

## **Slurry Phase DME Direct Synthesis Technology -100 tons/day Demonstration Plant Operation and Scale up Study-**

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### **1. Introduction**

Dimethyl ether (DME) is an innovative clean fuel which can be used for various sectors; household, transportation, power generation, etc. How to transport and utilize DME is extensively investigated in Japan, because DME could be a promising option to diversify energy resources in the future. DME has been used mainly as a propellant for spray cans. Recently, in China, they have started to use it as LPG substitute. Approximately 200,000 tons/year are produced worldwide by a dehydration reaction of methanol. In order to use DME as a fuel, it must be produced at low cost in large quantities.

As methanol, itself, is produced from synthesis gas (hydrogen and carbon monoxide), it would be more efficient to produce DME directly from synthesis gas. We have carried out the technical development of DME direct synthesis process from synthesis gas for the past 15 years.

In the fundamental research, a new efficient catalyst and slurry phase process for DME synthesis were developed [1]. On these fundamental results, five years development project using a 5 tons/day pilot plant was successfully conducted since 1997 with funds provided by the Ministry of Economy, Trade and Industry [2]. At this stage, a reformer technology to give adequate synthesis gas was also started to be developed.

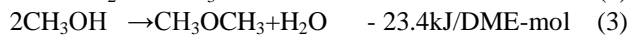
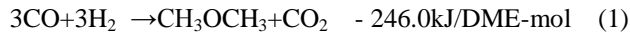
In 2002, five years development project using 100 tons/day demonstration plant has started by DME Development Co., Ltd. which is a consortium of nine Japanese companies and one French company; JFE, Taiyo Nissan Corporation, Toyota Tsusho Corporation, Hitachi Ltd., Idemitsu Kosan Co., Ltd, Marubeni Corporation, INPEX Corporation, LNG Japan Corporation, Japex Co., Ltd and Total, with funds provided by the Ministry of Economy, Trade and Industry [3].

From 2003 to 2006, continuous test operation for 2-3 months was done six times stably. Operation time reached to about one year and DME production amounted to about 20,000ton. Through these stable operations, the production technology and the catalyst performance are proved and the scale-up technology to a commercial scale plant was established.

## 2. Characteristics of DME direct synthesis and synthesis gas production

### 2.1. DME synthesis reaction and equilibrium conversion

The reactions and reaction heat concerning DME synthesis are as follows;



DME synthesis reaction (1) from synthesis gas ( $\text{H}_2$ ,  $\text{CO}$ ) is composed of three reactions; methanol synthesis reaction (2), methanol dehydration reaction (3), and water gas shift reaction (4). The overall reaction is exothermic and the reaction heat at methanol synthesis step is dominant.

Figure 1 shows equilibrium conversion of synthesis gas ( $\text{CO}$  conversion plus  $\text{H}_2$  conversion) calculated at the temperature  $260^\circ\text{C}$  and the pressure  $5\text{MPa}$  for DME synthesis reaction (1) and methanol synthesis reaction (2) as a function of hydrogen/carbon monoxide ratio ( $\text{H}_2/\text{CO}$ ) of the synthesis gas. In each reaction, the equilibrium conversion has its maximum peak where  $\text{H}_2/\text{CO}$  ratio corresponds to the stoichiometric value, that is, with  $\text{H}_2/\text{CO}$  ratio of 1.0 for DME synthesis reaction (1) and 2.0 for methanol synthesis reaction (2). The maximum equilibrium conversion for DME synthesis reaction (1) is much higher than that for methanol synthesis reaction (2).

