

Slurry Phase Reactor Technology for DME Direct Synthesis

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Abstract: Dimethyl ether (DME) is an innovative clean fuel that can be used in various ways in many different sectors including household, transportation, power generation, etc. In order to use DME as a fuel, it must be produced in a highly efficient manner. As part of fundamental research, a new efficient catalyst and slurry phase process for DME synthesis were developed. After testing was carried out at a pilot plant (5 tons/day), the demonstration plant (100 tons/day) project was implemented from 2002 to 2006. The conversion of DME in the slurry phase reactor is dominated by W/F (W: Charged catalyst weight, F: Gas flow rate in the reactor), regardless of reactor scale (1 kg/day – 100 tons/day). The gas hold up was measured by increasing the velocity of the gas up to 40 cm/s. Within this range, gas hold up increased smoothly without any sudden change of fluid phenomena or any negative effect on the chemical reaction. There is no clear dependence of the gas hold up on the reactor diameter. The mixing diffusion coefficient in the slurry phase and the heat transfer coefficient from slurry to heat exchanger tubes were determined. Based on these data, a process simulator has been developed that predicts that commercial scale production of 3,000 tons/day can be realized by a single reactor 7m in diameter and 50m high.

Introduction

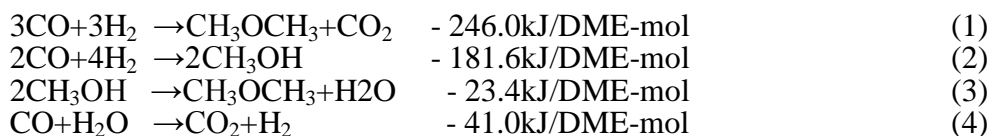
Dimethyl ether (DME) is an innovative clean fuel that can be used in various ways in many different sectors including household, transportation, power generation, chemical feedstock, etc. Up until now, DME has been used primarily as a propellant for spray cans. For such applications, approximately 200,000 tons/year are produced worldwide through the dehydration reaction of methanol. Recently, new DME plants to produce fuel grade DME have been constructed or are under consideration to be built such as at Fuel DME Production Company with 80,000 tons/year in Niigata, Japan, and many in China.

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 technical development of the DME direct synthesis process from synthesis gas for the past 20 years.

Part of fundamental research at JFE has seen the development of a new efficient catalyst and slurry phase process for DME synthesis as reported by Ohno (1997). After pilot plant (tons/day) testing as noted by Ohno (2001), the 5-year development project based on the 100 tons/day demonstration plant was started in 2002 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, Japan as reported by Ohno (2005).

DME synthesis reaction and equilibrium conversion

The DME synthesis reaction (1) from synthesis gas (H₂ and 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 in the methanol synthesis step is dominant.



Slurry phase reactor for DME synthesis and catalyst system

As the DME synthesis reaction is highly exothermic, it is more important to control the reaction temperature than in the case of methanol synthesis as shown in Equations (1) and (2). Figure 1 shows a comparison of equilibrium conversions of three reactions for methanol and DME syntheses. The proposed reaction shown in Equation 1 may have the maximum conversion at H₂/CO = 1 at the reaction condition. Therefore, we may expect a higher per-pass conversion than that by the other two reactions. This is because the higher equilibrium conversion of DME synthesis creates much more reaction heat that may create hot spots in the reactor and could damage the catalyst. The hot spots generally take place in a gas-solid phase and non-adiabatic packed bed tubular reactors. On the other hand, a slurry bed reactor can remove reaction heat by circulating slurry and easily maintains the uniform temperature.

