**Process Intensification for Dimethyl Ether Production by
Self-Heat Recuperation**

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ABSTRACT

Dimethyl ether (DME) is categorized as a green energy source and the demand for DME continues to increase. DME is commonly produced by two methods: indirect and direct DME synthesis. In the indirect method, methanol is produced and then converted to DME. In the direct method, DME is directly synthesized from syngas without methanol production. In this research, we investigated the feasibility of self-heat recuperation technology to the DME production process using the indirect method and developed an innovative process for DME production from an energy saving point of view, thereby considerably reducing the energy consumption of the thermal and separation processes.

KEYWORDS: Dimethyl ether production; Energy; Self-Heat Recuperation; Process Design

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38 **1. Introduction**

39 Recently, dimethyl ether (DME) has attracted interest because DME is categorized as
40 a green fuel [1]. It discharges low amounts of sulfur and particulate matter in the
41 exhaust gas produced by combustion [2]. DME contains 34.8% oxygenates and has a
42 higher heating value than natural gas [3]. Moreover, it is less toxic towards humans and
43 can be stored as a liquid fuel upon pressurizing or cooling [4].

44 DME is commonly produced from syngas during natural gas reforming and coal
45 gasification [5] or by biomass pyrolysis [6] and gasification [7] as known biomass
46 refinery [8] by either indirect [9] or direct DME synthesis methods [10]. In the indirect
47 method, otherwise known as the double-stage method, methanol is produced from
48 syngas and is converted to DME. In the direct method, otherwise known as the
49 single-stage method, DME is directly synthesized from syngas. The relevant series of
50 reactions are recognized as:

51 methanol synthesis

53 methanol dehydration

55 water gas-shift reaction

57 methanol synthesis from CO_2

59 All of these equations represent exothermic reactions. The reaction heat of the methanol
60 dehydration reaction, shown by Eq. (2), is $\Delta H_{298\text{K}} = -23.4 \text{ kJ/mol}$ under standard
61 conditions [11].

62 The direct method has been used and the methanol synthesis reaction from syngas
63 (CO and CO_2) takes place in the reactor according to the above-mentioned equations.
64 The main advantage of the direct method is that the CO transformation rate is higher
65 than that of the indirect method [10]. Because of this advantage, many investigators
66 have recently tried to analyze the kinetics [12] and to design reactors [13] for the
67 application of the direct method. Le Chatelier's principle reveals that this higher CO
68 transformation occurs because of the series of reactions that take place in the reactor.
69 The methanol product converts to DME immediately upon dehydration in the reactor
70 and this leads to a shift in the reaction equilibrium towards the product side. This means
71 that the same high CO transformation rate may be obtained by the indirect method
72 compared to the direct method. As shown in Eq.1, this requires that the methanol

product be removed, from the reaction field immediately by separation or by an increase in the methanol dehydration reaction rate, as shown in Eq. 2. This is done by adjusting the recycle flow rate and conditions (low temperature is preferred according to Le Chatelier's principle).

Many DME direct and indirect production processes use a reactant recycle system with product separation to shift the reaction equilibrium towards the product side. This increases the overall conversion ratio in the reactor. Distillation processes have often been industrially used for this product separation from the reactant recycle stream. However, it is well known that these distillation processes are energy-intensive processes because latent heat (vaporization and condensation heat) is used for gas-liquid separations in columns. Thus, many chemical engineers and investigators have analyzed the reaction kinetics [14] and conditions [15], and developed catalysts that give high conversion from reactant to product in the reaction, for decreasing the reactant recycle stream and whole process optimization, such as γ -Al₂O₃ with P₂O₅ [16] or Nb₂O₅ [17]. Alternatively, reactive distillation [18] and reactive distillation combined with a dividing wall column [19] have been used for DME production in order to reduce the energy of distillation process.

Recently, self-heat recuperation technology based on minimizing the loss of exergy to reduce energy consumption in chemical processes has been developed. The application of self-heat recuperation technology to chemical processes has resulted in the latent heat and the sensible heat of the process stream being circulated in these processes without any heat addition [20]. The energy consumption and the loss of exergy in a process can be greatly reduced in the steady state [21]. This technology has been applied to several chemical processes as case studies [22] and large energy savings have been obtained in these processes [23]. From these previous studies it was found that thermal [24] and distillation processes [25] are suitable processes for self-heat recuperation.

We thus investigated the use of self-heat recuperation technology in the DME production process using the indirect method. This was done to demonstrate the energy savings potential of the distillation processes and to determine if the indirect DME production process is feasible.

