

CONTINUOUS PRODUCTION OF DMC OVER FIXED-BED K/MgO CATALYST IN A PILOT SCALE REACTIVE DISTILLATION

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Introduction

Dimethyl carbonate (DMC) is a versatile and nontoxic chemical substance, which is an important chemical material in the current chemical industry and in the motor fuel industry. It has been proposed as a methylating agent for aromatic compounds, to replace methyl halides and dimethyl sulfate, which are both toxic and corrosive, and as an intermediate in the synthesize polycarbonates and isocyanates, thereby avoiding the need to use phosgene. DMC is also a candidate for replacing tertiary butyl ether (MTBE) as an oxygen-containing additive for gasoline because it has high oxygen content, a good blending octane, low toxicity, and quick biodegradation [1].

A number of DMC synthesis processes have been suggested and some processes have already been commercialized. The classic route to DMC involves the use of phosgene. This route is disadvantaged by the safety problem of handling highly toxic phosgene and the environmental problem of disposing of sodium chloride. Further, DMC can be synthesized concurrently with ethylene glycol (EG) by the transesterification process between methanol and ethylene carbonate (EC). [2]

MgO has been used as a primary solid catalyst as well as a support in many fields of heterogeneous catalysis reaction. Bhanage *et al.* reported that MgO as a basic oxide catalyst showed a high activity in a two-step synthesis of DMC from epoxides, carbon dioxide and methanol at 150°C [2]. It is also reported that the basic homogeneous catalysts such as KOH, K₂CO₃, NaOH and LiOH were effective for DMC synthesis from EC and methanol [3, 4].

Reactive Distillation is a unit operation, in which two operations can occur, chemical reaction and distillation. Reactive or catalytic distillation has captured the imagination of many recent processes, because of the demonstrated potential for capital productivity improvements (from enhanced overall rates, by overcoming very low reaction equilibrium constants and by avoiding or eliminating difficult separations), selectivity improvements (which reduce excess raw materials use and byproduct formation), reduced energy use, and the reduction or elimination of solvents.

The objective of this work has been to investigate the continuous production of DMC concurrently with ethylene glycol through transesterification of ethylene carbonate with methanol in the presence of K/MgO Raschig-ring form catalyst using a pilot scale reactive distillation column.

Experimental

MgO (Source: Mirae Ceratec Co., Ltd.) pellet was prepared as support. MgO pellet was made from its powder through a series of procedure. The produced MgO pellets were impregnated with K₂CO₃ aqueous solution for 5 h, dried in an oven at 100°C overnight and calcined in an electric furnace at 300-550°C for 5 h.

All experiments were conducted in a pilot scale reactive distillation (RD) column, which has inner diameter of 3 inches, and total height of 7 meters including boiler and condenser. The column was made from stainless steel SUS316. A condenser is directly connected at the top of the column, and a boiler at the bottom. The whole distillation column is insulated to avoid heat loss. **Fig. 1** shows a general scheme of RD system

RD column is divided to three sections, rectifying, reacting and stripping section. The stripping and rectifying sections were packed with stainless-steel Raschig-ring, while the reacting section was

packed with Raschig-ring formed K/MgO catalyst. **Fig. 2** and **Fig. 3** show the stainless steel Raschig-ring and K/MgO pellet, respectively.

The experiments were carried out under operating pressure of 7 atm. Reboiler temperature and reboiler duty were changed from 195 to 240 °C and from 1655 to 4150 Watt, respectively. Feed molar ratio between methanol and ethylene carbonate was varied from 4 to 12, while the feed flowrate of ethylene carbonate was changed from 0.056 to 0.148 l/h (0.833 – 2.220 mol/h).

The output product was analyzed using a gas chromatograph (Gow-Mac 550P) equipped with a TCD detector and a Carbowax column (1/8 in. × 2m, Chrom W-HP, 80/100).

Results and discussions

The effect of reboiler temperature is shown in **Fig. 4**. DMC yield decreases with the increase of reboiler temperature in both EC flowrates. The highest DMC yield can be obtained in the reboiler temperature range from 198 – 205 °C. So, for the following experiments we kept reboiler temperature in that range. **Fig. 5** shows the effect of feed molar ratio between methanol and ethylene carbonate. The ratio changes from 4 to 12. It can be seen that DMC yield increases with the increase of feed molar ratio. DMC yield more than 80% can be obtained by molar ratio of 12. Nevertheless, a suitable value should be determined in consideration of energy consumption.

