NEW CLEAN FUEL FROM COAL- DIMETHYL ETHER -

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1. Introduction

In Asian countries and regions including China, ASEAN and NIES , high speed economic growth is spurring a rapid increase in energy consumption, which means that there is a high probability of this part of the world eventually facing [1] a tight energy supply and demand situation and [2] serious environmental problems (CO2,SOx, NOx, etc.).

On the energy supply side, an increase is forecast in the total volume of crude oil and oil products imported from the middle east and other production regions outside this part of Asia, but it will be necessary to also use unexploited energy resources as lignite, sub-bituminous coal, coal bed methane and unexploited small deposits of natural gas within the region.

Looking at the environmental preservation situation, to deal with existing solid pollutant sources such as relatively large electric power plants and factories ,desulfurization and denitrification plants are effective. For the consumption of fuel in residential and commercial sector and transportation sector, as the sources of pollutants are widely dispersed, measures to clean the fuel itself must be taken.

Forecasts of sharp rises in demand for the clean fuels, natural gas (LNG) and LPG, have aroused fears of a jump in the prices of these products. For this reason, the production of dimethyl ether (DME)--a clean fuel as convenient to transport as LPG--by synthesizing from gas obtained by coal gasification at coal mine for shipment to users in the surrounding countries and regions is extremely significant from the point of view of environmental preservation.

Recently, the DME synthesis from H2/CO has been studied for coproduction with methanol to increase the productivity beyond the methanol equilibrium(3,4).

NKK, which has been studying the synthesis of DME from H2/CO since 1989 (1,2) , is now conducting research on a 50kg/day bench plant.

In this report, we present an overview of the physical properties, uses and synthesis reaction of DME, and an estimation to commercial plant of DME.

2. Physical Properties and Uses of DME

2.1 Physical Properties of DME

Table 1 shows the physical properties and combustion characteristics of DME and various fuels. DME, a colorless gas with a boiling point of -25℃ , is chemically stable and easily liquefied. With properties similar to those of propane and butane, which are principal constituents of LPG, it can be handled and stored using the same technology used to handle and store LPG.

While its net calorific value of 6.903 kcal/kg is lower than that of propane, butane, and methane, it is higher than that of methanol. In gaseous state, its net calorific value is 14,200 kcal/Nm3, which is higher than that of methane. Turning to its combustion properties, its explosion limit is wider than those of propane and butane, but almost identical to that of methane and narrower than that of methanol. Its cetane number is high, ranging from 55 to 60, so that it can be used in diesel engines. Actual engine tests show that its fuel consumption rate is lower than that of diesel oil at the same NOx level and confirm that it is an extremely clean fuel, generating an extremely small quantity of soot(5). Its flame is a visible blue flame similar to that of natural gas, and it can be used just as it is in an LPG cooking stove, and it does not produce aldehyde.

A toxicity study of its use as a propellant for spray cans to replace fluorocarbons has confirmed that its toxicity is extremely low; about the same as that of LPG (6). The study has shown that the toxicity of DME is even lower than that of methanol.

Table 1 Physical Properties and combustion characteristics of DME and other fuels

Properties	DME	Propane	n-Butane	Methane	Methanol
Chemical formula	CH_3OCH_3	C_3H_8	C_4H_{10}	CH_4	CH_3OH
Boiling point (℃)	-25.1	-42.0	-0.5	-161.5	64.6
Liquid density (g/cm³, 20℃)	0.67	0.49	0.57	–	0.79
Specific gravity (vs. air)	1.59	1.52	2.00	0.55	–
Heat of vaporization (kcal/kg)	111.7	101.8	92.1	121.9	262
Saturated vapor pressure (atm, 25℃)	6.1	9.3	2.4	246	–
Burning velocity (cm/s)	50	43	41	37	52
Ignition energy (10^{-4}J)	45	30	76	33	21
Ignition temperature (℃)	350	504	430	632	470
Explosion limit (%)	3.4~17	2.1~9.4	1.9~8.4	5~15	5.5~36
Cetane number	55~60	(5)	(10)	0	5
Net calorific value (kcal/Nm³)	14,200	21,800	28,300	8,600	–
Net calorific value (kcal/kg)	6,903	11,100	10,930	12,000	5,040

( ) : estimated Value

It does not corrode metal but it does corrode rubber type sealant, so these materials must be selected carefully (6).