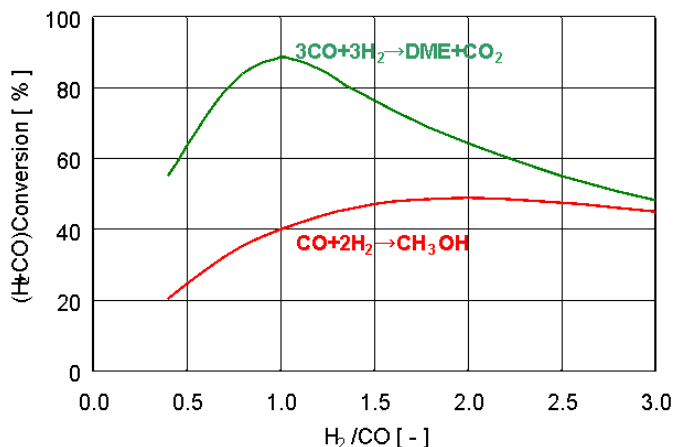


Figure 1. Equilibrium conversion for Methanol Synthesis and DME Synthesis at 260°C and 5MPa

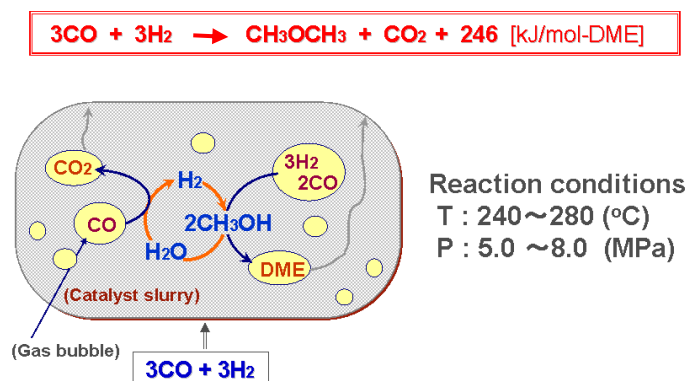


Figure 2. One-step DME Synthesis Mechanism

The mechanism of the reactions in the slurry composed of an inert solvent containing fine catalyst particles and the simplified schematic diagram is shown in Figure 2. The reactant gas or synthesis gas of CO and H₂ is supplied from the bottom of the reactor shown in Figure 3. Gas bubbles may be generated and diffuse into the solvent, and the chemical reactions take place on the surface of the catalyst. Firstly, the methanol synthesis reaction occurs and then methanol is dehydrated to produce DME. Water generated by the dehydration reaction quickly reacts with CO and is removed from the system. Therefore, no water remains on the surface of the catalyst. The heat of reaction is absorbed by the solvent, which has a large heat capacity, and thanks to the highly effective heat conductivity, the temperature distribution in the slurry could be homogeneous. The reaction heat is finally removed through the generation of steam.

In this connection, a catalyst that is appropriate for the slurry phase reactor has been designed and developed. In order to enable a large-scale test, mass production technology for the catalyst has also been developed. The inert solvent

is selected as a hydrocarbon fraction with a narrow and high boiling point range around 400°C, which may not influence the reaction performance and is not vaporized under reaction conditions.

The catalyst with the size of the order of 10-micron meters is suspended in the solvent. It is a mixed catalyst that has functions of methanol synthesis, dehydration and shift gas reactions, and contains CuO, ZnO and Al₂O₃. Water may damage the catalyst activity so that the water removal mechanism by the shift reaction to convert CO to CO₂ is very essential.

DME synthesis reactor effluent contains DME, CO₂ and the unreacted synthesis gas which are all in gas phase at the reactor outlet and are easily separated from the slurry phase so that the separation of liquid product and catalyst becomes unnecessary.

