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# Analysis of direct synthesis of dimethyl carbonate from methanol and $CO_2$ intensified by in-situ hydration-assisted reactive distillation with side reactor

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ABSTRACT

A reactive distillation (RD) process with a gas-phase side reactor potentially promoted by in-situ hydration is proposed to overcome the thermodynamic restriction of direct synthesis of dimethyl carbonate (DMC) from methanol and $CO_2$. A homogeneous RD model with fixed bed reactor is established in gPROMS platform. The feasibility of the process for direct DMC synthesis is analyzed. The important configuration parameters (e.g., side withdrawal stage and recycle stage) and operating conditions (e.g., reflux ratio and feed ratio) of the RD process are systematically studied. In-situ hydration of ethylene oxide occurring only in the column is introduced for further enhancement. With the process intensification, the conversion of methanol is both improved from approximately 10% in a one-step reactor to 99.5% of RD with and without EO hydration.

## 1. Introduction

Dimethyl carbonate (DMC), a value-added organic carbonate, plays a significant role in chemical industry [1]. DMC is considered as a green solvent and an appropriate alternative for volatile and toxic organic solvents in painting, dyeing, and organic synthesis because of its unique properties, such as low viscosity, low toxicity, and good solvency power [2]. DMC is also regarded as a benign fuel additive for both gasoline and diesel, attributing to its high blending octane number, low Reid vapor pressure, and easy biodegradable ability [3]. Moreover, DMC possesses a variety of functional groups, including methyl, methoxyl, and carbonyl, which promises considerable applications of DMC used as an environmentally friendly building block in many organic synthesis reactions, especially for methylation and carbonylation [4].

Up to now, there have been at least five typical routes to synthesize DMC [5], namely phosgenation of methanol, oxy-carbonylation of methanol, transesterification of ethylene carbonate, transesterification of urea, and carbonylation of methanol. Among them, carbonylation of methanol, also known as direct synthesis of DMC from methanol and $CO_2$, is promising in both gas phase and liquid phase [6], which is a simple way of high atom economy to convert $CO_2$ into value-added products. However, for this reaction, thermodynamic restriction results in low DMC yield [7]. With respect to such reversible reaction producing water, the removal of water has a positive effect on conversion. Consequently, both physical [8–10] and chemical [11–13] dehydrants were widely explored to intensify the reaction.

Although high selectivity and yield have been achieved by liquid-phase reaction in autoclaves with the assistance of dehydrants [14], long residence time and limited reaction space result in low efficiency. For industrial application, continuous production on a large scale is preferred. Reactive distillation (RD) is a highly integrated process that has been successfully applied in many equilibrium-limited reactions [15], e.g., esterification [16], etherification [17], alkylation [18], hydrogenation [19], hydrolysis [20,21], and transesterification [22]. This technology has the potential to overcome chemical equilibrium limitations, improve conversion and yield, improve energy efficiency, and reduce flowsheet complexity [23], which is appealing to the direct synthesis of DMC.

In conventional RD processes, catalysts are soaked with liquid, leading to a reasonable integration of liquid-phase reaction and distillation in one single column [24]. However, the finite internal space of conventional RD column cannot provide enough holdup and sufficient residence time, which is not suitable for reactions of low reaction rate like the direct synthesis of DMC where methanol slowly reacts with $CO_2$ [25]. Moreover, the mild condition of its gas-phase reaction over liquid-phase reaction leads to easier integration with distillation.

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## Nomenclature

| | |
|---|---|
| $a,b,c$ | Binary interaction parameters |
| $B$ | Bottom mole flowrate ($mol \cdot s^{-1}$) |
| $C$ | Heat capacity coefficients |
| $C_{p,m}$ | Mole heat capacity under constant pressure ($J \cdot K^{-1}$) |
| $f$ | Feed mole composition |
| $F$ | Feed mole flowrate ($mol \cdot s^{-1}$) |
| $G$ | Vapor mole flowrate of side streams ($mol \cdot s^{-1}$) |
| $G_m$ | Mole Gibbs free energy ($kJ \cdot mol^{-1}$) |
| $h$ | Number of components |
| $Hm$ | Mole enthalpy ($kJ \cdot mol^{-1}$) |
| $i,j,k$ | Component indexes |
| $j$ | Stage number |
| $J$ | Ratio of product to reactant |
| $K$ | Equilibrium constant |
| $l,q,s$ | Structural parameters of UNIQUAC parameters |
| $L$ | Liquid mole flowrate ($mol \cdot s^{-1}$) |
| $m$ | Tie-line index |
| $n$ | Phase index |
| $N$ | Total number of data points |
| $p$ | Pressure (Pa) |
| $Q$ | Heat exchange on stages (kJ) |
| $r$ | Reaction rate ($mol \cdot s^{-1} \cdot cm^{-3}$) |
| $R$ | Gas constant ($J \cdot K^{-1} \cdot mol^{-1}$) |
| $S$ | Liquid mole flowrate of side streams ($mol \cdot s^{-1}$) |
| $S_m$ | Mole entropy ($J \cdot K^{-1} \cdot mol^{-1}$) |
| $t$ | Time (s) |
| $T$ | Temperature (K) |
| $T_b$ | Boiling point (K) |
| $U$ | Liquid holdup on stages (mol) |
| $V$ | Vapor mole flowrate ($mol \cdot s^{-1}$) |
| $x,y$ | Mole fractions of liquid phase and vapor phase |
| $z$ | Coordination number |

