

# Innovative Design of Diphenyl Carbonate Process via One Reactive Distillation with a Feed-Splitting Arrangement

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This paper proposes an innovative design for diphenyl carbonate (DPC) synthesis using dimethyl carbonate (DMC) and phenyl acetate (PA) as reactants. DPC synthesis is an environmentally-friendly method for polycarbonate production and avoids the use of highly toxic phosgene. DPC production is a two-step and reversible reaction. An ideal model was established to simulate the thermodynamic behaviour. Kinetic parameters were chosen by the previous paper. The excess reactant design was used for the reaction mechanism in their research, and a thermal coupling arrangement was implemented to improve the conventional process design. However, this paper proposes an even newer design, delivering an equivalent performance with lower operating costs and energy requirements. The specifications for the product DPC and by-product methyl acetate (MA) were set as 99.5 mol % for industrial usage, and the optimal configuration of the DPC process was determined according to the minimum total annual cost (TAC). Compared with the results determined by Cheng et al. (2013), the proposed design reduced energy consumption by 59.54 % for condenser duty and by 71.07 % for reboiler duty, resulting in a 57.99 % lower TAC.

## 1. Introduction

Polycarbonate (PC) is a general plastic raw material widely used in the optical, automotive, electronics and chemical industries. Diphenyl carbonate (DPC) is a necessary precursor for PC production. The conventional process for manufacturing DPC uses phosgene and bisphenol-A as reactants and dichloromethane as the solvent. For environmental protection considerations, a phosgene-free process was presented by Sikdar (1987). In addition, Kim et al. (1999) reported a transesterification reaction from dimethyl carbonate (DMC) that offers a green route to generate DPC. Therefore, the transesterification reaction has attracted extensive attention in recent years.

Beckhaus (1921) published a reactive distillation (RD) concept that was largely ignored. Later, Agreda and Partin (1984) developed a methyl acetate (MA) homogeneous RD system by reforming the traditional multi-unit process into an RD system. Thus, RD has become an increasingly important topic since 1984. RD studies have focused on discussing system phenomena (Barbosa and Doherty, 1988) and steady-state analysis (Kaymak and Luyben, 2004). Steady-state multiplicities often appear in RD design (Ciric and Miao, 1994). In addition, Malone and Doherty (2000) explored RD steady-state design and comprehensively described recent studies. During the past few years, numerous studies have been published on feed-splitting. Jan (2006) investigated an n-butyl propionate process with feed-splitting, Lee et al. (2010) detailed a feed-splitting strategy with RD in butyl propionate synthesis.

The objective of the present study was to simulate a DPC process using a single RD column with a feed-splitting arrangement. The remainder of this paper is structured as follows. Thermodynamic and kinetic models are presented in Section 2, and a transesterification reaction from DMC to produce DPC using an RD design with the feed-splitting is explained in Section 3, including the optimal configuration determined according to TAC and the requirement of high-purity products and by-products. Section 4 presents concluding remarks concerning the entire DPC process.

## 2. Thermodynamic and kinetic models

### 2.1 Thermodynamic model

The ideal model for the DPC process, with phase equilibrium data from Yao (2012), is described as follows. The Antoine equation, presented in Eq(1), was used to derive the vapour pressure of each component; its parameters are described in Cheng et al. (2013), and they are presented in Table 1. In addition, the simulation results revealed no azeotropic point and no two-phase region in the residue curve maps. Table 2 orders the components according to their boiling points.