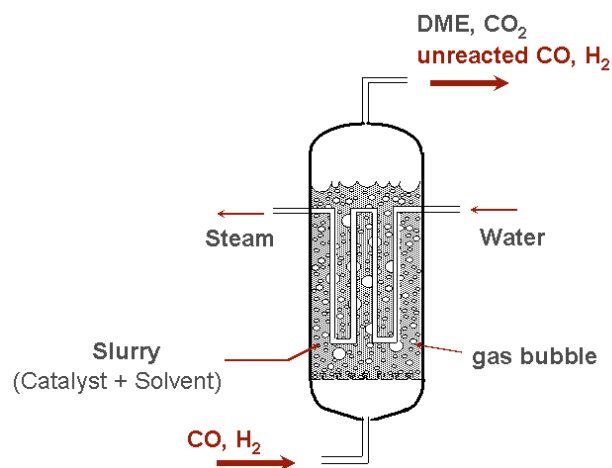


Figure 3. Slurry Phase Reactor for DME Synthesis

DME 100 tons/day demonstration plant

In order to validate DME synthesis in the slurry phase reactor, process development was carried out at JFE starting with a 50kg/day bench scale plant followed by a 5 tons/day pilot scale plant installed at Kushiro in the north of Japan utilizing coal bed methane and propane as the feedstocks. Then, a demonstration plant with a capacity of 100 tons/day was constructed, also near Kushiro. Figure 4 shows a simplified process flow diagram of the 100 tons/day demonstration plant. This demonstration plant uses natural gas for the feedstock which is converted to synthesis gas by an autothermal reformer, ATR, which is then converted to DME in the DME synthesis section.

Natural gas is reformed in the ATR at the following conditions; the outlet temperature is 1000-1200°C and the inner pressure is 2.3MPa with oxygen, steam and carbon dioxide recycled from the carbon dioxide removal unit and the purification unit to give synthesis gas of H₂/CO=1. Synthesis gas is quickly cooled and compressed, carbon dioxide is removed by methanol absorption, and

the treated syngas is supplied to the DME synthesis reactor. There are two reactors positioned in parallel: the main reactor which has a 2.3m inner diameter, and is 22m in height, and a small reactor with a 0.65m inner diameter and 28m in height. The small reactor is equipped to obtain various engineering data for higher gas velocity conditions. Reaction heat is removed by the internal heat exchanger coils to generate steam. The standard reaction condition is at a temperature of 260°C and a pressure of 5MPa. The reactor effluent is cooled and chilled to separate DME and by-products: CO₂ and methanol from the un-reacted gas, which is recycled to the reactor. DME is purified in two distillation columns and stored in a pressurized tank (1,000tons). By-product methanol is recycled to the DME synthesis reactor after water removal to be converted into DME. Figure 5 shows a picture of a DME 100 tons/day demonstration plant.

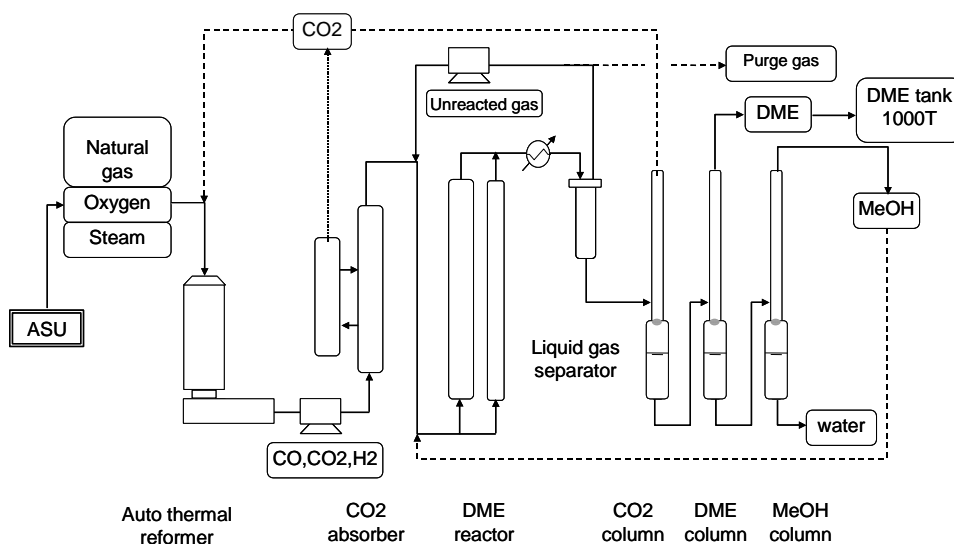


Figure 4. Process Flow Diagram of 100 tons/day DME Synthesis Plant

Operation results of 100 tons/day demonstration plant

The design and construction of the 100 tons/day demonstration plant started in 2002 and was completed in November 2003. As shown in Table 1, 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 scale-up technology for the commercial plant design.

Although the first run experienced some mechanical difficulties, subsequent operations were very stable for both synthesis gas production and DME synthesis. The total duration of the operation was almost one year (346 days). The cumulative DME production reached approximately 20,000 tons. The product DME was supplied for various development projects of DME utilization. The fourth and fifth runs were conducted continuously to obtain long term performance data for the catalyst.



