

## Design of Diphenyl Carbonate Process via Reactive Distillation Configuration

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This study designed a process for synthesizing diphenyl carbonate (DPC) by using diethyl carbonate (DEC) through reactive distillation (RD). DPC is commercially produced using phosgene, which is highly toxic. Transesterification is a possible alternative for producing DPC by DEC. In this study, two types of reactant excess designs for RD configurations were investigated for obtaining the minimum total annual cost (TAC). Furthermore, the NRTL (non-random two-liquid) model was used to for simulating the thermodynamic behaviours. The overall kinetic mechanism can be divided into two reversible reactions. The purity of DPC and the specification of ethyl acetate (EtAc) were set at 99.5 % for industrial applications. The optimal steady-state design was successfully investigating by applying two configurations. The TAC and energy requirement of excess phenyl acetate configuration were approximately 29.53 % and 9.57 % lower than those of the others.

### 1. Introduction

Polycarbonate (PC) is a durable material with excellent mechanical, optical, electrical, and heat resistance properties. The primary commercial method of PC synthesis is through the interfacial polycondensation of bisphenol A (BPA) and phosgene. However, synthesis using phosgene is not feasible for sustainable development, and the secondary product hydrogen chloride damages the equipment. Diphenyl carbonate (DPC) is a nontoxic and nonpolluting component. Sikdar et al. (1987) revealed that the transesterification of DPC and BPA provides a phosgene-free route for PC synthesis. Consequently, DPC synthesis gained impetus as an alternative precursor to PC production because of the aforementioned environmental and economic advantages.

Kim et al. (2004) prepared DPC by transesterifying dimethyl carbonate (DMC) and phenol; however, this reaction has some drawbacks. First, the equilibrium constant for the transesterification of DMC and phenol to the intermediate methyl phenyl carbonate and the by product methanol is only  $3 \times 10^{-4}$  at 180 °C (Tundo et al., 2002). Therefore, transesterifications are thermodynamically unfavourable, have a low yield, and are sensitive to DPC. Second, DMC and methanol form an azeotrope and require more distillation columns for separation. Third, side reactions such as methylation, which forms methyl phenyl ether, can occur in the reaction between DMC and phenol. To avoid these drawbacks, diethyl carbonate (DEC) and phenyl acetate (PA), and not DMC and phenol, were used in our study for producing DPC and the by product ethyl acetate (EtAc). The benefits of this DPC synthesis method include a higher equilibrium constant and the lack of azeotropes and side reactions. According to our review of relevant literature, until date, no study has proposed a DPC synthesis method involving a reaction between DEC and PA. Ryu (2013) reported DPC production by reacting DEC with phenol. The advantages of producing DPC by DEC include the low energy and material input for constructing a plant. The overall equation is shown as Eq(1). This process eliminates the requirement for a solvent-based extractive distillation, which is commonly required for producing DPC from DMC.



Reactive distillation (RD) is an extensively studied intensification method. Taylor and Krishna (2000) and Karacan et al. (2014) have reported the advantages of RD, which include improved selectivity, increased conversion, optimal heat control, effective utilization of reaction heat, scope for difficult separation, and no azeotrope formation. The reaction of DPC and PA is a typical equilibrium limit reaction. Therefore, RD was operated with excess reactant in this study for improving the resultant DPC. Two approaches were used for obtaining excess reactants in the RD column of the DPC synthesis process: excess PA and excess both DEC and PA. In this study, optimal plan-twide processes using excess quantities of reactants were designed and evaluated. The optimum operating condition of each plan-twide RD process was studied for minimizing the total annual cost (TAC). By using the same level of product purity, an optimal plant-wide RD process can be obtained by the minimum TAC.

The thermodynamic and reaction kinetic models are presented in Section 2. The design of RD processes with excess DEC or PA reactant for producing high-purity products are described in Section 3. The conclusions are provided in Section 4.

## 2. Thermodynamic and reaction kinetic models

In the optimal design of RD processes, the effects of chemical reaction and phase equilibrium on the entire system must be considered.