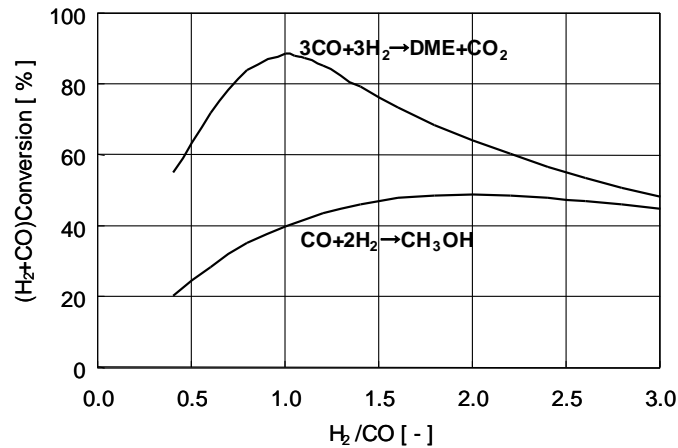


Figure 1 Equilibrium Conversion ( $260^\circ\text{C}$ ,  $5\text{MPa}$ )

## 2.2. Slurry phase reactor for DME synthesis and catalyst system

As the reaction of DME synthesis is highly exothermic, it is more important to control the reaction temperature than in the case of methanol synthesis, because the higher equilibrium conversion of DME synthesis gives much more reaction heat, and hot spot in the reactor could damage the catalyst.

In the slurry which is composed of an inert solvent containing fine catalyst particles, the reactant gas forms bubbles and diffuses into the solvent, and chemical reaction takes place on the catalyst. The reaction heat is quickly absorbed by the solvent, which has a large heat capacity, and thanks to the high effective heat conductivity, the temperature distribution in the slurry could be homogeneous.

There is less restriction on the shape and strength of the catalyst in the slurry phase reactor than in the fixed bed reactor. Catalyst is replaceable during operation.

In the slurry phase reactor, as catalyst particles are surrounded by the solvent, mass transfer mechanism of reactants and products is different from that in the fixed bed reactor. A catalyst system adequate to the slurry phase reactor has been developed. In order to enable a large scale test, a catalyst mass production technology has been also developed.

The slurry phase reactor for DME synthesis is simpler than that of FT synthesis because DME synthesis reaction products are all in gas phase at the reactor outlet and liquid product and catalyst separation is not required.

## 2.3. Separation of products from unreacted synthesis gas

By-product of reaction (1) is CO<sub>2</sub>, actually with methanol and a very small amount of water, separation of liquid product and unreacted synthesis gas is efficiently done at chilled temperature. By produced CO<sub>2</sub> can be removed by dissolving in produced DME.

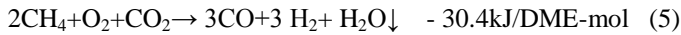
In recent SRI report [4], an evaluation of so called JFE process is introduced. However, unfortunately the process described as JFE process is quite different from the actual our process, especially for CO<sub>2</sub> separation, maybe due to lack of information.

JFE's basis is to use a physical absorption based on DME - CO<sub>2</sub> vapor liquid relations. On the other hand, SRI uses a chemical absorption based on MDEA. In SRI's process, due to the chemical absorption, neither methanol nor DME is allowed in synthesis gas for the MDEA absorber, the separation of the product such as DME and methanol from synthesis gas is very strict and therefore, -51C refrigerant is used. There are two distillation columns are provided for this separation.

The separation sequence is also different. In SRI's process, the sequence is the synthesis gas-product separation, the water removal and the DME-methanol separation, while JFE's the synthesis gas-product separation, the DME purification and the methanol-water separation and by this sequence, the methanol-water separation becomes smaller than that of SRI's. In total, SRI's process requires six columns in the separation and purification section and the very severe separation, while JFE's requires only three columns.

#### 2.4. Newly developed autothermal reformer with recycled CO<sub>2</sub> for synthesis gas production

The synthesis gas (H<sub>2</sub>/CO=1) adequate for DME synthesis can be produced in an autothermal reformer (ATR) with O<sub>2</sub> and recycled CO<sub>2</sub> from DME synthesis itself by the following reaction;



The burner top structure and furnace inner profile were designed to enhance mixing of feed in order to realize both higher thermal efficiency and much lower soot formation and residual methane at the same time. Water cooled burner and well designed refractory works are applied to keep its robustness.