2.2 Uses of DME

Some is used as solvents, refrigerants, etc., but most is used as a propellant (paint, chemical fertilizers, cosmetics), with 8,000 tons/year produced in Japan and about 100,000 tons/year produced world wide. Its only use as a fuel has been as an intermediate product during the conversion to synthetic gasoline, but to take advantage of its properties similar to those of LPG, China has begun producing DME by dehydration reaction of methanol as a fuel substitute for LPG. Table 2 shows potential uses of DME as a fuel and the energy it will replace. When it is possible to produce it cheaply from coal or natural gas, it will be used widely as a clean fuel which is as convenient to transport as LPG.

Table 2 Potential use of DME as substitute fuel

Transportation	: diesel oil
Domestic use	: coal, coal briquette, fuel gas from coal, natural gas, LPG
Power generation	: coal, natural gas, heavy oil, LPG

3. Synthesis of DME

3.1 DME Synthesis Reaction

Table 3 shows the reactions concerning DME synthesis and the heat of reaction. As shown in Table 3, the DME synthesis reaction (e) from H2/CO consists of three steps: the methanol synthesis reaction (a), the dehydration reaction(b), and the shift reaction (c). Without the shift reaction, the reaction can be carried out following the formula(d) which is given by combining reactions (a) and(b). Because generally the methanol synthesis catalyst encourages the shift reaction(c), the total reaction is likely to proceed between (d) formula and (e) formula.

Because the total reaction is highly exothermic, if the excess reaction heat is not efficiently removed and the reaction temperature is not carefully controlled, there is a risk of the catalyst deactivation by the rising temperature.

Table 3 Reaction concerning DME synthesis and reaction heat

	Reaction			Reaction heat (kcal/mol-DME)
(a)	$2CO + 4H_2$	→	$2CH_3OH$	+ 43.4
(b)	$2CH_3OH$	→	$CH_3OCH_3 + H_2O$	+ 5.6
(c)	$CO + H_2O$	→	$CO_2 + H_2$	+ 9.8
(d)	$2CO + 4H_2$	→	$CH_3OCH_3 + H_2O$	+ 49.0
(e)	$3CO + 3H_2$	→	$CH_3OCH_3 + CO_2$	+ 58.8

Figure 1 shows how the (H2 + CO) equilibrium conversion for these two DME synthesis reaction formulae (d) and (e) and methanol synthesis reaction(a) varies as function of the initial H2/CO ratio and reaction pressure. In each reaction ,the equilibrium conversion has its peak where the H2/CO ratio of the reactant gas corresponds to the stoichiometric value, that is , H2/CO = 2 (reaction (d) and reaction(a)) and with H2/CO = 1 (reaction(e)). The equilibrium conversion of DME is higher than that of methanol. For DME synthesis, the maximum value of the equilibrium conversion is higher for the reaction formula (e). This clearly indicates the significance of the fact that the shift reaction (c) proceeds in response to reaction (a) and reaction (b).

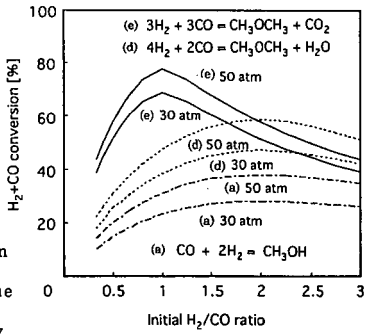


Fig.1 Equiliblium (H_2+CO) conversion to DME or methanol as function of initial H_2/CO ratio and pressure (at 280 ℃)

3.2 Slurry Bed Reactor

The reactor types for catalytic reaction are categorized in fixed bed, fluidized bed and slurry bed. Because DME synthesis reaction is highly exothermic, a fluidized bed and a slurry bed reactor are recommended. Their heat transfer characteristic is so excellent that the temperature distribution in the reactor is flat and that the structure of reactor can be simple.

