Abstract—This study investigated the energy-saving design and control of diphenyl carbonate (DPC) reactive distillation (RD) process by using phenyl acetate (PA) and diethyl carbonate (DEC) through a thermally coupled arrangement. A thermally coupled arrangement eliminates the remixing effect and reduces the total energy. Two cases of DPC synthesis through RD configuration have been discussed in a previous study. However, a remixing effect can be observed between the RD and separation columns through composition profile analysis. To decrease the total heat duty, the remixing effect must be eliminated. This paper presents two cases of the proposed thermally coupled arrangement. After reducing the total heat duty through thermal coupling, the minimum TAC was determined in order to implement dynamic control. The product DPC as well as the byproduct EtAc was met the industrial specifications by temperature controller under the ±10% throughput and −5%, −10% composition disturbances.

I. INTRODUCTION

Diphenyl carbonate (DPC) is a nontoxic and nonpolluting precursor in polycarbonate (PC) synthesis. Sikdar (1993) proposed a phosgene-free method for PC production by using the precursor DPC. In 2004, Kim et al. synthesized DPC by using the transesterification reaction of dimethyl carbonate (DMC) and phenol (Kim et al., 2004). However, this reaction has some disadvantages. First, Tundo et al. stated that the equilibrium constant for the transesterification reaction of DMC and phenol was only 3 × 10^{-4} at 180 °C (Tundo et al., 2002). Therefore, these transesterification reactions are thermodynamically unfavorable and limited by the low yield of DPC. Second, an azoetope of DMC and phenol requires a larger distillation column. Third, side reactions occur during the reaction between DMC and phenol. To overcome these drawbacks, diethyl carbonate (DEC) and phenyl acetate (PA) were used in our previous study for the production of DPC and byproduct ethyl acetate (EtAc). This method has the following advantages: the reaction has a higher equilibrium constant, no azoetropes are formed, and no side reactions occur.

Conventional processes combined with the thermally coupled configuration can reduce heat energy. An example of a thermally coupled distillation column is the divided-wall column, which is separated into three kinds of types: direct sequence, indirect sequence, and prefractionator arrangement. In the stripping section or rectifying section, the components initially increase and then suddenly decrease; this is referred to as the remixing effect. The purpose of using a thermal coupling design is to eliminate the remixing effect. First, the thermally coupled direct sequence configuration is designed by the removal of the reboiler from the first column. And energy is provided from the side vapor stream of the second column. By the same principle, the thermally coupled indirect sequence configuration is designed by the removal of the condenser from the first column. The overhead vapor of first will feed into the second column directly. Third, the prefractionator arrangement eliminates the condenser and reboiler and provides energy from the recycled steam of the second column. In this study, the main purpose is to design a thermally coupled RD configuration for DPC process. Moreover, this process are also performed to find a better control structure for two kinds of disturbances.

II. THERMODYNAMICS AND KINETICS

A. Thermodynamic model

Distillation is a widely used unit for separating mixtures on the basis of the boiling point of the components. For the simulation of the RD process, selection of the thermodynamic model is crucial to describe the vapor–liquid equilibrium (VLE) or liquid–liquid equilibrium (LLE). According to Ho’s results in 2014, the NRTL is the best model for DPC process. There are five components in this process: the reactants (PA and DEC), intermediate (EPC), product (DPC), and byproduct (EtAc). The parameters of NRTL are presented in Table I (Ho 2014), and the boiling points are listed in Table II. Notice that no azoetop is found in this process.

<table>
<thead>
<tr>
<th>TABLE I. PARAMETERS OF NRTL MODEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i,j)</td>
</tr>
<tr>
<td>a_{ij}</td>
</tr>
<tr>
<td>b_{ij}</td>
</tr>
<tr>
<td>c_{ij}</td>
</tr>
<tr>
<td>d_{ij}</td>
</tr>
<tr>
<td>e_{ij}</td>
</tr>
</tbody>
</table>

1: EtAc, 2: DEC, 3: PA, 4: EPC, 5: DPC

<table>
<thead>
<tr>
<th>TABLE II. ORDER OF BOILING POINT AT 1 ATM</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtAc</td>
</tr>
<tr>
<td>Boiling-point (°C)</td>
</tr>
</tbody>
</table>