In the reactive distillation column, the top product is generally azeotrope mixture of methanol and DMC, which correspond to a ratio of methanol to DMC of 6.5. So, the feed ratio of the reactive distillation column must be greater than 8.5, because the stoichiometric methanol/EC ratio of the transesterification reaction is 2. Moreover, along the column, from the top to the bottom, methanol/EC ratio changes in a broad range, and close to infinity in the bottom.

Fig. 6 shows the effect of EC flowrate on DMC yield. DMC yield increases with the decrease of EC flowrate. However, the increase of DMC yield with the decrease of EC flowrate from 0.111 to 0.056 l/h is lower than 3%, while the decrease of EC flowrate from 0.148 to 0.111 l/h affects to the increase of DMC yield around 12%. The effect of reboiler duty on DMC yield is shown in **Fig. 7**. DMC yield increases along with reboiler duty and reaches the highest value of around 91% at reboiler duty of 4150 Watt and EC flowrate of 0.056 l/h.

References

- [1] Pacheco, M. A., C. L. Marshall: *Energy & Fuels*, **11**, 2 – 29 (1997)
- [2] Bhanage, B. M., S. Fujita, Y. He, Y. Ikushima, M. Shirai, K. Torii and M. Arai: *Catalysis Letters* **83**, Nos. 3 – 4, 137 – 141 (2002)
- [3] Han, M. S., B. G. Lee, B. S. Ahn, K. Y. Park, and S. I. Hong: *Reaction Kinetics and Catalysis Letters*, **73**, 33 – 38 (2001).
- [4] Knifton, J. F. and R. G. Duranleau: *Journal of Molecular Catalysis*, **67**, 389 – 399 (1991).