Figure 5. DME 100 tons/day Demonstration Plant

Table 1. 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 |

The cold gas efficiency (calorific value of produced DME /calorific value of feed natural gas as raw materials) of the overall process was evaluated as 69.4% from the operational data. This value is sufficiently high for the demonstration plant that of the efficiency of the commercial scale plant can be estimated to be 71%. The cold gas efficiency of the ATR section and the DME synthesis section were 84.9% and 81.7%, respectively.

DME synthesis reactor performance

Before start-up, the catalyst slurry was charged into the reactor by a pump. The reactor was heated 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 no hot spots were observed. The following performance was demonstrated; Total conversion: 96% (target: 95%), DME/ (DME+MeOH) (carbon mole ratio): 91 % (target: 90%) and Production rate: 109 tons/day (target:

100 tons/day). The purity of produced DME was higher than 99.8%, which satisfied the target purity (higher than 99%: Tentative specification proposed by Japan DME Forum).

Figure 6 shows the evolution of the catalyst activity for 152 days in the fourth and fifth runs which were continuously operated. The catalyst activity change was high for the first 1,000 hours. It seems that activity stabilization occurs after 3,000 hours on stream. Increasing the temperature is expected to make catalyst life at least one year for a commercial scale plant to maintain desired conversions.

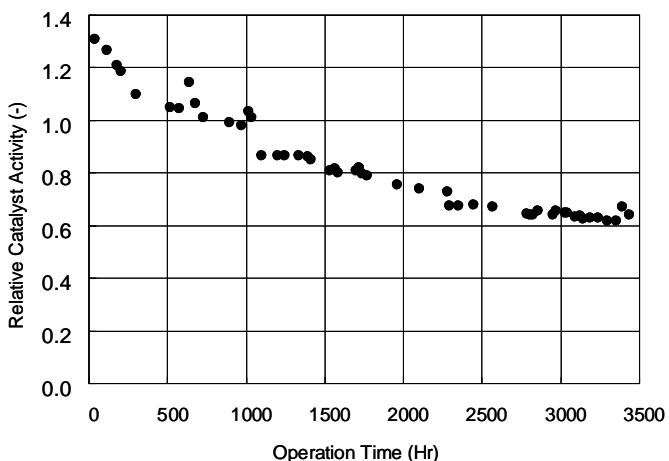


Figure 6. DME synthesis catalyst activity change

The slurry temperature of up to 280°C in the reactor is homogeneous and stably controlled by steam drum pressure. Due to the high heat transfer characteristic of the slurry phase reactor, the temperature profiles for different temperature operations are very uniform under the slurry surface as shown in Figure 7. Therefore, it is considered that the DME synthetic reactions are performed in an isothermal way.

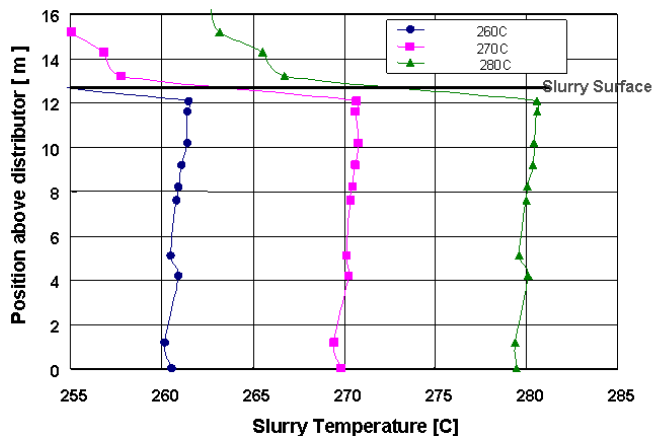


Figure 7. Slurry Temperature Distribution in DME Reactor

Process parameters of DME synthesis slurry phase reactor

Figure 8 shows the process parameters governing the DME synthesis slurry phase reactor. Various operation parameters affect the phenomena inside the reactor and the reactor performance characteristics such as feed gas consumption, reactor capacity and control system.