Reforming catalyst bed is located at the lower part of ATR to have role of completing reforming and gas distribution. Synthesis gas going out of ATR is rapidly quenched to prevent Boudouard reaction. Synthesis gas production (5) and DME synthesis reaction (1) give the following overall reaction:



which indicates that DME and water is generated by a kind of partial oxidation of methane.

#### 2.5. Comparison of Direct DME synthesis and Indirect DME synthesis

Table 1 shows a comparison of “Direct synthesis” and “Indirect synthesis”. Indirect synthesis is two step process of methanol synthesis by reaction (2) from synthesis gas and DME production by dehydration reaction (3).

The synthesis gas (H<sub>2</sub>/CO=2) adequate for methanol synthesis can be produced in an autothermal reformer (ATR) with O<sub>2</sub> and steam by the following reaction;

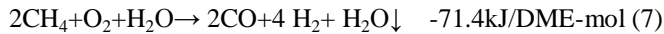


Table 1 Characteristics of Two DME process

Process	Direct (JFE)	Indirect (Two Step)	
		Methanol	Dehydration
Reaction pressure(MPa)	5	8-10	1-2
Reaction temperature(°C)	240-280	180-270	300-340
One through conversion(%)	50	38	70
Reaction by-product	CO <sub>2</sub>	-	Water
(Water+MeOH)/DME (molar ratio)	0.1	-	1.9
Reactor	Slurry Phase	Fixed Bed	Fixed Bed
Cold gas efficiency(%)	71(83)	57(83)	
( ) – Theoretical cold gas efficiency(%)	66(83)	66(84)	87(98)

The combination of (5) and (1) gives the same overall reaction formula (6).

The methanol synthesis is done actually at pressure 8-10MPa because the equilibrium conversion of the methanol synthesis is low at pressure 5MPa as shown in Figure 1.

Dehydration reaction is conducted at temperature 300-340°C and the pressure 1-2 MPa. One through conversion is high, around 70%, but energy requirement for evaporation of liquid methanol and separation of three components, DME, by-produced water and unreacted methanol is large. Taking account of this energy requirement, the cold gas efficiency of dehydration process goes down to 87% and the overall cold gas efficiency of DME production from natural gas is estimated about 57%.

The calculated theoretical value of cold gas efficiencies of the DME production from methane, the methanol production from methane, and the dehydration of methanol is shown in Table 1. In this table, estimated values for actual plant are indicated; an evaluated value from operation results of an actual plant of the methanol synthesis, a predicted value by process simulation for the methanol dehydration and the direct DME synthesis.

It is understood that the direct synthesis could have big advantages of the lower synthesis pressure and the higher cold efficiency.

### 3. Operation results of 100 tons/day demonstration plant

#### 3.1. DME 100 tons/day demonstration plant

Figure 2 shows simplified process flow diagram of 100 tons/day demonstration plant located at Kushiro in the north of Japan.