### 2.1 Kinetic model

Lin (2014) reported DPC synthesis and its overall kinetic mechanism, which can be divided into two parallel-series and reversible reactions, and titanium (IV) ethoxide was used as the homogeneous catalyst. The entire reaction is divided into two steps. The first step involves the transesterification of DEC and PA into ethyl phenyl carbonate (EPC) and EtAc Eq (2), and the second step involves the transesterification of EPC and PA into DPC and EtAc, as shown in Eq(3).



Table 1: Kinetic parameters of synthesis (Lin, 2014)

	$k_0$ (l/min.mol)	$E_a$ (kJ/kmol)	AARD
$k_1$	$1.691 \times 10^7$	83,973.9	
$k_{-1}$	$3.708 \times 10^2$	46,960.6	
$k_2$	$1.467 \times 10^3$	49,979.9	0.93 ~5.13 %
$k_{-2}$	6.146	22,675.9	

Eq(4) and Eq(5) are the reaction rate expressions used in Aspen Plus. The Arrhenius Eq(6) is used for describing the reaction rate constant. The kinetic parameters are presented in Table 1. And their absolute average relative deviation (AARD) to conversion of experiment data is between 0.93 ~ 5.13 % from the result of Lin (2014).

$$r_1 = k_1 C_{DEC} C_{PA} - k_{-1} C_{EPC} C_{EtAc} \quad (4)$$

$$r_2 = k_2 C_{EPC} C_{PA} - k_{-2} C_{DPC} C_{EtAc} \quad (5)$$

$$k_j = k_0 e^{-E_a/RT} \quad (6)$$

### 2.2 Thermodynamic model

Before designing the process configuration, thermodynamic properties must be considered. In this study, we used five components: DEC, PA, EPC, EtAc, and DPC. Ho (2014) also used similar components: DEC-PA, DEC-EtAc, DEC-DPC, PA-EtAc, PA-DPC, and EtAc-DPC. Moreover, the NRTL model and binary parameters by ASPEN Plus were applied for simulating the thermodynamic behavior from data of the aforementioned study. However, no experimental data are present on other binary components, such as DEC-EPC, PA-EPC, EPC-EtAc, and EPC-DPC; therefore, the thermodynamic properties of the UNIFAC estimation can be referred to. After designing the thermodynamic model, the pure boiling points of components were calculated by the extended Antoine equation Eq (7); the parameters of this equation are

shown in Table 2. The boiling points of all components in this process are ranked in the ascending order in Table 3. No azeotropes were formed in the DPC synthesis process.

$$\ln P_i^* = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{C_{7i}} \quad (7)$$

Table 2: Parameters of the extended Antoine equation for each component

	DPC	EPC	PA	EtAc	DEC
C <sub>1i</sub>	82.8987	73.27864	79.78307	55.31107	197.6371
C <sub>2i</sub>	-12,708.4	-10,573.6	-10,074	-6,227.6	-12,732
C <sub>3i</sub>	0	0	0	0	0
C <sub>4i</sub>	0	0	0	0	0
C <sub>5i</sub>	-9.57617	-8.44466	-9.4831	-6.41	-28.31
C <sub>6i</sub>	1.74×10 <sup>-18</sup>	2.83×10 <sup>-18</sup>	3.87×10 <sup>-18</sup>	1.79×10 <sup>-17</sup>	2.93×10 <sup>-5</sup>
C <sub>7i</sub>	6	6	6	6	2

Table 3: Boiling point of DPC production process

Component	B.P. (at 1 atm)
EtAc	77.20 °C
DEC	126.82 °C
PA	195.67 °C
EPC	239.49 °C
DPC	302.00 °C