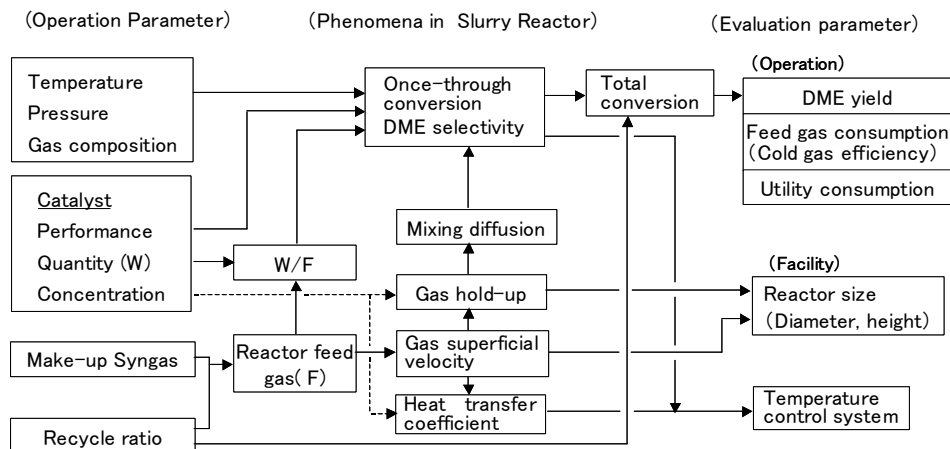


Figure 8. Process Parameters of Slurry Phase Reactor for Direct DME Synthesis

The operating data for conversion were compared with those of the smaller scale processes including the autoclave reactor. The conversion varies as a function of W/F, W: Charged catalyst weight in the reactor (g-catalyst), and F: Gas flow rate through the reactor (mol/h). As shown in Figure 9, conversion data for a very wide range of reactor scale are almost the same for the same W/F. The plant scale has little effect on the conversion. Although the same catalyst size, which defines the internal diffusion resistance and the same gas velocity, are

adopted for the different reactor scales, the production rate is proportional to the catalyst weight in the reactor.

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

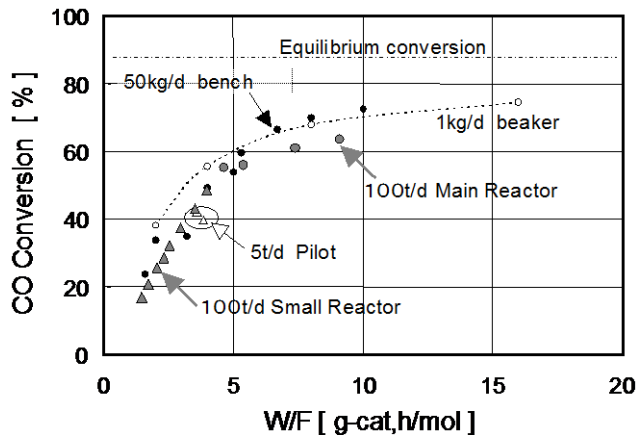


Figure 9. Effect of W/F on Once-through CO Conversion

Fluid dynamic phenomena in slurry phase reactor

The gas hold up (ϵ_g) was measured for increasing gas velocities (U_g) up to 0.40m/s. Within this range, the gas hold up increased smoothly without any sudden change as shown in Figure 10.

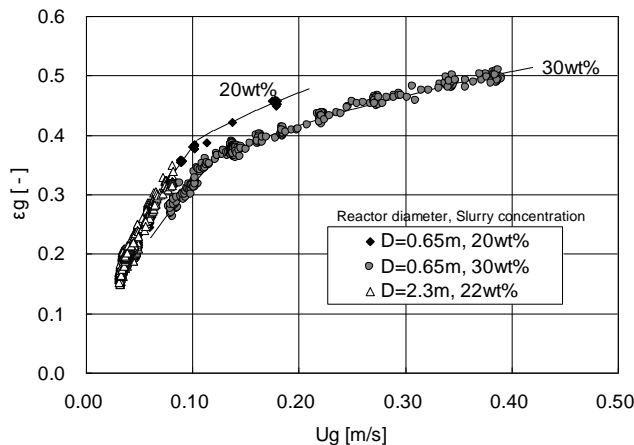


Figure 10. Effect of Superficial Gas Velocity on Gas Hold-up

Furthermore, the gas hold-up decreases by 0.05 with slurry concentration increasing 20% to 30%. There is no clear dependence of the gas hold up on the reactor diameter at the range of $U_g = 8 \sim 18$ cm/s. Although the experimental data