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

Table 1: Parameters of the Antoine equation for each component

	MA	DMC	PA	MPC	DPC
C <sub>1i</sub>	49.74	46.51	79.77	18.61	82.89
C <sub>2i</sub>	-5618.6	-5991.3	-10074	-10121.3	-12708.4
C <sub>3i</sub>	0	0	0	0	0
C <sub>4i</sub>	0	0	0	0	0
C <sub>5i</sub>	-5.65	-5.10	-9.48	-7.82	-9.58
C <sub>6i</sub>	2.1E-17	1.34E-17	2.84E-18	2.54E-18	1.74E-18
C <sub>7i</sub>	6	6	6	6	6

Table 2: Components ranked in ascending order of boiling point

Component	Boiling point (°C)
MA	57.1
DMC	90.2
PA	195.7
MPC	234.7
DPC	302.0

### 2.2 Kinetic model

DPC production is a two-step reversible reaction. The kinetic parameters were established following Cheng et al. (2013). Tetra-n-butyl orthotitanate (Ti (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) is a homogeneous catalyst in this process, which involves five other components: the reactants DMC and phenyl acetate (PA), the intermediate methyl-phenyl carbonate (MPC), the product DPC, and the by-product MA. In the first-step of the reaction, presented in Eq(2), DMC reacts with PA to form MPC and MA. In the second step, presented in Eq(3), the MPC and PA transesterification reaction produces DPC and MA. The overall reaction is presented in Eq(4).



The overall reaction:



The reaction rates of the DPC process are provided in Eq(5) and Eq(6), where  $k_1$  and  $k_2$  are the forward reaction constants and  $k_{-1}$  and  $k_{-2}$  are the reverse reaction constants. In addition, the Arrhenius equation (Eq(7)) describes the equilibrium constant of the reaction rate. The kinetic parameters of the DPC process are listed in Table 3. Notice that  $E_a$  is activation energy and  $k_0$  is pre-exponential factor.

$$r_1 = k_1 C_{DMC} C_{PA} - k_{-1} C_{MPC} C_{MA} \quad (5)$$

$$r_2 = k_2 C_{MPC} C_{PA} - k_{-2} C_{DPC} C_{MA} \quad (6)$$

Arrhenius equation:

$$k_j = k_0 e^{-E_a/RT} \quad (7)$$

Table 3: Kinetic parameters of the DPC process (Cheng et al., 2013)

	$k_0$ (m <sup>3</sup> /kmol·s)	$E_a$ (kJ/kmol)
$k_1$	135	54200
$k_{-1}$	52	54900
$k_2$	1210	61500
$k_{-2}$	611	56200

### 3. Process flowsheet

This section is divided into two parts. The first part describes previous work on DPC process and compares the conventional process with the heat integration process (Cheng et al., 2013). The second part presents a new design for DPC process, based on the boiling point ranking of the components.

#### 3.1 Conventional RD process and thermal coupling design

On the basis of the kinetic parameters, the design involves multiple columns. Cheng et al. (2013) designed a process with one RD column (C1) and one separation column (C2), with excess DMC in the RD section. Figure 1 compares the conventional design (Figure 1(a)) with the thermally coupled configuration of the DPC process (Figure 1(b)). The thermal coupling design removes the condenser at the top of the RD column, sending the steam instead to the distillation column (C2) instead. Subsequently, the side stream is extracted from C2 for RD. This heat integration method can eliminate the remixing effect and save 24.5 % of the energy consumption of the total reboiler duty compared with the conventional design.