*Greek letters*

| | |
|---|---|
| $\gamma$ | Activity coefficient |
| $\Delta$ | Variation |
| $\Delta f$ | Variation of formation |
| $\Delta r$ | Variation of reaction |
| $\varepsilon$ | Volume of liquid holdup ($cm^3$) |
| $\theta,\tau,\phi$ | Modified UNIQUAC parameters |
| $\Theta$ | Standard status |
| $\nu$ | Stoichiometric coefficient |
| $\chi$ | Conversion |

For the water-containing systems, the hydration of ethylene oxide (EO) yielding ethylene glycol (EG) is regarded as an auxiliary approach for process intensification. Typical example is the separation of ethanol-water azeotrope, realizing high purity of ethanol produced from the top [26]. Notably, the hydration of EO is a non-catalytic liquid-phase reaction [27], which easily takes place in a distillation column and can be used as an auxiliary reaction for RD promotion. It was activated as an auxiliary reaction to reduce the energy consumption in the RD process of ester production [28].

In this work, two process intensification strategies, integrated distillation with gas-phase side reactor and in-situ hydration of EO are used to intensify the direct synthesis of DMC. By using a homogenous RD model with fixed bed reactor in gPROMS platform, the significant configuration parameters and operating conditions of the RD process are optimized considering in-situ hydration of EO. Analysis and comparison are made to highlight the effect of EO hydration.

## 2. Proposed RD process for direct synthesis of DMC from methanol and $CO_2$

The principle of the proposed RD process is shown in Fig. 1. The process integrates a distillation column for separation and EO hydration with a gas-phase side reactor for direct DMC synthesis. Methanol and $CO_2$ are fed to the distillation column, the vapor phase withdrawn from the upper column with stoichiometric reactant of methanol and $CO_2$ is then introduced into the gas-phase side reactor to form DMC, and the output of the reactor flows back to the column.

For the case with EO hydration, it takes place only in the liquid phase of the column. EO is introduced into the system for water removal and fed in between methanol and $CO_2$. The unconverted $CO_2$ gas and methanol distillate are separated from the top of the column; while DMC, water, and the auxiliary product EG are produced at the bottom.

## 3. Analysis model and fundamental

### 3.1. RD model

Equilibrium stage model is a widely used approach for the process analysis and simulation of distillation column with the assumption of constant mole overflow. The combination of material balance, vapor-liquid phase equilibrium, mole fraction of normalization, and heat balance (MESH equations) is used to describe a dynamic equilibrium stage model considering finite reaction rates [29]. The four sets of equations of stage $j$ are readily derived as follows.

The material balance of component $i$ (M equation):

$$\frac{dU_jx_{i,j}}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_jf_{i,j} - (V_j + G_j)y_{i,j} - (L_j + S_j)x_{i,j} + \sum_{i=1}^{h} \nu_i r_j \varepsilon_j \tag{1}$$

The vapor-liquid equilibrium (E equation):

$$y_{i,j} = K_{i,j}x_{i,j} \tag{2}$$

The mole fraction of the normalized equation (S equation):

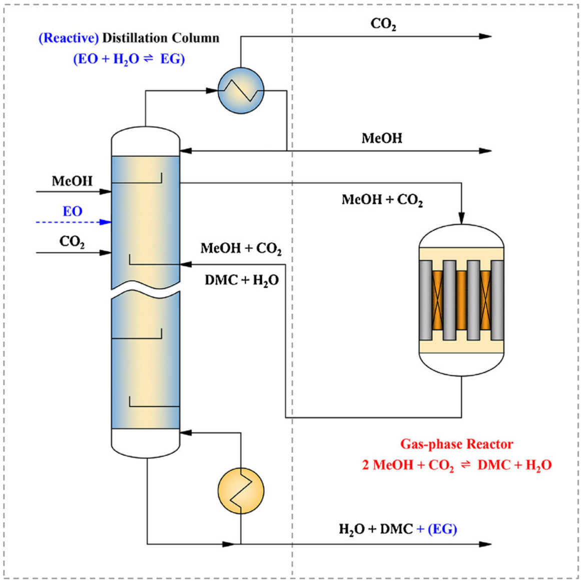

**Fig. 1.** Concept of proposed reactive distillation process.