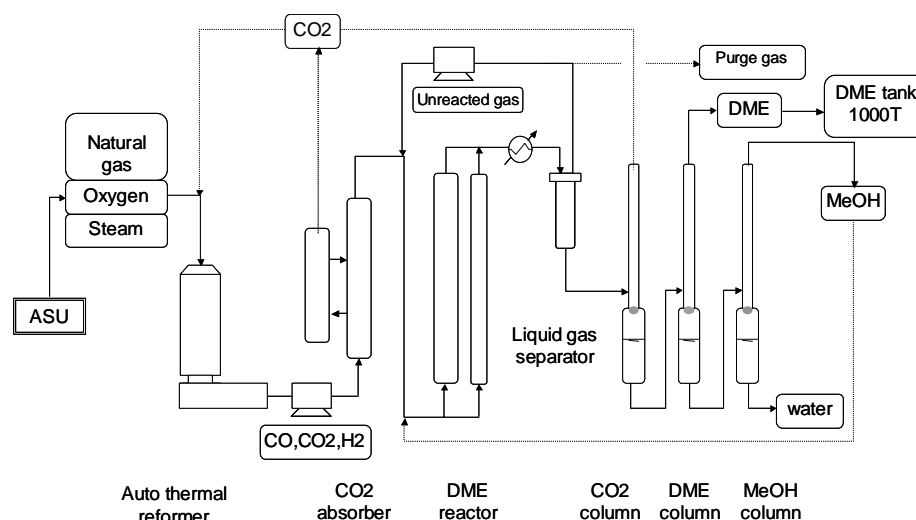


Figure 2 Process Flow Diagram of 100 tons/day DME Synthesis Plant

Natural gas is reformed in an auto-thermal reformer at the condition; the outlet temperature is 1000-1200C and the inner pressure is 2.3MPa with oxygen, steam and carbon dioxide recycled from a carbon dioxide removal unit and a purification unit to give synthesis gas of  $H_2/CO=1$ . The synthesis gas is cooled, compressed and carbon dioxide is removed by methanol absorption and supplied into DME synthesis reactor. There are two reactors in parallel; main reactor is 2.3m in inner diameter and 22m in height, small reactor is 0.65m in inner diameter and 28m in height. Small reactor is equipped to get various engineering data with higher gas velocity condition. Reaction heat is removed by internal heat exchanger coils to generate steam. The standard reaction condition is temperature: 260C and pressure: 5MPa. The effluent of the reactor is cooled and chilled to separate DME from unreacted gas, which is recycled to the reactor. DME is purified in two distillation columns and stored in pressurized tank (1,000tons). By-produced methanol is recycled to the DME synthesis reactor after water removal to be converted into DME.

### 3.2. Operation results of 100 tons/day demonstration plant

The design, manufacturing and construction of 100 tons/day demonstration plant started in 2002 and completed in November 2003.

As shown in Table 2, six test runs were carried out during 2003-2006 to demonstrate the viability of the technology and to obtain various engineering data aimed to establish the scale-up technology to commercial plant.

Table 2 Results of Test Operation

RUN NO.	Period	Duration (day)	DME production(t)
RUN100	2003/12/12-2004/1/26	43	1,240
RUN200	2004/6/20-7/31	39	2,500
RUN300	2004/10/6-12/16	72	4,230
RUN400/500	2005/6/15-11/13	152	9,070
RUN600	2006/4/1-5/12	40	2,480
(Total)		346	19,520

Although the first run had some mechanical troubles, after that, the operations were very stable for both synthesis gas production and DME synthesis. The total operation time is almost one year (346 days). The cumulative DME production reached to about 20,000 tons. The product DME was supplied for various development projects of DME utilization. The fourth run and the fifth one were conducted continuously to get the long term performance data of the catalyst.

Cold gas efficiency (Calorific value of produced DME /Calorific value of fed natural gas as raw materials) of overall process is evaluated 68.9% from operational data. This value is sufficiently high for demonstration plant and that of commercial scale plant is

estimated 71%, which satisfies the assumed value in Table 1. Cold gas efficiency of ATR section and DME synthesis section was 85.1% and 80.7%, respectively.

### 3.3. ATR performance

At the start-up of ATR, it was supplied with preheated natural gas, steam and oxygen, and the gas temperature at the outlet of ATR was controlled mainly by steam addition. After DME synthesis started up, by-produced CO<sub>2</sub> was recycled to ATR and, replacing steam, H<sub>2</sub>/CO ratio of synthesis gas was adjusted to 1.

