale bench plant was constructed on the premises of the Taiheiyo Coal Mining Co., Ltd. (of the time) in Kushiro, Hokkaido with support from the Center for Coal Utilization, Japan. Research and development were continued, and the element technologies of the JFE Process as a whole, including the synthesis gas generating equipment, were completed. Beginning in 2002, a 100 t/d demonstration plant project was carried out for the purpose of technical development for commercialization of the JFE Process as a funded project of the Agency for Natural Resources and Energy.

5. 100 t/d Demonstration Plant Project

In Dec. 2001, DME Development Co., Ltd. was established as the entity responsible for implementing the 100 t/d demonstration plant project by a group of 10 companies, including the former NKK, Nippon Sanso Corp., Toyota Tsusho Corp., Hitachi Ltd., Marubeni Corp., Idemitsu Kokan Co., Ltd., INPEX Corp., LNG Japan Corp., TotalFinaElf, and Japan Petroleum Exploration Co., Ltd. A large number of persons with experience

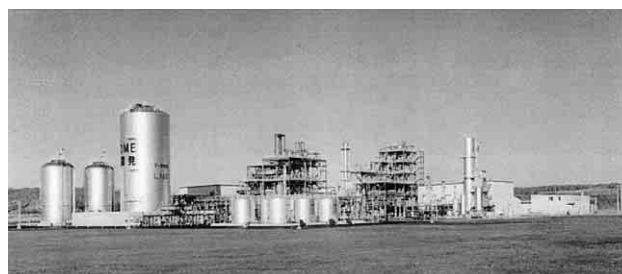


Photo 1 Over view of DME 100 t/d plant

Table 1 Master plan of test operation

Test number	Period	Duration (month)	Main objective
Run 100	Dec. 2003–Jan. 2004	1.5	Overall plant trial operation
Run 200	June 2004–July 2004	2	100% Load plant overall operation
Run 300	Sept. 2004–Dec. 2004	2.5	Engineering data for scale up
Run 400	June 2005–Sept. 2005	3	Continuous plant operation over 3 months
Run 500	Oct. 2005–Dec. 2005	2	Plant operation to verify scale up technology
Run 600	June 2006–Aug. 2006	2.5	Additional advanced engineering data

in the development of the JFE Process are participating in DME Development Co., Ltd., and following the decision of the basic plant specifications and equipment design/construction management and completion, have been engaged in operational research. In Aug. 2002, JFE Engineering, and Nippon Sanso Corp. received the order for the plant design and construction from DME Development Co., Ltd. and began construction work in Shiranuka-cho, Hokkaido in Sept. of the same year. Detailed design and construction of the equipment were carried out under the general supervision of JFE Engineering with the cooperation of the JFE Group. Construction of the equipment was completed at the end of Nov. 2003 after a short period of 15 months. A general view of the 100 t/d demonstration plant is shown in **Photo 1**. Overall trial operation was carried out from Dec. of the same year through Jan. 2004. As scheduled in the master plan shown in **Table 1**, during the period from fiscal year 2004 to 2006, verification of the technology will be carried out by conducting 5 continuous runs of 2–3 months each, and various kinds of engineering data will be collected for establishment of the technology for scaling-up to a commercial plant.

5.1 Outline of 100 t/d Demonstration Plant Equipment

A process flow diagram of the 100 t/d demonstration plant is shown in **Fig. 1**. This demonstration plant has been designed to carry out demonstration tests for