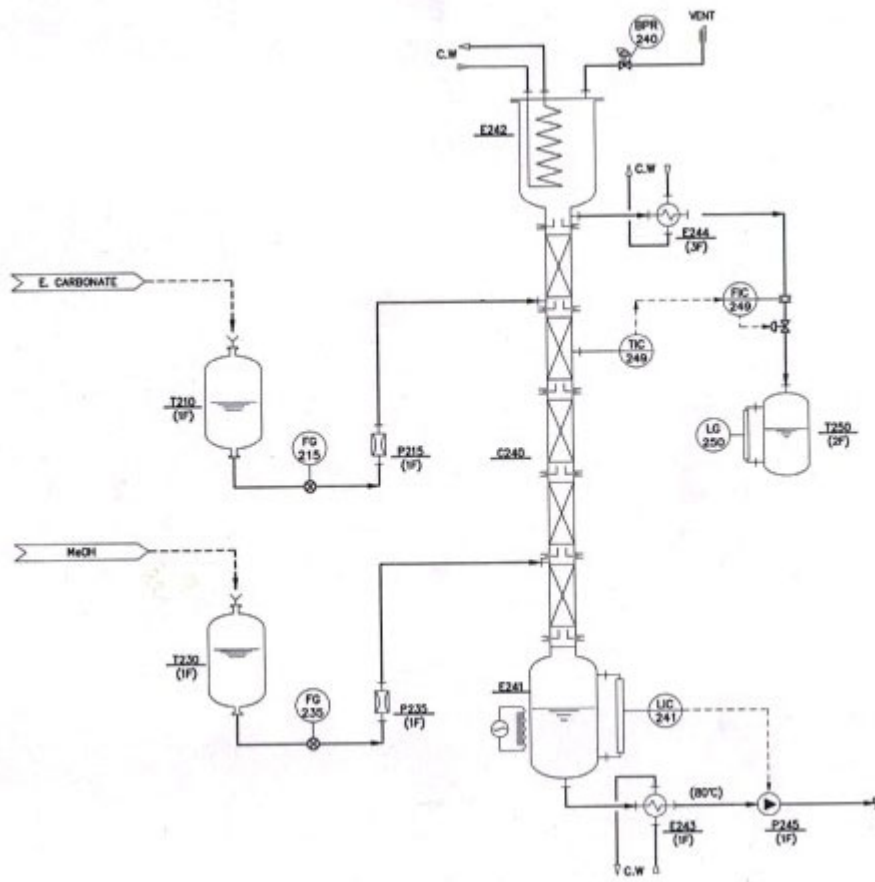


Fig. 1. General scheme of reactive distillation system



Fig. 2. Stainless steel Raschig-ring



Fig. 3. Raschig-ring formed K/MgO catalyst

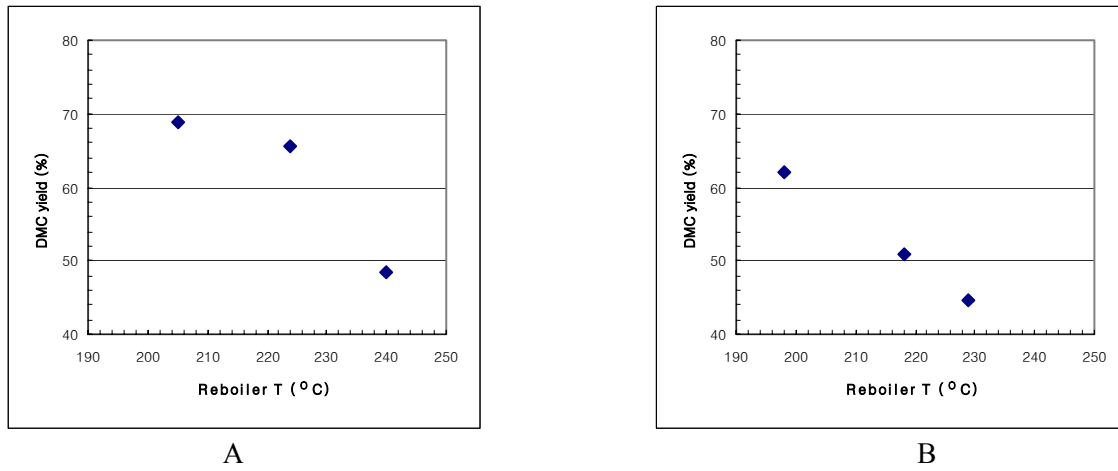


Fig. 4. Effect of reboiler temperature on DMC yield by EC flowrate: A. 0.111 l/h, B. 0.222 l/h

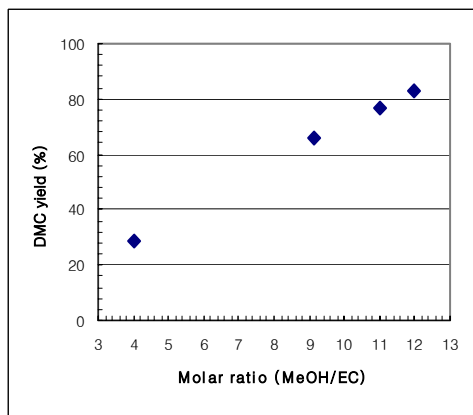


Fig. 5. Effect of feed molar ratio on DMC yield

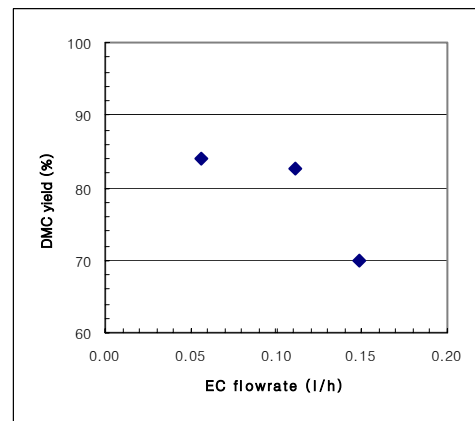


Fig. 6. Effect of EC flowrate on DMC yield

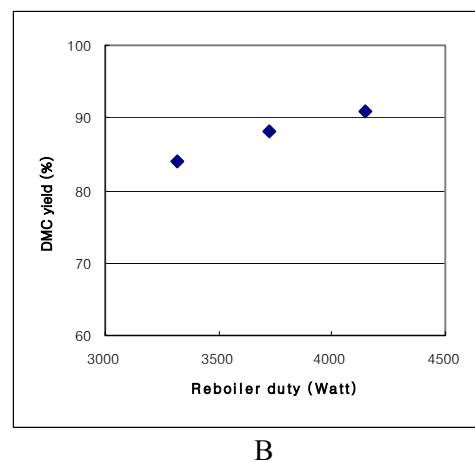
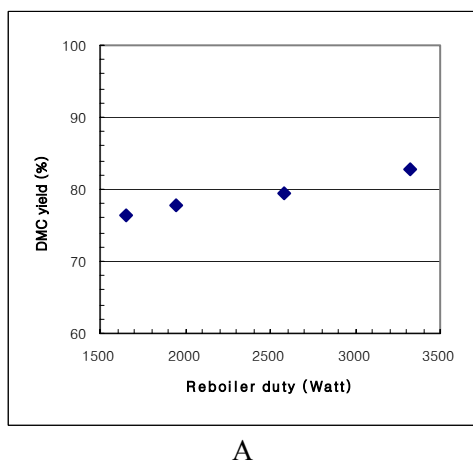


Fig. 7. Effect of reboiler duty on DMC yield by EC flowrate of A. 0.111 l/h, B. 0.056 l/h