2. Conventional DME production using the indirect method

Figure 1 shows a flow diagram for the conventional DME production process using the indirect method [26]. The process was divided into three parts: the reaction, product

DME distillation, and methanol-water distillation for the recycling of methanol. These are designated R1, D1, and D2 and are surrounded by broken lines in Fig. 1. A simulation was conducted using PRO/II Ver. 9.0 (Invensys, SimSci) to examine the energy required for the conventional process [27]. In this simulation, the Soave-Redlich-Kwong equation was selected for the state equations, the UNIFAC model was used for equilibrium calculations and 100% adiabatic efficiency was assumed for the compressors. Additionally, the minimum temperature difference for the heat exchangers was set to 10 K for all the heat exchangers and the heat and pressure losses from the system were negligible.

2.1. Reaction part (R1)

Figure 2 shows a detailed flow diagram of the reaction part of DME production. Note that the arrows show energy inputs (above the device) and outputs (below the device) in the system and that the outlined arrows represent work and the gray arrows represent heat. Initially, feed methanol at a standard temperature (25 °C) and at 2.0 MPa was mixed with recycled methanol at 25 °C and 2.0 MPa and fed to R1. In R1, the stream was heated to 130 °C by a heater and fed to the reactor. For the simulation, 27.6 kW was supplied to the heater. This reactor was assumed to be an isothermal reactor at 130 °C. In the reactor, the methanol dehydration reaction, as shown in Eq. 2, takes place

in the liquid phase and methanol is converted to DME and water. The DME conversion ratio was 0.42. The exothermic reaction heat was 20.7 kW (Exergy was 5.4 kW). This reaction heat can partially be used to supply the heat duty of the reactor. The product stream from the reactor was cooled to 25 °C and fed to DME distillation (D1). The cooling duty was 34.3 kW.

2.2. DME distillation (D1)

DME was separated as distillate from the methanol-DME-water mixture (reaction product stream from the reactor) by distillation column (Distillation 1), as shown in Fig.

3. In the simulation, the product DME flow rate was 4.2 kmol/h at 2.0 MPa. The reflux ratio of the column was set to 1.2 on a mole basis. The number of stages in the distillation column was 15 and the feed stage was the 8th stage from the top. The DME composition of the distillate was 0.999 (pure DME) and the bottom of the distillation column contained a methanol-water mixture. The bottom was depressurized by a valve (0.1 MPa) to separate pure methanol and water by subsequent distillation (D2). From the simulation, the reboiler and condenser duties of Distillation 1 were 65.5 and 21.0 kW, respectively.

2.3. Methanol-water distillation (D2)

Recycled methanol was separated from the methanol-water mixture (the bottom of Distillation 1) as a distillate, as shown in Fig. 4. In the simulation, the flow rate of the recycled methanol was set to 1.0 kmol/h at 0.1 MPa. The reflux ratio of the column was set to 5.0 on a mole basis. The number of stages in the distillation column was 15 and the feed stage was the 10th stage from the top. Then methanol composition of the distillate was 0.999 (pure methanol) and the bottom of the distillation column was water (methanol-water mixture). The methanol composition of this methanol-water mixture was 0.126. In the simulation, the reboiler and condenser duties of Distillation 2 were 44.6 and 58.8 kW, respectively.

The total heat duty was 137.7 kW (27.6 for the heater and 65.5 for the reboiler in Distillation 1 and 44.6 for the reboiler in Distillation 2) and the work was 0.0 kW for the pump.

3. Proposed DME production using the indirect method

To determine the energy required for the DME production process based on self-heat recuperation, a simulation was conducted using the same assumptions as those of the simulation for the conventional process.

3.1. Reaction part (R1)

An isothermal reactor at 130 °C was used in this simulation, which is the same as in the simulation of the conventional process. This reaction takes place in the liquid phase. All the streams around the reactors are in the liquid phase. However, this reaction takes place in the vapor phase at higher temperature (250–400 °C) in many industrial plants for DME production with the indirect method [28]. Thus, some DME production processes are integrated with methanol production processes by heat integration or generate middle pressure steam (30 MPa) by using reaction heat. Although some researchers have managed to develop new exergy recuperative systems for self-heat recuperation such as heat circulators with magnetocaloric or electrocaloric effects, or thermoelectric devices [29], self-heat recuperation with adiabatic compression is the only current industrially feasible system. To increase the temperature by adiabatic compression for heat circulation in the process it is necessary that a part of process must be in the vapor phase at lower temperature range. Therefore, we only applied conventional heat recovery to this reaction as shown in Fig. 5. Using conventional heat recovery, the heat (24.2 kW) in the reaction product stream is exchanged with the heat in the feed stream. Furthermore, additional heat (3.4 kW) is required to heat the feed stream to the set temperature (130 °C) because of temperature differences in the heat exchanger. The amount of exothermic reaction heat was 20.7 kW, which is the same as

that of the conventional process. This reaction heat can thus account for the heat duty of the heater. However, this reaction heat is not integrated into the heat duty of the heater, which would allow for heat recovery, as shown in Fig. 5.