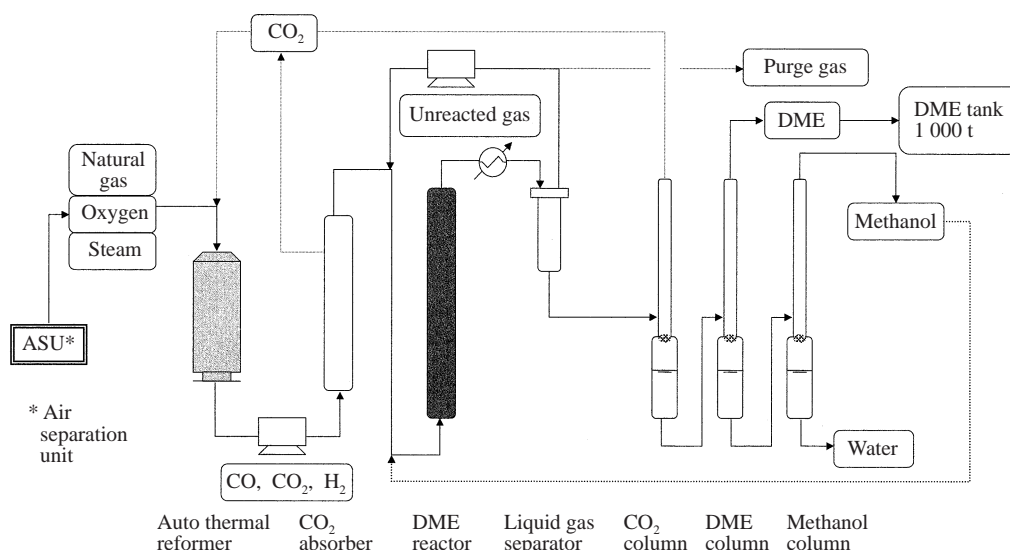


Fig. 1 Process flow diagram of 100 t/d DME synthesis plant

commercialization of the JFE Process using natural gas as the feedstock. The feedstock natural gas is supplied in the form of LNG from the Yufutsu Gas Field in Hokkaido. Natural gas is reformed by the ATR together with oxygen and steam, and CO_2 recycled from the downstream process. The ATR operates at a pressure of 2.3 MPa and forms synthesis gas with a ratio of $\text{H}_2/\text{CO} = 1$. The synthesis gas is quenched with a waste heat recovery boiler and pressurized to 5 MPa, which is the reaction pressure. After CO_2 generated during reforming is removed by the CO_2 absorber, the gas is supplied to the DME reactor. In the DME reactor, DME and CO_2 are formed by action of the catalyst. Unreacted synthesis gas is separated by a gas-liquid separator and recycled to the reactor. The liquid component is sent to the CO_2 stripper, where the CO_2 formed during the reaction is separated. The separated CO_2 is recycled to the ATR as a submaterial. After CO_2 has been separated from the crude DME, methanol is removed by the DME column, and the resulting DME is stored in the DME tank as product DME. In treating methanol, after water is removed in the methanol column, the methanol is recycled to the reactor and converted to DME.

5.2 History and Results of Overall Trial Operation

ATR preheating began on Dec. 10, 2003, and the ATR was put into actual operation on Dec. 12. The CO_2 absorber was then started up, and recycling of CO_2 to the ATR was begun. Next, synthesis gas was introduced into the DME reactor, and DME was successfully produced on Dec. 21. The gas feed rate to the DME reactor was increased while continuing to perform various adjustment work, and on Dec. 31, the plant achieved 100% load operation at a reaction pressure of 5 MPa

and temperature of 260°C. In order to use the produced DME effectively, beginning on Jan. 5, 2004, the plant was shifted to natural gas/DME mixed feedstock operation. Operation was continued until Jan. 26, when the overall trial operation was completed. On the whole, stable operation was realized through the 46-day overall trial operation period, and the target production rate of 100 t/d and DME purity of 99.6% were achieved. The ATR successfully produced synthesis gas with a molar ratio of $\text{H}_2/\text{CO} = 1$ under a pressure of 2.3 MPa, while recycling by-produced CO_2 as a partial carbon source. Leak methane and soot formation during this period were both minimal. Stable temperature control was realized in the DME reactor by steam pressure control, and the temperature distribution in the reactor was extremely uniform. Total conversion was 93% (target: 95% or higher) and DME selectivity was 91% (target: 90%), thus approximately achieving the target values. It may also be noted that total conversion of 96% was achieved during Run 200, which was carried out in June–July 2004. Where the quality of the product DME is concerned, as shown in Table 2, the product composition satisfied the producer's guarantee specification (tentative proposal) of the Japan DME Forum.