Under the condition of  $m = 0.34$  ( $m$  is oxygen ratio,  $m=1$  for complete combustion),  $S/C=0.25$ , outlet gas temperature = 1,050C and pressure = 2.3Mpa, 90% reforming reaction took place before the catalyst bed, the amount of soot formation and residual methane is very low; 0.2mg/Nm<sup>3</sup> (target: 10mg/Nm<sup>3</sup>) and 0.15%, respectively. No damage of burner and refractory found after one year.

### 3.4. DME synthesis reactor performance

Before start-up, catalyst slurry was charged into the reactor by pump. The reactor was heated up by steam and the catalyst was first subjected to pre-reduction by synthesis gas. The reactor temperature was controlled stably by steam drum pressure up to 280°C. The temperature distribution in the slurry was very homogeneous and there was no hot spot observed. The following performances were demonstrated; Total conversion: 96% (target: 95%), DME/ (DME+MeOH) (carbon mole ratio): 91 % (target: 90%) and Production rate: 109tons/day (target: 100tons/day). The purity of produced DME was higher than 99.8% which satisfied target purity (higher than 99%: Tentative specification proposed by Japan DME Forum).

Figure 3 shows an evolution of the catalyst activity for 152days in the fourth and fifth

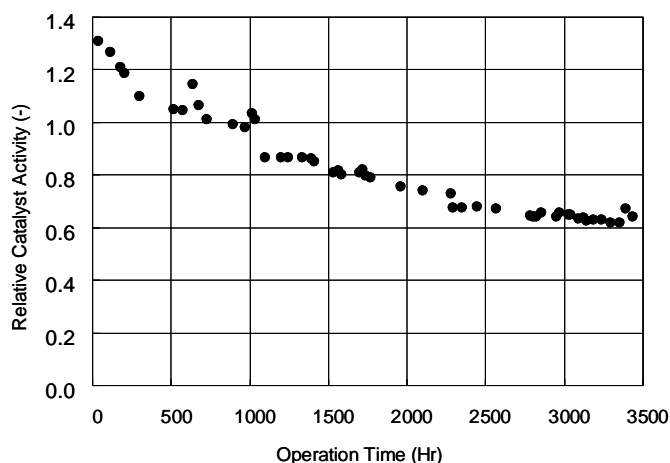


Figure 3 DME synthesis catalyst activity change

runs continuously operated. The catalyst activity change was high for the first 1,000 hours, but later looks like stabilized. The catalyst life is expected at least one year for commercial scale plant.

#### 4. Scale up of slurry phase reactor

##### 4.1. Process parameters of DME synthesis slurry phase reactor

Figure 4 shows process parameters governing the DME synthesis slurry phase reactor. Various operation parameters affect the phenomena inside the reactor, and finally the reactor performances such as feed gas consumption, reactor capacity and control system.