3.2. DME distillation (D1)

The operating pressure of DME distillation was decreased to 0.5 MPa from 2.0 MPa for separation purposes, as shown in Fig. 6. Because of this modification the temperature difference between the top and the bottom of the distillation column are similar and the temperature of the reboiler decreases. The use of exhaust heat thus increases. Following the proposed self-heat recuperative distillation design [30, 31], the temperature and the enthalpy value (q) of the column feed were ~~was~~ adjusted where $q = \{\text{heat needed to vaporize one mole of feed}\} / \{\text{molar latent heat of feed}\}$. The heat of the distillate and the bottom stream from Distillation 1 was thermally integrated using adiabatic compression. All of the process heat can thus be circulated to D1, leading to remarkable energy savings. However, three compressors are required to apply self-heat recuperation in this part, leading to an increase in capital costs for this modification. The pressure of the distillate stream is similar to that of the critical pressure. The amount of condensation heat may be too small for heat exchange with the vaporization heat in the reboiler, leading to a marked decline in energy efficiency of the system. It is thus

necessary to reduce the pressure of the bottom part and to add a compressor to refeed the bottom part to the column after the heat exchange. This results in an increase in the number of compressors. The work required for the three compressors in this part is 15.4 kW ($= 4.9 + 7.1 + 3.4$).

3.3. Methanol-water distillation (D2)

In addition to DME distillation (D1), the temperature and the enthalpy value (q) of the column feed to methanol-water distillation (D2) were adjusted by following the self-heat recuperative distillation design, as shown in Fig. 7. All of the process heat is thus circulated to D2. According to the simulation, the work required for the two compressors in this part is 9.2 kW ($= 0.3 + 8.9$). Figure 8 shows a temperature-heat diagram for the heat exchangers in D2. From this figure, all the heat from the process stream is well circulated. However, this figure also shows that further reduction of the process energy is possible from the exergy point of view for heat transfer especially at latent heat exchange.

Table 1 summarizes the energy required for each part of this process. The required energy required reduces to about 18% that of the conventional process. If we compared the energy required as a primary energy calculation in Japan, the conventional process requires 137.7 kW ($= 137.7 + 0.0 \times 1/0.369$) and the proposed process requires 70.0 kW

(= $3.4 + 24.6 \times 1/0.369$). Note that 0.369 is the power generation efficiency from the Japanese energy savings law. Therefore, the installation of self-heat recuperation provides a substantial energy savings potential to DME production. In addition, we found some issues to solve for further increase of the energy efficiency by application of self-heat recuperation at R1 and D1. If this process is combined with the methanol synthesis process based on self-heat recuperation [32], an appropriate economic analysis of the proposed process design reveals that the indirect method incorporating this process should be an additional option for DME synthesis from syngas.

5. Conclusions

We examine the feasibility of applying self-heat recuperation technology to DME production using the indirect method. An innovative integrated process design is reported from an energy savings point of view. The use of self-heat recuperation technology for DME production leads to about 80% reduction in energy consumption in the process. In addition, we found the possibility of further energy improvement of the DME production with development of exergy recuperative systems and with heat integration of the proposed process with methanol production and reformer based on self-heat recuperation.

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330 **Figure Legends**

- 331 Figure 1 Flow diagram for DME production by the indirect method. 22
- 332 Figure 2 Detailed flow diagram of the reaction part. 22
- 333 Figure 3 Detailed flow diagram of DME distillation. 23
- 334 Figure 4 Detailed flow diagram of methanol-water distillation. 23
- 335 Figure 5 Detailed flow diagram of the reaction part using heat recovery. 24
- 336 Figure 6 Detailed flow diagram of DME distillation based on self-heat recuperation.

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Figure 7 Detailed flow diagram of methanol-water distillation based on self-heat recuperation.

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Figure 8 Temperature-heat diagram in the heat exchangers for methanol-water distillation based on self-heat recuperation.

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Table 1 Summary of the energy required

	Conventional		Proposed	
	Heat	Work	Heat	Work
R1 [kW]	27.6	0	3.4	0
D1 [kW]	65.5	0	0	15.4
D2 [kW]	44.6	0.0*	0	9.2+0.0*
Total [kW]	137.7	0.0	3.4	24.6

Adiabatic efficiency of compressor and pump: 100%

*0.0 kW is required for pump (22.5 W)

Fig. 1. Flow diagram for DME production by the indirect method

Fig. 2. Detailed flow diagram of the reaction part

Fig. 3. Detailed flow diagram of DME distillation

Fig. 4. Detailed flow diagram of methanol-water distillation

Fig. 5. Detailed flow diagram of the reaction part using heat recovery

Fig. 6. Detailed flow diagram of DME distillation based on self-heat recuperation

Fig. 7. Detailed flow diagram of methanol-water distillation based on self-heat recuperation

Fig. 8. Temperature-heat diagram in the heat exchangers for methanol-water distillation based on self-heat recuperation