Based on the satisfactory results of the overall trial operation, technical development for commercializa-

Table 2 Composition of product DME

	(mass%)			
	DME	CO_2	Methyl formate	Methanol
Tentative specification	≥ 99.0	≤ 0.1	≤ 0.01	≤ 0.1
Composition of product DME	99.6	N.D.	N.D.	0.06

tion of the JFE Process will be carried out in accordance with the original project plan. The second test run (Run 300) was conducted from early Sept. 2004, and various data necessary for the study of plant scaling-up were collected.

6. DME-fueled Large-scale Diesel Engine Power Generating System

6.1 Outline of Development

For practical application of DME fuel, development of an economical mass-production manufacturing process and development of use technologies for the product DME are essentially interrelated. Among applications of DME, fuel for power generation is particularly promising because creation of large-volume demand can be expected. Therefore, development for practical application as a fuel for gas turbines and diesel engines is being carried out.

In comparison with other power generating engines such as gas turbines and gasoline engines, the diesel engine offers excellent efficiency, but with conventional diesel fuels such as heavy oil and light oil, diesel engines have the disadvantage of high contents of NO_x and PM in the exhaust gas. Particularly in Tokyo, Osaka, and other urban areas in Japan, the exhaust gas NO_x concentration is strictly regulated under independent municipal ordinances, making the introduction of diesel engines realistically impossible at present. However, by using DME as a fuel, a broad improvement in exhaust gas characteristics can be expected, while also maintain-

ing the advantage of high power generating efficiency.

JFE Engineering, in joint work with Daihatsu Diesel MFG. Co., Ltd. and Iwatani International Corp., is currently developing a DME-fueled large-scale diesel generating system under a 5-year plan which began in fiscal year 2002. This effort is supported by the Ministry of Economy, Trade and Industry (METI) under its DME-fueled Machinery Development Funding Project.

Figure 2 and Table 3 show the significance and performance targets of this development, respectively.

6.2 Development of Element Technologies

6.2.1 Engine fuel injection and combustion analysis

Commissioned research on the basic combustion characteristics of engines is being carried out by the Clean Power System Group (Director, Dr. Shinichi Goto), National Institute for Advanced Industrial Science and Technology, and includes calculation of the physical properties of DME, visible analysis in the combustion chamber, and numerical simulation.

Engine development problems related to the physical properties of DME include the following.

- (1) Because the volumetric heat value of DME is small, a fuel injection rate approximately double that with oil-based fuels is necessary.
- (2) Due to high compression, injection delay tends to occur easily.
- (3) Due to the low boiling point of DME, atomized DME is easily vaporized and dispersed, resulting in weak penetration in the combustion chamber.

It is necessary to obtain a quantitative understanding of these characteristics of DME in the fuel injection system and combustion system and create the optimum design for the engine configuration and fuel injection control.

As one example of the experimental apparatus used

Table 3 Target of performance

Capacity	1 000 to 5 000 kW _e
Efficiency	Equivalent to existing diesel 42 to 45% low heat value
NO _x in exhaust gas	Less than 110 ppm at 13% O ₂