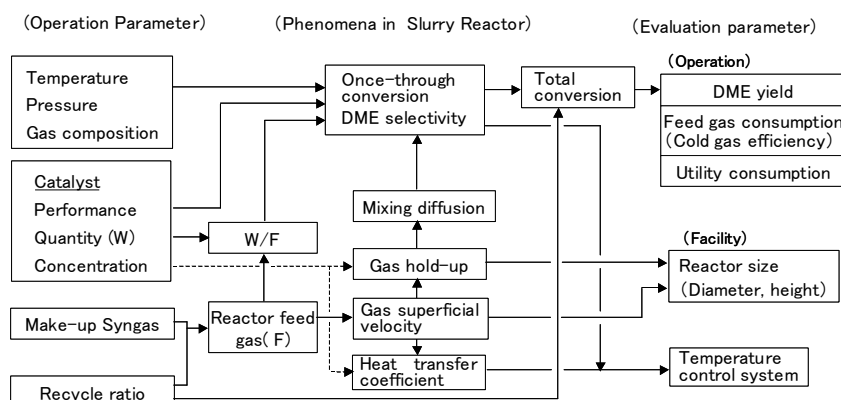


Figure 4 Process Parameters of Slurry Phase Reactor for Direct DME Synthesis

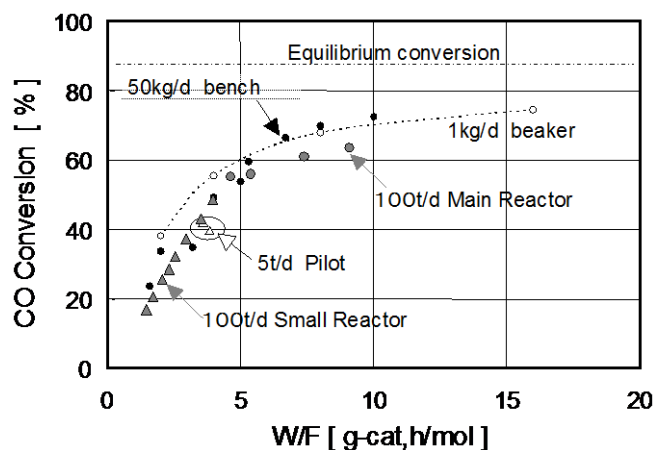


Figure 5 Effect of W/F on Once-through CO Conversion



The operation data of conversion were compared with those of smaller scale plant including auto-clave. The conversion varies as a function of W/F, W: Charged catalyst weight in the reactor, F: Gas flow rate through the reactor. As shown in Figure 5, the data of conversion for very wide range of reactor scale are almost the same for the same W/F. Plant scale has little effect on conversion. It means that overall reaction is mainly controlled by chemical reaction and the production rate is proportional to the catalyst weight in the reactor.

By this principle, the volume of 100 tons/day reactor had been decided almost 20 times larger than 5 tons/day pilot plant reactor. This simple principle was confirmed by above operation results, and can be applied to a commercial scale reactor design.

#### 4.2. Fluid dynamic phenomena in slurry phase reactor

The flow regime of slurry phase reactor varies as a function of reactor diameter and gas superficial velocity in the reactor as shown in Figure 6. The operating points of pilot plant (5 tons/day, diameter: 0.55 m), demonstration plant (100 tons/day, diameter: 2.3 m) and also planned commercial plant (3,000 tons/day, diameter: 7 m) are located in the same region of heterogeneous flow.

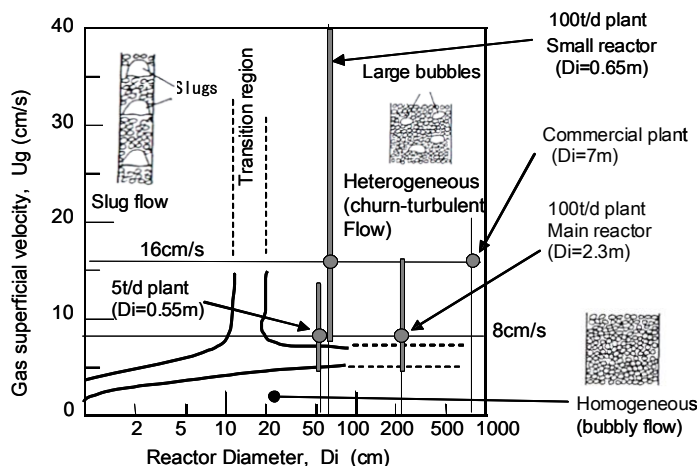


Figure 6 Flow Regime Map

The gas hold up ( $\epsilon_g$ ) was measured in increasing gas velocity ( $U_g$ ) up to 40 cm/s. Within this range, gas hold up increased smoothly without any sudden change as shown in Figure 7. As for the synthesis reaction with higher gas velocity, DME production yield by catalyst weight is almost constant up to 40 cm/s.

The gas hold-up decreases by 0.05 with slurry concentration increasing 20% to 35%.

There is no clear dependence of the gas hold up on the reactor diameter.