A slurry bed does not restrict the shape and mechanical strength of the catalyst compared with a fluidized bed. The catalyst in the slurry bed can be easily exchanged by slurry pomp without disturbing the operation when the activity of catalyst decreases. But in the slurry bed, the solubility in the solvent of the water generated on the dehydration catalyst is low, the most of water emerges directly into the gas bubbles and there is a strong tendency for it to emerge from the reactor without reacting with the CO, and overall, the CO conversion becomes low. So adding a shift reaction function to the dehydration catalyst to

convert generated water with the CO immediately to H2 and CO2 has been designed. Because H2 has high solubility and diffusion rate in the solvent, it is consumed by the methanol synthesis reaction, and overall it is possible to obtain a high CO conversion (1,2).

3.3 DME Synthesis Reaction Test

A bench scale experiment was performed based on beaker scale research (1,2). An outline of the test plant is presented in Figure 2. The reactor is a slurry bed bubble tower with an internal diameter of 90 mm and a height of 2 m. The plant capacity is of 50 kg/day of DME. Figure 3 and Figure 4 present, as examples of the results of the experiment, the CO conversion and selectivity of all constituents of the product (CO2 is excluded and the total of DME, methanol, CH4 is considered to 100%) produced in one through operation. There is no other heavy byproduct than methanol and methane.

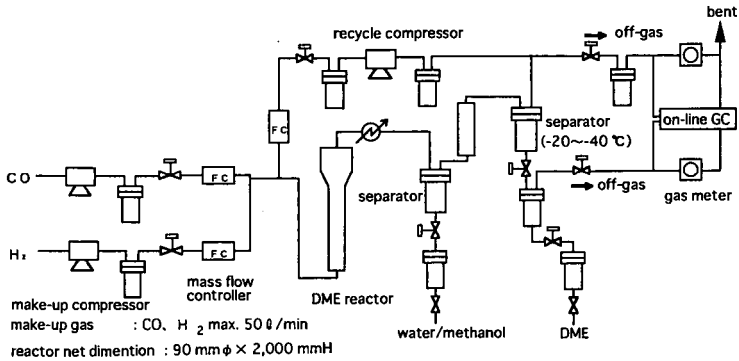


Fig.2 Flow diagram of Bench Plant

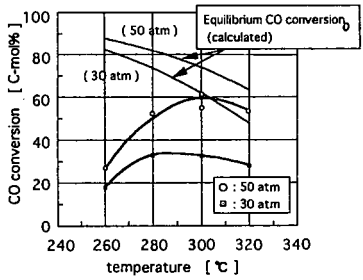


Fig. 3 CO conversion as function of temperature and pressure(one-through,make-up H2/CO=1)

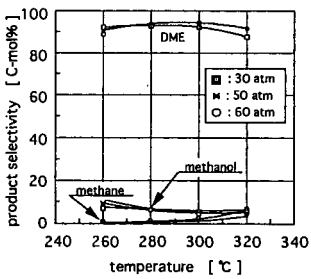


Fig. 4 Product selectivity as function of temperature and pressure

The CO conversion rises as the temperature climbs, and it has the maximum value. This is considered to represent the effect of the equilibrium restrictions caused as the conversion approaches the equilibrium and of the fall in the soluhility of the reaction gas as the temperature rises. A CO conversion greater than 50% and a DME selectivity in excess of 90% were obtained at a pressure of 50 atm and a temperature of 300℃.

As for the catalyst life, as shown in Figure 5 ,during 700 hours of consecutive testing, no deactivation was observed.