are limited for this comparison, we may expect that the difference may be smaller for the higher gas velocity since the gas hold up may be saturated. According to Krishna (2000), if 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 $D=0.65\sim 2.3\text{m}$, $db=3\sim 5\text{mm}$ estimated by Akita (1974) equation. As for the synthesis reaction with higher gas velocity, DME production yield by catalyst weight is almost constant up to 0.30m/s as shown in Figure 11.

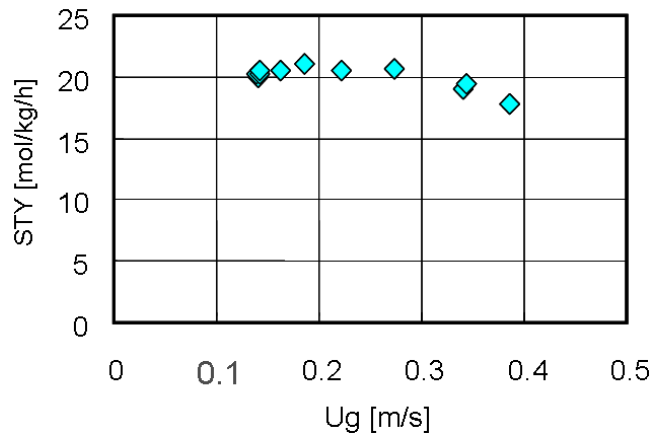


Figure 11. Effect of Gas velocity on DME Yield

The mixing diffusion coefficient in the liquid phase was estimated by a one dimensional reactor model simulation and also by a fluid dynamics model simulation for liquid and gas bubbles movement. Both simulators were developed at DME Development Co.

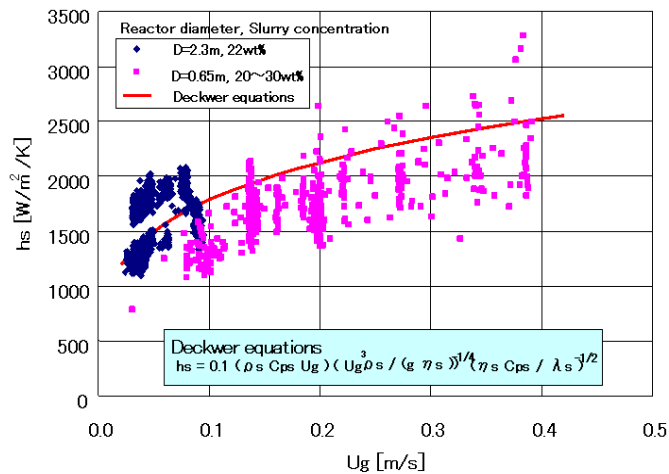


Figure 12. Effect of U_g on Slurry Heat Transfer Coefficient, h_s

The heat transfer coefficient from the slurry to heat exchanger tubes was also evaluated from the heat balance data of the reactor. The Deckwer (1982) equation for the heat transfer coefficient agrees with the operational data with some allowance as shown in Figure 12. According to this agreement, it was discovered that the Deckwer equation can be applied to a scale-up to a commercial plant.

In this one-dimensional simulation, the reaction and the heat transfer were simulated in changing a factor for the mixing diffusion coefficient calculated by the Deckwer equation. The calculated mixing diffusion coefficients are shown in Figure 13 of which depends on the reactor diameter and the gas velocity.