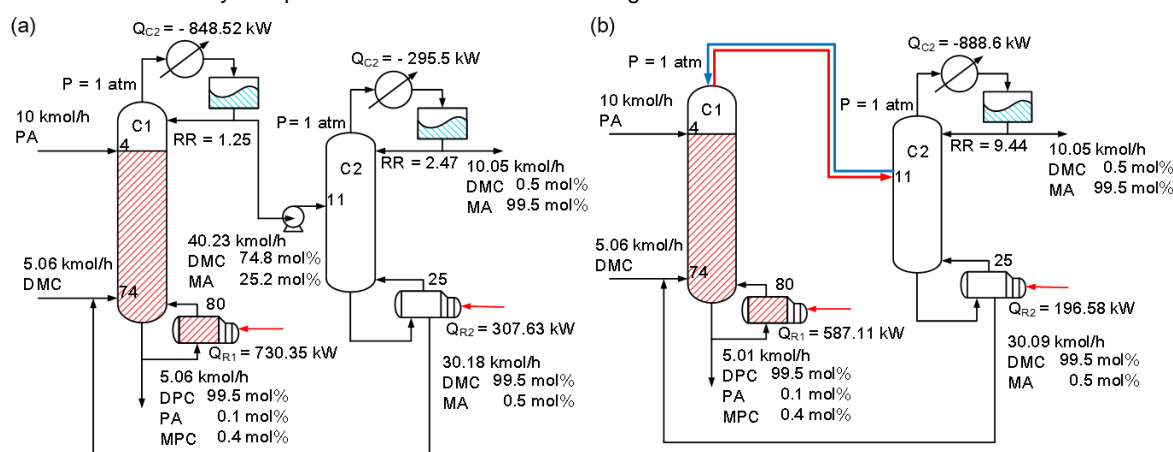


Figure 1: Comparison of DPC flowsheet designs: (a) conventional (b) thermally coupled (Cheng et al., 2013).

#### 3.2 Proposed design

This paper presents a design that delivers performance equivalent to the two aforementioned designs, but with lower costs and more efficient use of energy. This is achieved by using a feed-splitting arrangement to adjust the molar flow rate. According to the boiling point ranking, the first PA inlet stage must be set above the DMC inlet stage because DMC has a lighter boiling point than PA; therefore, PA would move downwards and DMC would move upwards. The first-step of the reaction occurs at the top section of the reactive zone to generate MPC and MA. Although MPC is a heavier component than PA. To achieve a counter-current flow for the reactants in the second-step of the reaction, the second PA inlet stage was positioned at the lower section of the reactive zone to produce DPC and MA. Hence, high-purity MA and DPC could be obtained and drained from the top and bottom of the RD column, respectively.

The Aspen Plus V8.6 simulation software was used to propose a new configuration to achieve 99.5 mol % DPC and 99.5 mol % MA for industrial uses through a single RD column with a feed-splitting arrangement. This process involved seven design variables, which are shown in Figure 2(a), namely the total number of stages ( $N_T$ ), number of reactive stages ( $N_{rxn}$ ), column pressure ( $P$ ), split ratio ( $SR$ ) of the PA feed, first PA feed stage ( $NF_{1PA}$ ), second PA feed stage ( $NF_{2PA}$ ), and DMC feed stage ( $NF_{DMC}$ ).  $SR$  was defined as first PA feed flow rate over the total PA feed flow rate.

The catalyst tetra-n-butyl orthotitanate was used in its liquid phase; its boiling point is higher than the other components in this process. This homogeneous catalyst moves downwards with gravity. Because the temperature in stage 71 was higher than the catalyst's decomposition temperature, it was presumed that no reaction would occur from stage 71 to the final RD stage. This system is illustrated in Figure 2(b).

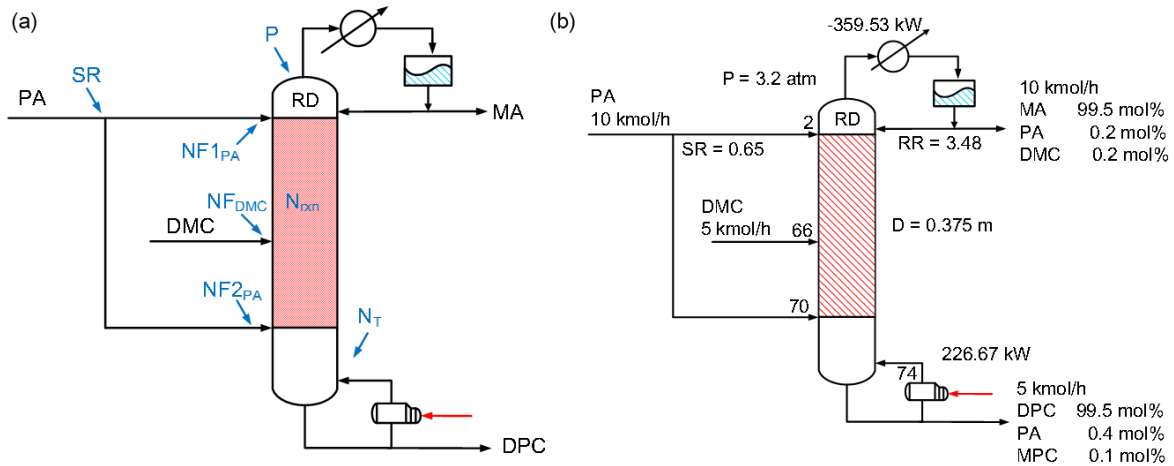


Figure 2: (a) Design variables of proposed DPC process (b) Flowsheet of proposed DPC process.