According to Krishna [5], the ratio of gas bubble size ( $db$ ) to reactor diameter ( $D$ ) is smaller than 0.125, reactor diameter has no effect on the gas holdup. In our case, the ratio ( $db/D$ ) is less than 0.05; for  $D=0.65$ - $2.3$  m,  $db=5$ - $30$  mm (estimated by fluid dynamic simulation with increasing  $U_g$ ).

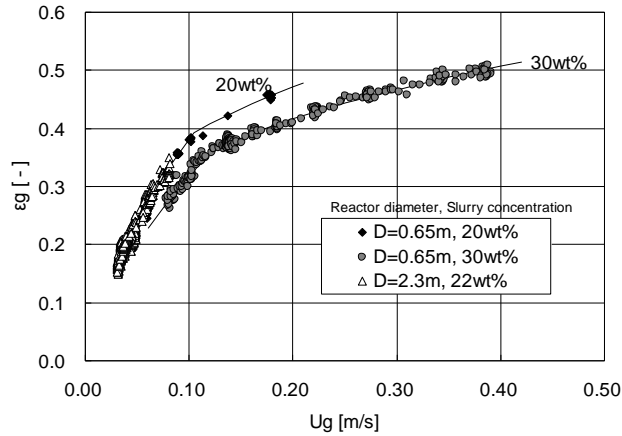


Figure 7 Effect of Superficial Gas Velocity on Gas Hold-up

The mixing diffusion coefficient in liquid phase was estimated by one dimensional reactor model from measured temperature distribution and also by a fluid dynamics model for liquid and gas bubbles movement.

Figure 8 shows a comparison of the temperature distribution measured and simulated. In this one dimensional simulation, the reaction and heat transfer was simulated in changing a factor for the mixing diffusion coefficient calculated by Deckwer [6] equation. With factor of 0.5-1.0, the simulated temperature distribution and conversion at the outlet is similar to the measured ones.

The heat transfer coefficient from the slurry to heat exchanger tubes was also evaluated from heat balance data of the reactor as shown in Figure 9. In this figure, Deckwer equation for heat transfer coefficient agrees with the operational data with some allowance.