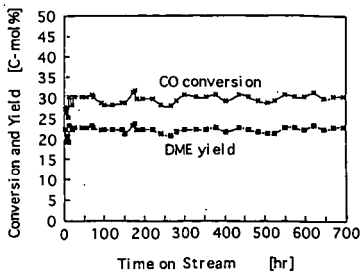


Fig. 5 Catalyst activity as function of time on stream (H2/CO=1,280g,30atm,W/F=12g-cat hr/mol)

4. Synthesis of DME from Coal and Natural Gas and its Uses

4.1 DME Synthesis Process Flow

Figure 6 shows a block diagram to produce DME from coal. Because the H2/CO ratio of synthesis gas obtained by the coal gasification ranges from 0.5 to 1.0, the gas composition is adjusted by the shift reaction so that H2/CO = 1, and it is then supplied for DME synthesis. In this synthesis step where the reaction (e) (H2/CO=1) is achieved, the difference of H2/CO ratio to be adjusted is so narrow in comparison with the reaction(d) (H2/CO=2) that the equipment size and utility consumption for the shift conversion step are smaller.

The effluent from the slurry reactor is cooled and chilled in order to separate the liquid phase (DME , CO2 and small amount of methanol and water) from the gaseous phase containing unreacted H2 and CO. Most of the separated gas is recycled to the reactor. Because the one-through reaction rate is high, the recycle ratio is sufficient at 1:1. After CO2 removal, the product DME is obtained by removing the impure water and methanol to a required level.

In case of natural gas, it can be converted to synthesis gas of H2/CO = 1 by means of CO2 reforming and used to the DME synthesis.

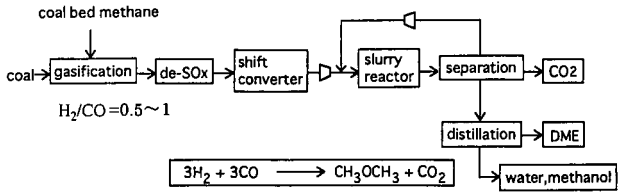


Fig. 6 DME synthesis from coal derived synthesis gas

4.2 Uses of DME

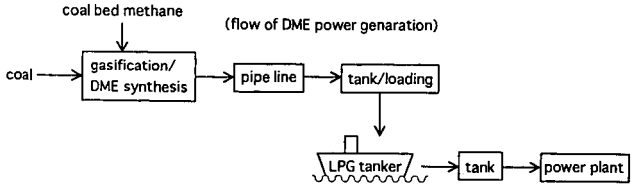
It is expected that DME will be introduced as a LPG-like home use fuel to replace coal and coal briquette and as an engine fuel to replace the light oil used in diesel engines in China, India, Indonesia, and other heavily populated countries with rich coal resources.

In Japan, 25 million tons of non-coking coal is imported to Japan to be consumed in electric power plants. It is forecasted that the future construction of more coal-burning power plants will be accompanied by an increase in the amount of coal consumed for this purpose to 57 million tons/year by 2005; three times as much as that is consumed now.

In Asian region besides Japan, the electricity demand is expected to increase at a rate of 7-8%/year and the coal consumption for power plant will be immense and the environmental pollution will be aggravated.

A concept of a system in which coal is gasified and converted to DME at coal mine, then transported to final consumption area as Japan for use in electric power production has been created as shown in Figure 7 . This system would provide the following potential benefits in comparison with the conventional coal flow.