### 3. Process layout analysis and cost estimation

The reaction kinetics yielded two chemical reactions, which may require more than one RD column depending on the properties of the equilibrium constant and reaction rates. Consequently, at least two RD columns should be used for obtaining DPC and EtAc under specifications. By contrast, the approximate molar ratio of the two reactants PA and DEC should be 2:1 for the overall stoichiometric balance in the process. Therefore, PA and DEC were supplied at 10 and 5 kmol/h, and the purity of DPC and EtAc were set at 99.5 % for industrial usage. The objective function for the process design is based on the TAC, which includes the operating and annualized capital costs. The operating cost includes the steam for the reboiler, cooling water for the condenser, catalyst cost, and operating cost for the compressor. For estimating the catalyst cost, the unit price was assumed to be 7.7 US\$/kg and was revised every three months. The assumed capital charge factor for three years is presented in Eq(8). A detailed cost calculation is provided in Appendix E of Douglas (1988) and a sequential optimization method is used from Tang et al. (2005).

$$\text{TAC} = \text{TAC}_{\text{operating}} + \text{TAC}_{\text{capital}}/3 \quad (8)$$

Two possible design configurations, involving excess PA and DEC, were used for the RD column. A reactant excess design reveals an excess of one reactant in the RD column. However, the ratio of the overall reaction is stoichiometrically balanced in the entire process. Aspen Plus was used as the process simulator in this study.

#### 3.1 Configuration 1: The PA excess design

As presented in Figure 1, the last distillation column (CD) is used for separating the EtAc collected at the top and the unreacted PA at the bottom. The purity of the unreacted PA is set at 99.9 mol% for recycling it to the first and second RD columns (hereafter referred to as RD1 and RD2). If the PA/DEC molar ratios in both RD columns are more than 2, this design is called the PA excess reactant design.

In total, RD1 involves 75 stages, and reactions occur in stages 5-75. In RD1, the heavier fresh PA and recycled PA from the bottom of the CD are fed into stage 5, and lighter fresh reactant DEC are fed into stage 66. Furthermore, for RD1, the distillate specification of EtAc is set at 99.5 mol% and that of the DEC remaining at the bottom is set at 0.01 mol% to be fed into RD2. The stream, which contains 7.9 mol% of the intermediate component EPC from the bottom of the RD1 is fed into the stage 14, and the lighter component PA from the bottom of the CD is fed into the stage 20 for the conversion of EPC to DPC in RD2. RD2 includes a total of 25 stages, with reactions occurring in stages 14-25. In RD2, the purity of the EPC distillate is set at 0.01 mol% to be fed into CD and that of the DPC from the bottom of RD2 is set at 99.5 mol%. Moreover, CD is used for separating the main products EtAc and PA. CD includes 10 stages,

and feed is used in stage 5. The purity of the EtAc distillate is set at 99.5 mol%. The splitting ratio of the flow rate of the PA at the CD bottom to RD1 and RD2 is a critical variable for the reactions in both RD columns. The reflux ratio and reboiler duties of all columns are presented in Table 4.