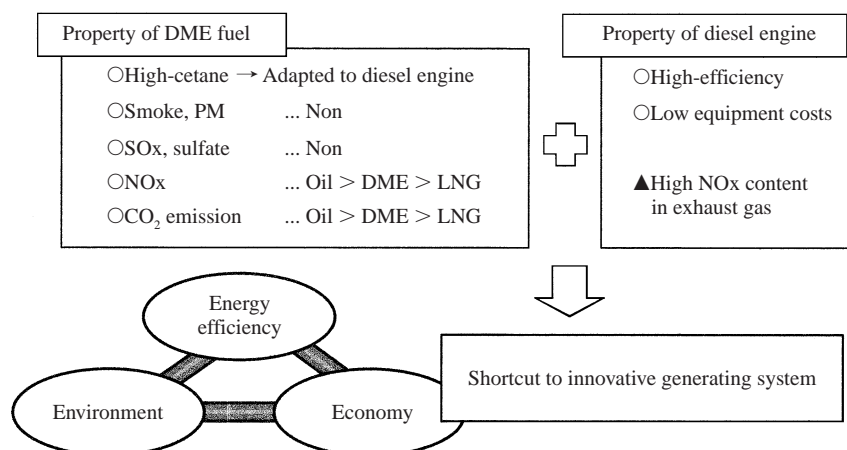


Fig.2 Significance of DME diesel electric generation system

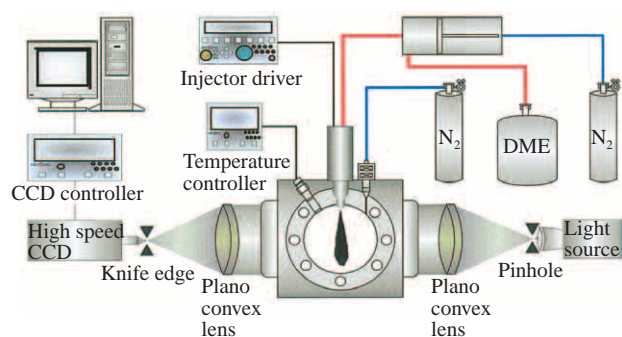


Fig. 3 Configuration of visualization apparatus for fuel injection behavior

in this work, **Fig. 3** shows the configuration of the visualization apparatus for DME fuel injection.

6.2.2 Small-scale engine combustion experiments

The JFE Group was among the first to begin technical development for application of DME to automotive diesel engines and has actual results as the first in Japan to carry out running tests on public roads with a DME automobile. **Photo 2** shows the small-size engine test bench which is the basis for this development and is currently being used in fundamental experiments for development of large-scale engines. The main items in experiments now in progress are as follows.

- (1) Collection of fundamental data on the combustion characteristics of DME engines
- (2) Preliminary tests of exhaust gas recirculation(EGR)
- (3) Evaluation of de-NOx catalyst performance with actual exhaust gas

6.2.3 Exhaust gas treatment by selective catalytic reduction of NOx with DME

In order to improve the exhaust gas characteristics of the engine itself and reduce exhaust gas NOx in the equipment as a whole, a new nitrogen oxides removal

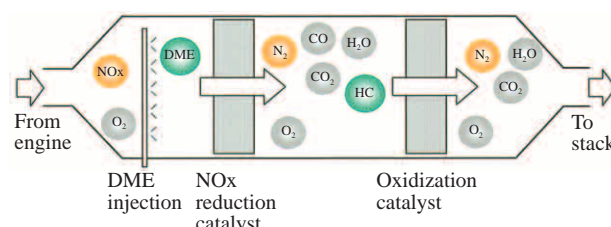


Fig. 4 Mechanism of DME-SCR (selective catalytic reduction)

(de-NOx) system is being developed. In conventional exhaust gas de-NOx devices, ammonia or urea is used as the reducing agent, but because these are difficult to handle and operating costs are high, they were difficult to apply in distributed generation equipment. Here, a new selective catalytic reduction system for NOx is being developed using the DME fuel itself as the reducing agent (**Fig. 4**).

Catalyst development is being carried out in joint research with Prof. Akio Tada of the Dept. of Applied and Environmental Chemistry, National University Corp. Kitami Institute of Technology.

6.3 Demonstration Power Plant

For an overall verification of the results of the various element experiments described above, a 1 250 kW demonstration power plant was constructed at JFE Engineering's Tsurumi Works (**Photos 3, 4**). Daihatsu Diesel MFG. Co., Ltd., which was a joint development partner, was responsible for engine development, and improved an existing oil-fueled DK series engine for use of DME. The basic specifications of the equipment as a whole are shown in **Table 4**.

Table 5 shows the schedule of this development. All tests are scheduled to be carried out by fiscal year 2006, targeting practical application of the world's first megawatt-class large-scale DME diesel engine.

