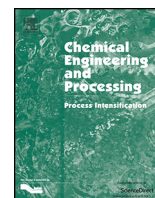




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## Design and control of reactive dividing-wall column for the synthesis of diethyl carbonate



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### ABSTRACT

In this study, dimethyl carbonate (DMC) and ethanol (EtOH) are used to synthesize diethyl carbonate (DEC) by transesterification. In order to have sufficient activity for application in reactive distillation (RD) column, homogeneous catalyst sodium ethoxide is used and can be recycled to reuse. Due to the presence of azeotrope in the reaction system, feed location is discussed and an unusual feed location is used: the heavier DMC feed should be located in the middle of the reaction section, while the lighter EtOH feed should be located at the top part of the reaction section. A conventional RD process is developed and optimized by minimizing the total annual cost (TAC). A reactive dividing-wall column (R-DWC) is also designed with the same number trays, feed conditions and product specifications. The results show that the R-DWC can save 18.7% of the energy consumption and 13.9% of the TAC compared with the conventional RD process. The control structure for the R-DWC is investigated to control the product composition. The proposed control structure can maintain the product purities close to the set point when disturbances in the feed flow rate and feed composition are introduced.

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### 1. Introduction

Diethyl carbonate (DEC), one of the most important carbonates, has been widely used in the chemical industry. Due to the environmental impact, DEC has been regarded as an ideal candidate for methyl *tert*-butyl ether (MTBE) as a promising fuel additive since its oxygen content is higher than that of MTBE [1]. In comparison to two other potential fuel additives, dimethyl carbonate (DMC) and ethanol (EtOH), DEC has a more favorable gasoline/water distribution coefficient [2]. Besides being used as a fuel additive, DEC is mainly used as a solvent for cellulose nitrate, resin, some drugs and intermediate for preparing norfloxacin, a broad-spectrum antibiotic [3]. DEC can also be used as the electrolyte of lithium ion battery [4].

Several chemical routes have been reported for the preparation of DEC: the phosgene route [5], oxidative carbonylation of EtOH [6], the reaction between ethyl nitrite and carbon monoxide [7], and alcoholysis of urea [8]. The drawback of them is either the use of poisonous gases or a low yield of DEC. Thus, we select DMC and EtOH to synthesize DEC by transesterification. The

transesterification reaction is a green process which does not produce pollutants, and has 100% of the atomic utilization. Since the transesterification reaction of DMC and EtOH is a reversible reaction, reactive distillation (RD) technology will be explored in the production of DEC.

RD combines reaction and separation in a single vessel. For many reversible reactions, RD can solve the limitation of chemical equilibrium, and obtain a high conversion. Sundmacher and Kienlev [9] surveyed various industrial applications and strategies in process design of RD. Luyben and Yu [10] listed 236 reactions that can be applied to RD in the Appendix of their book. All of these can indicate the importance and good application prospects of RD.

RD was used to synthesize DEC in previous studies [11,12]. Wei et al. [12] designed a traditional RD process. They used an RD column with DEC as bottom product and then a distillation column was used to separate the excess of ethanol and methanol. They compared the RD process with reaction and then separation process. Furthermore, the dynamic and control aspect of this RD process was studied. The two-column flowsheet can attain DEC and methanol (MeOH) at high purity.

The dividing-wall column (DWC) is a single column shell with a vertical partition wall in it. Due to its advantages of saving energy and capital investment, the DWC has received more and more attention. In recent years, the industrial application of the DWC is

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## Nomenclature

C1	Reactive distillation column
C2	Separation column
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DWC	Dividing-wall column
EMC	Ethyl-methyl carbonate
EtOH	Ethanol
MeOH	Methanol
NF <sub>DMC</sub>	DMC feed location
NF <sub>EtOH</sub>	EtOH feed location
NF <sub>2</sub>	Separation column feed location
NT <sub>n</sub>	Theoretical number of plates for column n
Q <sub>Cn</sub>	Condenser heat removal for column n (kW)
Q <sub>Rn</sub>	Reboiler heat input for column n (kW)
R-DWC	Reactive dividing-wall column
RR <sub>n</sub>	Reflux ratio for column n
SVD	Singular value decomposition
TAC	Total annual cost
K <sub>C</sub>	Gain, %/%
τ <sub>1</sub>	Integral time, min

gradually increasing, and there are about 100 to put into use [13]. Dejanovic et al. [14] gave a complete overview of research and implementation of DWCs based on published papers and patents. Olujić et al. [15] showed several application examples of DWC and Asprión et al. [16] reviewed fundamentals, limitations and recent advances of DWC. DWC usually can offer about 30% cost savings in capital and energy compared to conventional configurations [17].