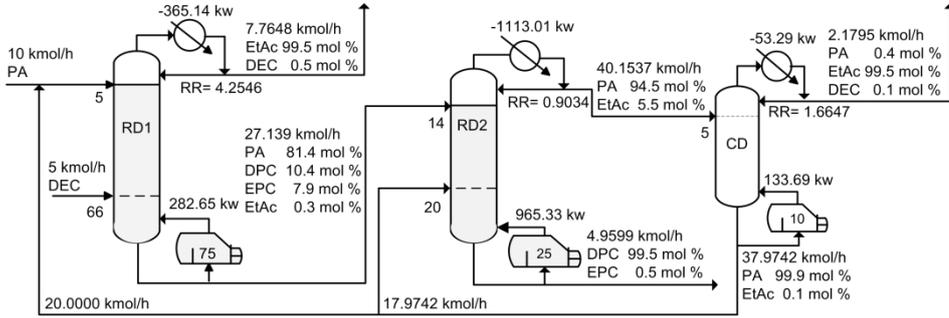


Figure 1: Flowsheet of configuration 1

Table 4: Reflux ratio and heat duties of reboiler for configuration 1

	RD1	RD2	CD
Reflux Ratio	4.2546	0.9034	1.6647
Heat Duty (kw)	282.65	965.33	133.69

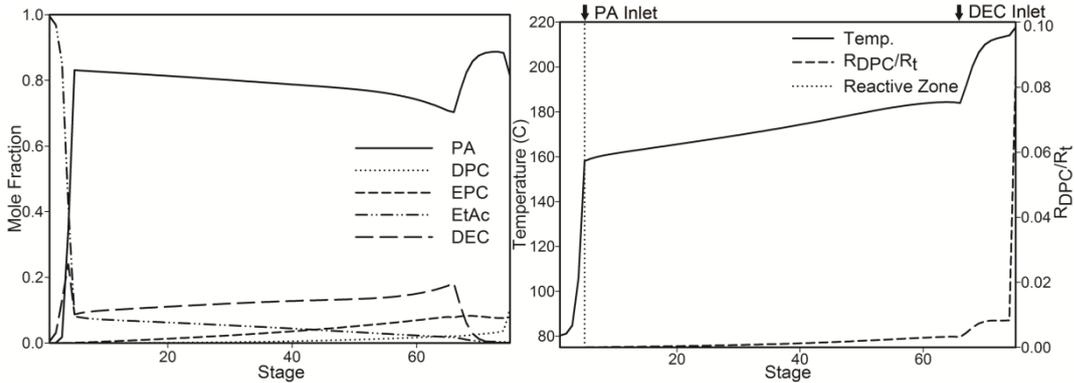


Figure 2: Composition and temperature profiles of the RD1 of configuration 1

The liquid composition and temperature profiles for both RD1 and RD2 are shown in Figures 2 and 3. The dashed line in Figure 2 and 3 represents the DPC reactive ratio, which represents the DPC production rate in each stage divided by the overall production rate in RD1. Stage 75 revealed the highest reactive ratio, implying that most reactions occurred in stages. Higher compositions of both PA and DEC (Figure 3) induced a higher reaction rate because of the second order reaction, as shown in Eq(2) and Eq(3).