RD involved 74 stages in total. The reactive section was from stage 2 to stage 70. In the RD process, the fresh PA stream was set as 10 kmol/h and split into two streams: the first PA feed stage (NF<sub>1PA</sub>) and the second PA feed stage (NF<sub>2PA</sub>). NF<sub>1PA</sub> was fed in stage 2 and NF<sub>2PA</sub> in stage 70. The SR was set as 0.65 to maintain a suitable mole fraction for the feed before it enters to RD. Overall, the ratio of PA to DMC was 2:1; therefore, the flow rate of DMC was set as 5 kmol/h, and DMC was fed in stage 66. The first stage of the transesterification reaction occurred in the upper portion of the reactive section, and the second stage occurred in the bottom portion. According to the boiling points, MA is the lightest component in this system. Thus, MA moves upward and drains from the top of the column. By the same principle, DPC drains from the bottom because it is the heaviest component.

Figure 3 presents the composition and temperature profile of the proposed design. In this study, the main purpose of RD was to complete the two transesterification reactions and generate DPC. In other words, DMC was consumed in the upper reactive section because of the first-step of the reaction occurs in the top of the RD column, whereas PA reacted in the centre of the column. Therefore, the mole fraction of PA had a downward trend in the centre of the column. The PA mole fraction tended to increase in the bottom portion of column because of the PA stream that was fed during stage 70. In addition, MPC exhibited a slight increase in the bottom column due to its higher boiling point. Furthermore, MPC and PA reacted at the bottom of the reactive zone. Following the same pattern, MA decreased from the top to the bottom of the RD column. By contrast, DPC rapidly increased at the bottom of the composition profile. Figure 3(b) indicates that the temperature gradually increased from the top to the bottom of the RD column.

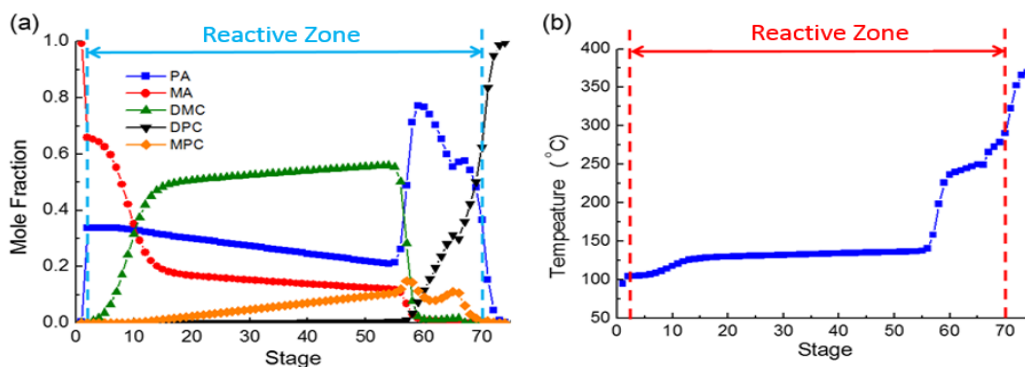


Figure 3. (a) Composition profile of proposed design. (b) Temperature profile of proposed design.

In the proposed design, the pressure of the RD column was slightly higher than atmospheric pressure. As shown in Figure 4(a), the process resulted in a lower TAC when the operating pressure was lower. However, to meet the specifications for both DPC and the MA by-product, the minimum operating pressure of the RD column is 3.2 atm. Figure 4(b) indicates that the DPC specification was fixed according to the reboiler duty; however, at lower operating pressures, the mole fraction of MA did not reach 99.5 mol % in spite of an increasing reflux ratio.