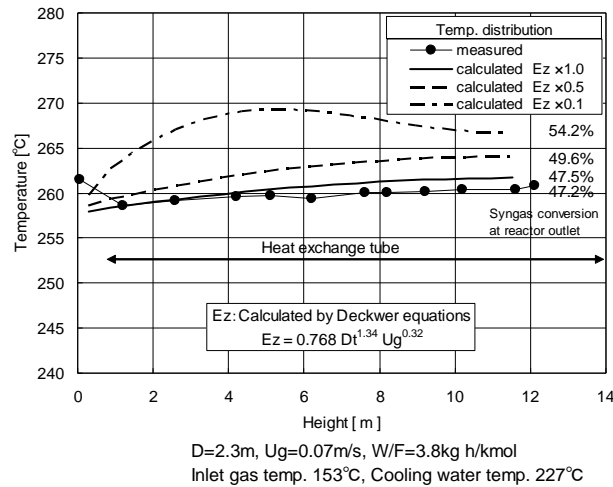


Figure 8 Comparison of Measured with Calculated by 1-D Reactor Simulator

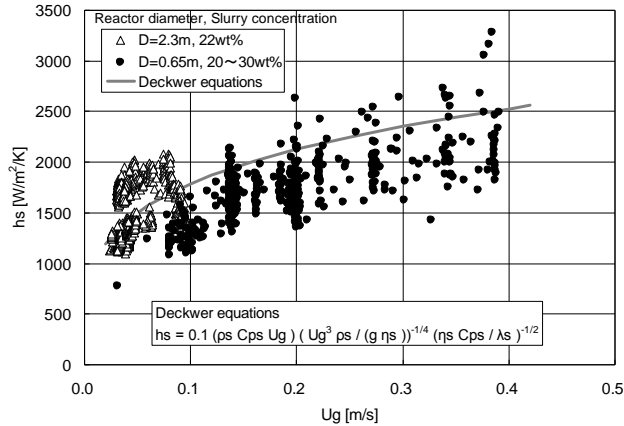


Figure 9 Effect of Superficial Gas Velocity on Slurry Heat Transfer Coefficient

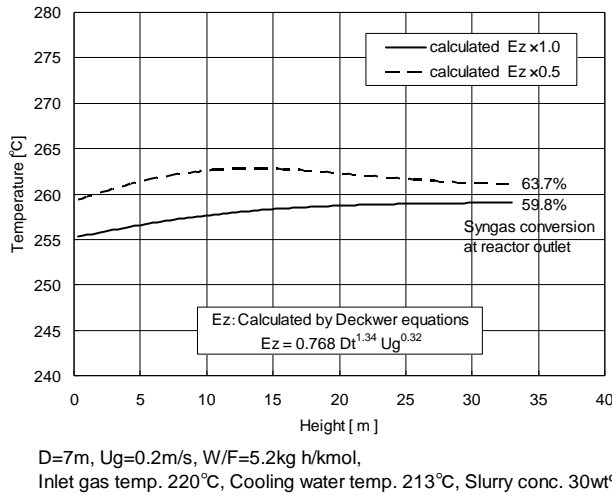


Figure 10 Example of 1-D Reactor Simulation for commercial scale plant

Based on these data, a commercial scale production of 3,000tons/day could be realized by a single reactor of 7m diameter and 44m height. Figure 10 shows an example of simulation for a commercial scale reactor, the temperature distribution is homogeneous and conversion is sufficient.

### 4.3. Application to natural gas with high CO<sub>2</sub> concentration

In JFE process, CO<sub>2</sub> is recycled from down stream to ATR in order to adjust H<sub>2</sub>/CO ratio=1. In case of natural gas highly containing CO<sub>2</sub>, the amount of CO<sub>2</sub> recycled can be reduced to compensate the increase of input CO<sub>2</sub> in natural gas and keep thermal

efficiency constant and plant configuration up to  $\text{CO}_2=40\%$  as shown in Figure 11. This characteristic could be applied to such stranded gas resources.

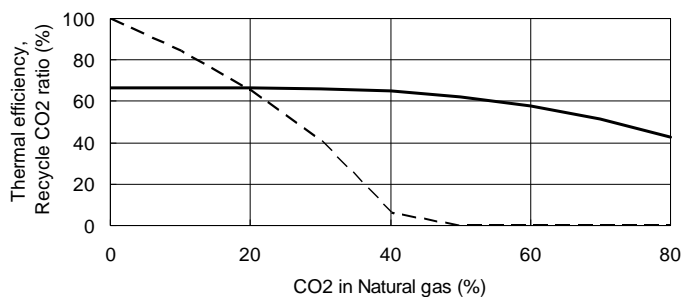


Figure 11 DME production from  $\text{CO}_2$  rich natural gas

## 5. Conclusion

DME is an excellent clean fuel, easy to transport, and could be used extensively in various sectors as household, transportation and power generation. DME can be produced from various raw materials such as natural gas, coal or coal bed methane etc. through synthesis gas.

JFE has completed the development of Direct DME synthesis process and  $\text{CO}_2$  recycle type ATR. DME is synthesized from synthesis gas of  $\text{H}_2/\text{CO}=1$ , which is produced by the ATR from natural gas with by-produced  $\text{CO}_2$ . This ratio is suitable for synthesis gas from gasification of coal ( $\text{H}_2/\text{CO}=0.5-1.0$ ) or biomass ( $\text{H}_2/\text{CO}\approx 1$ ).

JFE has developed own efficient catalyst system and its mass production technology. Process technology has been confirmed by long term operation of 100t/d demonstration plant. Catalyst performance in slurry phase reactor was stable. Conversion and DME selectivity were high. Scale-up technology has been established.

JFE is ready for the licensing and catalyst supply.

## Reference

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