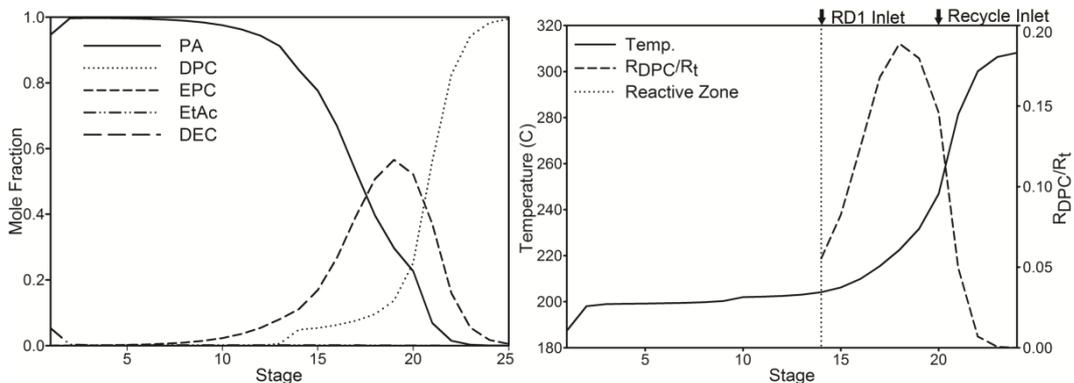


Figure 3: Composition and temperature profiles of the RD2 for configuration 1

### 3.2 Configuration 2: Both DEC and PA excess designs

As shown in Figure 4, in Configuration 2, the reactant PA was fed through two inlets: 8.5 and 1.5 kmol/h into RD1 and RD2. PA was fed in the top and bottom streams of RD1. The top stream of RD1 contained only EtAc and unreacted DEC, which were then fed into CD1 for separation. The separated product was obtained at the top of CD1, and heavier DEC was recycled to RD1 from the bottom of CD1. Furthermore, the flow rate of fresh DEC was set at 5 kmol/h. A molar ratio of PA/DEC less than the overall stoichiometric condition is considered as the DEC excess reactant design for RD1. The bottom of RD1 contained heavy components, EPC and DPC, which were fed to RD2 for further reaction. DPC having a purity of 99.5 mol % was observed in the bottom of RD2. The unreacted PA and EtAc at the top of RD2 were fed to CD2 for separation. The EtAc product was obtained at the top of CD2, and the unreacted PA obtained from the bottom of CD2 was recycled to RD2. The molar ratio of PA/EPC was observed to be more than the stoichiometric balance value of the second reaction. The feed condition of RD2 is called the both DEC and PA excess reactant design.

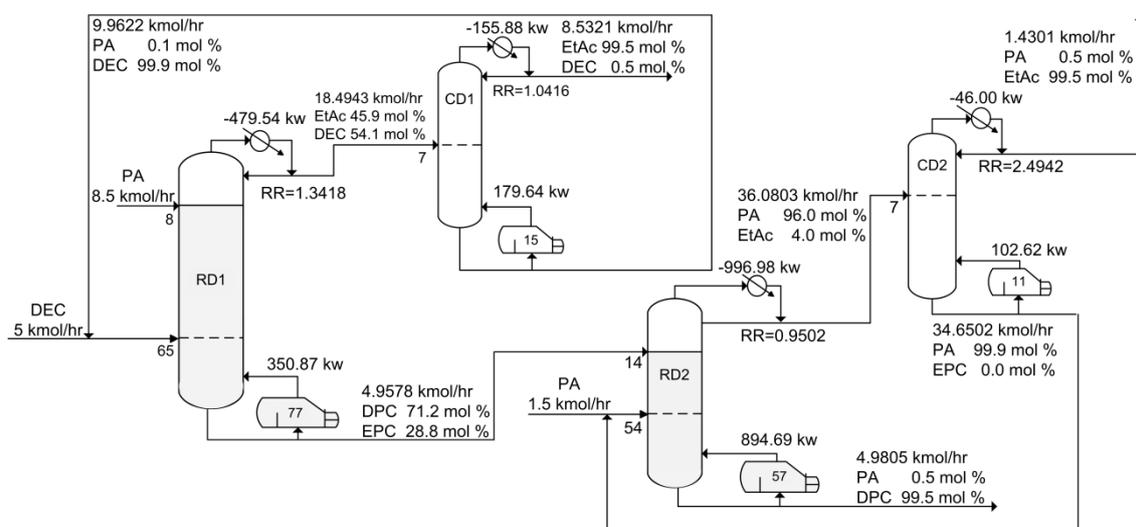


Figure 4: Flowsheet of configuration 2

The optimal result of this configuration obtained through the optimization process is depicted in Figure 4. In RD1, lighter DEC and recycled DEC stream were fed into stage 65, and heavier PA was fed into stage 8. In total, RD1 includes 77 stages, and reactions occur in stages 8 - 77. The PA component was consumed in the first reaction. Therefore, the purity of the distillate and bottom compositions of PA was set at 0.01 mol%. The distillate of the RD1 is sent to the CD1, and the bottom flow is sent to RD2. The total stage number of CD1 is 15, a stream connects to stage 7 from the distillate of RD1. The CD1 distillate specification of EtAc was set at 99.5 mol%, and DEC from the bottom stream was recycled to RD1, with the purity set at 99.9 mol% for combining with the fresh DEC. For the RD2, the fresh PA with the recycle stream which from the CD2 feeds into stage 54, and the other inlet from the bottoms flow of RD1 feed into stage 14. In total, there are 57 stages, and reactions occur in stages 14-57. CD2 has 11 stages and stage 7 is the feed location. The reflux ratio and reboiler duties of all columns are listed in Table 5.