At coal mine , [1] coal is prepared to reduce transportation costs and provide assurance of sufficient quality, but coal preparation would be unnecessary and all could be used effectively. [2] It would be possible to use low quality coal, for example, lignite coal with high moisture content or inflammable coal which is inadequate to the transportation. [3]Coal bed methane produced as a byproduct of coal mining is generally an unexploited energy resource. As it has a higher greenhouse effect than CO2, its proper treatment will be necessary. Although the coal bed methane generation varies over time, it could be used effectively by injecting it into the coal gasification reactor in which the methane is reformed to synthesis gas.



condition		· DME 2,500 t/d (over sea) · 500,000 k W power plant
DME production	plant cost	55 ~ 75 billion yen
	DME cost	2.2 ~ 2.9 yen/10^3 kcal
power genaration cost		8.2 ~ 9.4 yen/kWh

Fig. 7 Power generation through DME flow system and its cost estimation

At the transportation stage, [1] it could be handled in the same way as LPG, so the shipping and receiving base equipment could be simple, and would produce no dust.
In final consumption area , [1] the use of this ash-free clean fuel would eliminate the need for desulfurization and ash disposal treatment, [2] as a gaseous fuel, it would be sure to provide high power generation efficiency with combined cycle power generation, and the problems of providing a coal yard and dealing with ash would be resolved so it could be constructed in the suburbs of cities, thereby reducing transmission power loss.

4.3 Cost estimation of DME production and Electricity from DME burning power generation

Figure 8 shows an example of DME production cost (at coal mine and Japan CIF) in a case where equipment cost varies according to DME plant size with DME production of 910,000 tons/year as a constant condition. As the plant size increases, the cost of producing DME falls to the same level as the price of light oil and of LPG, whose cost is forecast to rise, in regions near coal mine at a production rate of 2,500 tons/day.
In this calculation, the cost of the total plant for DME production from coal is estimated to be 55 billion yen. If the plant costs climb from 55 billion to 75 billion yen, as shown in Figure 7, the DME production cost will be 2.22 yen/10 3 kcal to 2.86 yen/10 3kcal at the production site, while the electric power generation cost rises from 8.2 yen/kwh to 9.4 yen/kwh in Japan. These costs of electricity would be either equal to or lower than the cost of coal burning power generation.

4.4 Comparison of the Environmental Load of Coal burning and DME burning Power generation

The total environmental load produced between the coal production stage in coal mine over sea and the production of power and disposal of waste material in Japan has been compared. Figure 9 shows a result of this study. A switch over to DME flow system is sure to sharply cut the environmental load as follows.
[1] The volume of CO2 emissions would remain almost unchanged. When coal bed methane is emitted in the air, its effective utilization in the coal gasification reactor can cut 20% equivalent to CO2.
[2] No sulfur compounds would be discharged into the atmosphere in the DME flow system.
[3] As DME does not contain nitrogen, there would be no fuel NOx. By incorporating denitrification measures, the amount discharged into the atmosphere could be cut to approximately 1/9 of that discharged from a coal powered plant.
[4] Ash would be discharged as molten slag, it would be easier to use than fly ash, and no heavy metal elution would occur.

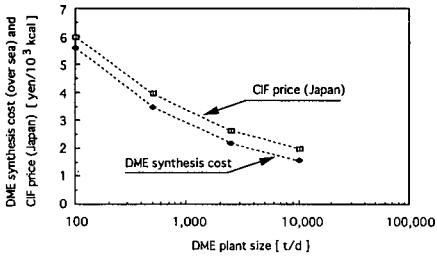


Fig. 8 Cost estimation of DME production

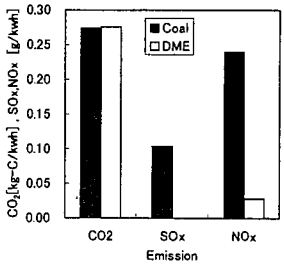


Fig.9 Environmental load of DME flow system and coal flow for power generation

5. Summary

If DME is developed to the stage where it is a practical product and is then distributed as an energy source for home use, transportation, and electric power generation, it will make a significant contribution to the resolution of energy and environmental problems, not only in the country using it for these purposes, but in other Asian countries.
Because DME is not a standard fuel which is already in use, integrated all-encompassing efforts must be made to prepare for its introduction and use from the production through the distribution stage.

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