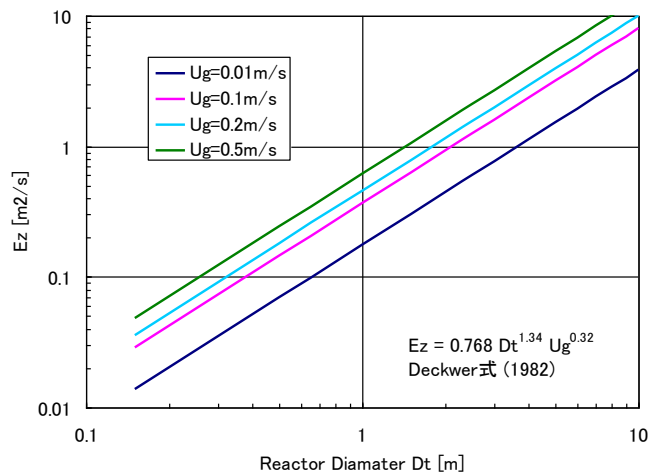
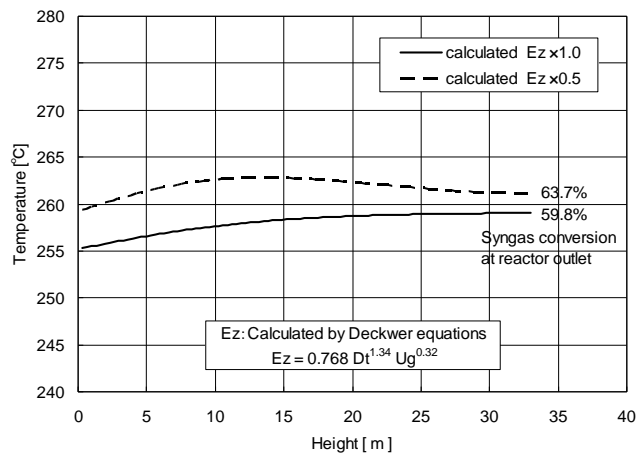


Figure 13. Estimated Mixing Diffusion Coefficients, E_z



$D=7\text{m}$, $U_g=0.2\text{m/s}$, $W/F=5.2\text{kg h/kmol}$,
 Inlet gas temp. 220°C , Cooling water temp. 213°C , Slurry conc. 30wt%

Figure 14. Example of 1-D Reactor Simulation for the commercial scale plant

Figure 14 shows examples of the simulations for the commercial scale reactor and it was discovered that the temperature distribution is homogeneous and that the synthesis conversion is sufficiently high. With factor of 0.5~1.0, the simulated temperature distribution and conversion at the outlet is similar to the measured ones.

Based on the parameters necessary for the design of the slurry phase reactor obtained during the operation of the demonstration plant as well as the analysis of the process data, a process simulator has been developed that predicts that commercial scale production of 3,000 tons/day can be realized by a single reactor 7m in diameter and 50m high.

Conclusion

DME is an excellent clean fuel, easy to transport, and could be used extensively in various sectors as household, transportation, power generation and petrochemical feedstock. DME can be produced from various kinds of raw materials such as natural gas, coal or coal bed methane, biomass and even municipal wastes through synthesis gas generated either by reforming steam or gasification processes.

This paper summarized the process development of a direct synthesis process for Dimethyl Ether (DME) laboratory scale though operation of an industrial demonstration plant. Learnings are applied to the design of a commercial scale plant and the scale-up technology have also been established.

DME Development Co. has also developed an efficient DME synthesis catalyst and associated mass production technology. The performance of the catalyst was confirmed by the long-term operation of a 100 tons/day demonstration plant. It was discovered that the catalyst activity is very high and stable. The conversion and DME selectivity were also very high.

Notation

| | |
|-----|--|
| D | Reactor diameter, m |
| db | Gas bubble diameter, mm |
| Ez | Diffusion coefficient, m ² /s |
| H/C | Hydrogen to carbon atom ratio |
| hw | Heat transfer coefficient, W/m ² /K |
| S/C | Steam to carbon ratio, g-mol/C-atom |
| STY | DME production rate per catalyst, g-mol/kg-cat/h |
| Ug | Gas superficial velocity, m/s |
| W: | Charged catalyst weight in the reactor, g |
| F: | Gas flow rate through the reactor, mol/h |

Greek Letter

| | |
|----|---------------|
| εg | Gas holdup, - |
|----|---------------|

Article in International Journal of Chemical Reactor Engineering 8(1) · January 2010
DOI: 10.2202/1542-6580.2267

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