As the most mature separation technology, distillation occupies a large part of the energy consumption in process industry. Due to the demand of energy saving, many researchers have focused on the process of strengthening. DWC and RD are two typical process intensification techniques. When RD and DWC are combined together, we can form the concept of the reactive dividing-wall column (R-DWC) [18]. Many papers have been published about R-DWC in recent years. Mueller et al. [19] developed a two-step approach to decompose the R-DWC into simple column sequences. Sun and Bi [20] developed a shortcut design method for the design of R-DWC. Kang and Lee [21] introduced a geometric design approach for the integration of reaction and distillation in a heat-integrated wall-divided column. Holtbruegge et al. [22] designed an R-DWC to synthesize DMC and showed that R-DWC can save approximately 35% in total operating cost and TAC compared to the base-case process. Many reactions have also been studied using R-DWC, such as esterification reactions [17,23–25], selective hydrogenation reaction [26], dimethyl ether synthesis [27], formic acid synthesis [28], methyl acetate hydrolysis [29] and transesterification reactions [30–32].

Because of the complex structure of R-DWC, its dynamic control is much more difficult than that of conventional process. There are many articles [33–37] to study the control of RD and DWC. They are helpful to control the R-DWC. Chung et al. [38] compared single-point temperature control and dual-point temperature control. The dynamic performances showed that dual-point temperature control can perform faster and handle throughput disturbances quite well. Ling and Luyben [39] thought there were four control

variables: reflux flow rate, liquid spilt ratio, vapor boil up, and sidestream flow rate in a DWC. They proposed a new control structure to control product compositions and minimize energy consumption simultaneously by manipulating liquid split. A few papers [17,40–42] on the control of R-DWC have been reported in recent years.

In this work, a conventional RD process is developed to synthesize DEC. Excessive EtOH is used in the RD column in order to obtain high-purity products. Then a distillation column is used to recover the excessive EtOH, which is recycled back to the RD column. The conventional RD process will be optimized in terms of total annual cost (TAC). Then an R-DWC is designed to attain products with the same purity. The R-DWC is compared with conventional RD process in terms of energy costs and TAC. At last, the control strategy of the R-DWC is also studied. A control structure for the R-DWC is proposed. Aspen Plus is used in the steady state design process. A rigorous distillation model is used and equilibrium stages are assumed in the steady state simulations. Aspen Dynamics is used in the dynamic control process.

## 2. Kinetic model and thermodynamic model

### 2.1. Kinetic model

The reactions, converting DMC to DEC are two consecutive transesterification reactions with the intermediate product of ethyl-methyl carbonate (EMC). These two reactions can be expressed as follows:



In order to have sufficient activity for application in an RD column, homogeneous catalyst sodium ethoxide is chosen to use in this study. The kinetic equations for these two reversible reactions catalyzed by sodium ethoxide, which can be expressed as follows [43]:

$$r_{R1} = x_{\text{cat}} [1.34 \times 10^{11} \exp(-36530/RT) \alpha_{\text{DMC}} \alpha_{\text{EtOH}} - 1.338 \times 10^{11} \exp(-38480/RT) \alpha_{\text{EMC}} \alpha_{\text{MeOH}}] \quad (3)$$

$$r_{R2} = x_{\text{cat}} [1.8 \times 10^{13} \exp(-54620/RT) \alpha_{\text{EMC}} \alpha_{\text{EtOH}} - 3.08 \times 10^{13} \exp(-53680/RT) \alpha_{\text{DEC}} \alpha_{\text{MeOH}}] \quad (4)$$

where  $r_{R1}$  and  $r_{R2}$  are the rates of the two reactions involved in the transesterification of DMC with EtOH, ( $\text{mol m}^{-3} \text{s}^{-1}$ ),  $\alpha_i$  is the activity of component  $i$  and  $x_{\text{cat}}$  represents the molar fraction of the homogeneous catalyst sodium ethoxide. The  $x_{\text{cat}}$  is set as 0.5%  $\text{mol}^{-1}$ .

### 2.2. Thermodynamic model

The UNIQUAC model is used to describe the phase equilibrium of the reaction system. In this reaction system, some information of the EMC is lacking in Aspen Plus databank. Therefore, EMC needed to be added so that the simulation can be started. The UNIQUAC parameters for ten binary pairs are listed in Table 1 [43]. Table 2 gives calculated azeotropic temperatures and compositions versus the experimental data. The maximal relative errors of azeotropic compositions and temperatures between the predicted values and experimental data are 2.09% and 0.105%, respectively. In addition,

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