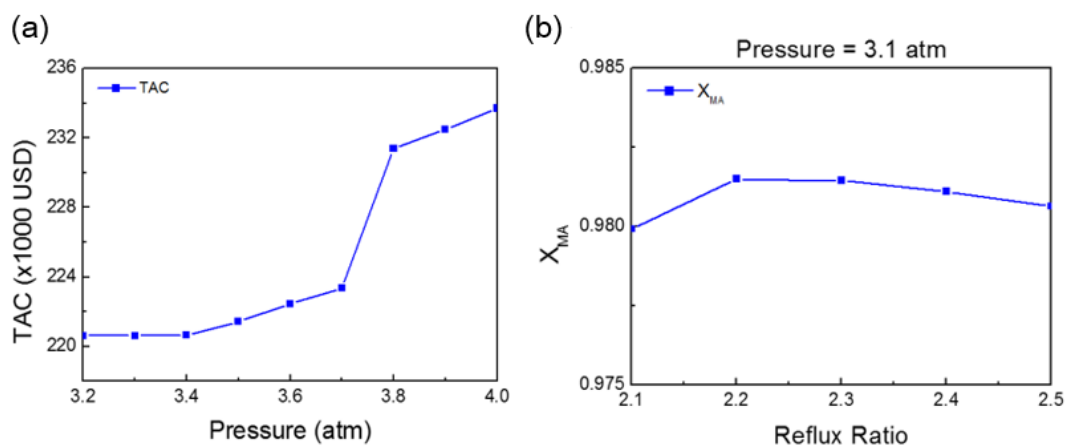


Figure 4: (a) Relationship between TAC and operating pressure. (b) Relationship between MA concentration and reflux ratio at an operating pressure of 3.1 atm.

The optimal configuration was determined by the total annual cost (TAC), which is defined in Eq(8). The formula for calculating TAC was taken from Douglas (1988) and the energy price was obtained from Turton et al. (2009). The specification for high-purity products and by-products was fixed at 99.5 mol % for industrial usage during optimization. This study assumed the payback period of 3 years. The TAC involves two parts, namely the equipment and the operating costs, including the steam use in the reboiler, the application of cooling water, and the catalyst.

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

Table 4 compares the DPC processes. Compared with the energy use of the design by Cheng et al. (587.11 kW and 196.58 kW for the single RD and single distillation column, respectively), the proposed design only used 226.67 kW, providing a 71.07 % energy saving. This resulted in a TAC of  $\$2.187 \times 10^5$ , a saving of 57.99 % compared with the TAC of the other design ( $\$5.207 \times 10^5$ ).

Table 4: Comparison of DPC processes.

	Cheng et al. (2013)		This study	Savings
	C1	C2	RD	
The total number of stages	80	25	74	
Number of reactive stages	75	--	69	
Reflux ratio	--	9.44	3.48	
Condenser duty (kW)	0	-888.6	-359.53	59.54%
Reboiler duty (kW)	587.11	196.58	226.67	71.07%
TAC	$\$ 5.207 \times 10^5$		$\$ 2.187 \times 10^5$	57.99%

#### 4. Conclusions

Effective DPC processes have been the focus of numerous studies in recent years. Several researchers have investigated technologies concerning the heat integration of DPC production, most notably Cheng et al. (2013), who demonstrated that a thermally coupled design is more effective than a conventional design for the DPC process. This paper presents an innovative design for synthesizing DPC that offers an environmentally-friendly method for PC production by using RD and a feed-splitting arrangement.

This study produced two major contributions. First, the proposed design combines single RD column and a single distillation column into one RD column. In contrast to Cheng et al. (2013), no remixing effect was observed in the proposed design. Second, the proposed system was observed to deliver equivalent performance

compared with those of previous studies with energy savings of 59.54 % for condenser duty and 71.07 % for the reboiler duty. This could reduce the TAC by approximately 58 %.

### Acknowledgments

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