Table 5: Reflux ratio and heat duties of reboiler for configuration 2

	RD1	CD1	RD2	CD2
Reflux Ratio	1.3418	1.0416	0.9502	2.4942
Heat Duty (kw)	350.87	179.64	894.69	102.62

The liquid composition, temperature profiles, and reactive ratio of DPC for RD1 and RD2 in the configuration are shown in Figures 5 and 6. The dashed line in Figures 5 and 6 represents the DPC reactive ratio. The highest reactive ratio was observed in stage 69 for RD1. In contrast to RD1, in RD2, two peaks of reactive ratio were observed on stage 14 and 52 (Figure 6).

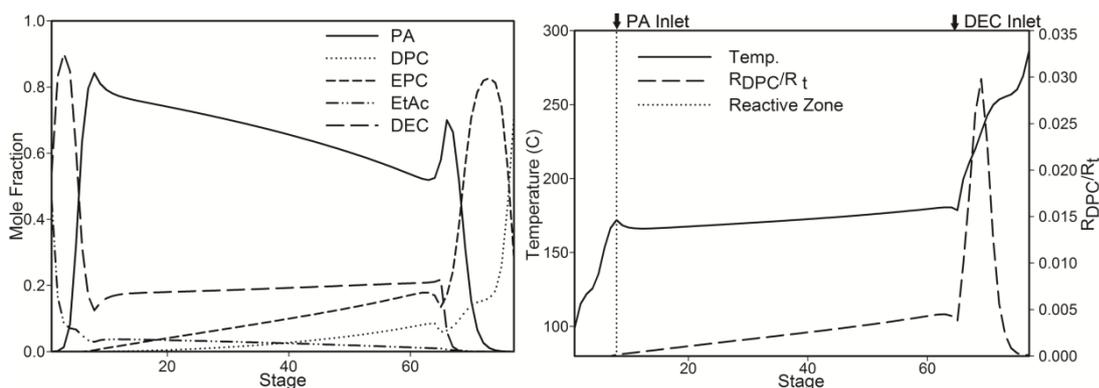


Figure 5: Composition and temperature profiles for the RD1 for configuration 2

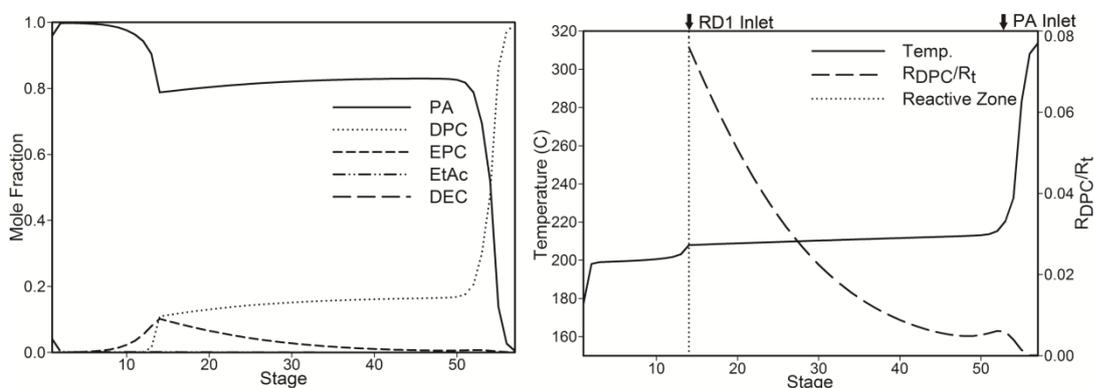


Figure 6: Composition and temperature profiles for the RD2 for configuration 2

#### 4. Conclusions

In this study, the optimal designs of the two configurations of the DPC synthesis process through RD were studied. Both DPC and EtAc satisfied the product specification set at 99.5 mol% for industrial usage. Both configurations were optimized by minimizing their TAC. Furthermore, results revealed that the total reboiler duty of configurations 1 and 2 were approximately 1,381.67 and 1,527.82 kW. The TAC of configurations 1 and 2 were approximately US\$1,344,473 and US\$1,907,917. The process simulation results revealed that the energy requirement and TAC of configuration 1 are less than approximately 9.57 % and 29.53 % for configuration 2.

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