An outline of the development of the DME diesel engine has been presented in the preceding sections

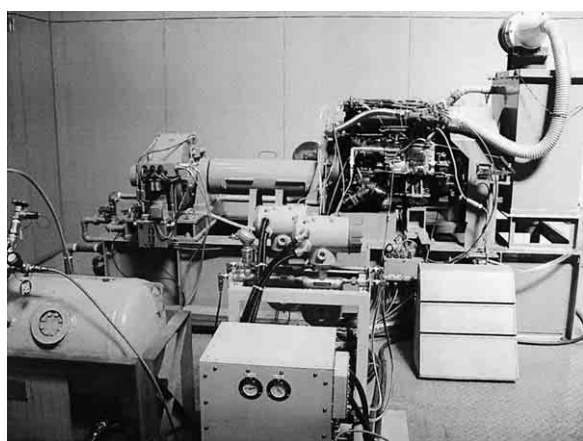


Photo 2 DME diesel engine test bench



Photo 3 DME diesel demonstration test facility

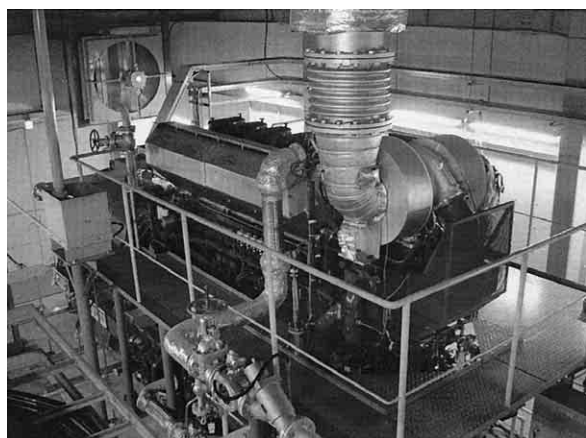


Photo 4 Outlook of DME diesel engine generator

Table 4 Basic specifications of DME diesel demonstration test facility

Category	Item	Data
Diesel engine	Manufacturer	Daihatsu Diesel Mfg. Co., Ltd.
	Number of cylinder	6
	Bore × Stroke (mm)	φ260 × 380
	Rotation speed (rpm)	750
	Shaft power (kW _m)	1 333
Generator	Type	Synchronous
	Voltage (V)	3 300
	Output power (kW _e)	1 250
DME storage	Type	Horizontal cylindrical
	Volume (m ³)	35 (20 t of DME)
DME supply	Feed pump	Centrifugal caned pump
	Booster pump	Reciprocating diaphragm
	Supply pressure (MPaG)	1.5
	Feed rate (m ³ /h)	0.6
Exhaust gas	DeNOx	DME-SCR
	Capacity (Nm ³ /h)	8 681 (Nominal)

of this paper. Technical details, including operational results of the demonstration power plant, are scheduled to be reported on another occasion.

7. Conclusion

Dimethyl ether (DME) is a new fuel which is expected to reach practical application in the near future. This report has described the physical properties of DME and its distinctive features as a fuel, the features of a direct synthesis process (JFE Process) which the JFE Group developed as a manufacturing technology, and the outline of a 100 t/d demonstration plant project and history of the overall trial operation of the plant. It also

Table 5 Schedule of development of large scale DME diesel generation system

Fiscal year	2002	2003	2004	2005	2006	2007
		★Project start	★100 t/d Operation start			
(1) Basic research		Engine combustion study				
		Exhaust gas deNOx study				
(2) Demo plant construction		Basic design Work I	Detail design Work II	★Operation start (Aug.)		
(3) Demo plant operation			Performance test			
				Duration test		

includes an outline of the development of a DME-fueled large-scale diesel engine power generating system as a use technology and the content of element research, and the condition of installation of the demonstration test facility. The JFE Group intends to forcefully promote research and development of the DME manufacturing technology and use technologies, aiming at early commercialization of DME.

The authors wish to express their deep appreciation to all those concerned, and particularly to the members of the Coal Division and Petroleum Distribution and Retail Division, Natural Resources and Fuel Department, Agency for Natural Resources and Energy, who provided much generous support in this research and development, and request their continuing guidance in the future.

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