B. Kinetic model

DPC synthesis is a two-step reversible reactions. In this process, titanium (IV) ethoxide is used as a catalyst (Lin, 2014). The first step is the transesterification of the reactants DEC and
PA to the intermediate EPC and byproduct EtAc in (1). Subsequently, EPC and PA are used as reactants to generate the product DPC and byproduct EtAc in (2).

\[
\begin{align*}
C_9H_{10}O_3 + C_4H_6O_2 & \rightleftharpoons C_9H_{10}O_4 + C_4H_8O_2 \\
(DEC) + (PA) & \rightarrow (EPC) + (EtAc) \\
C_9H_{10}O_3 + C_4H_6O_2 & \rightarrow C_{11}H_{10}O_3 + C_4H_8O_2 \\
(EPC) + (PA) & \rightarrow (DPC) + (EtAc)
\end{align*}
\]

(1) (2)

The overall reaction is as follows:

\[
DEC + 2PA \leftrightarrow DPC + 2EtAc
\]

(3)

The Arrhenius equation is presented for the reaction constant in (4), where \( r_i \) is the reaction rate (kmol/m\(^3\)∙s\(^{-1}\)) and \( k_i \) and \( k_i^{-1} \) are the forward and reverse reaction rate coefficients, respectively. The reaction rate is subsequent describing of (1) and (2) by (5) and (6). The kinetic parameters are presented in Table III.

\[
\begin{align*}
&k_i = k_i e^{-Ea/RT} \\
r_1 = k_1 C_{DEC} C_{PA} - k_1^{-1} C_{EPC} C_{EtAc} \\
r_2 = k_2 C_{EPC} C_{PA} - k_2^{-1} C_{DPC} C_{EtAc}
\end{align*}
\]

(4) (5) (6)

TABLE III. KINETIC PARAMETERS OF DPC PRODUCTION

<table>
<thead>
<tr>
<th>(k_i) (L/(min∙mol))</th>
<th>(E_a) (kJ/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>1.691×10(^7)</td>
</tr>
<tr>
<td>(k_2)</td>
<td>3.708×10(^4)</td>
</tr>
<tr>
<td>(k_3)</td>
<td>1.467×10(^4)</td>
</tr>
<tr>
<td>(k_4)</td>
<td>6.146</td>
</tr>
</tbody>
</table>

III. PROCESS DESIGN AND COST ESTIMATION

According to the results of the kinetic reaction, a two-step reaction requires at least two RD columns to achieve the specifications of DPC and EtAc. In this case, the stoichiometric ratio of the reactants should be 2 (PA: DEC = 2:1), and the specifications of DPC and EtAc are set at 99.5 mol\% for industrial application. Because titanium (IV) ethoxide is a homogeneous catalyst, it can be combined with fresh PA stream and fed to the RD column. In a previous study (Chen et al., 2015), we devised two configuration designs: excess PA configuration and excess DEC configuration. The overall reaction observe by stoichiometric ratio in whole process.

A. Excess PA design for DPC synthesis

As shown in Figure 1(a), the first and second reaction steps occur in RD1 and RD2 separately. Subsequently, PA is recycled from the distillation column (C3) and supplied to RD1 and RD2.

In RD1, the fresh PA and recycled PA are fed to the top portion of the column. The fresh DEC stream fed at stage 66 which stage is lower than PA stream because of the sequence of boiling point. Therefore, the first reaction step occurs in RD1. Incidentally, the specification at the top portion of the column is 99.5 mol% EtAc and that at the bottom portion of the column is 0.01 mol% DEC; the products are then fed to RD2.

The second reaction step occurs in RD2 by consuming the intermediate EPC. Simultaneously, RD2 produces the byproduct EtAc, and the excess PA is fed to the final column. The product specification at the bottom is 99.5 mol% DPC. The finial distillation column (C3) yields 99.5 mol% EtAc at the top and 99.9 mol% excess PA at the bottom of the column. Subsequently, the excess PA is fed to RD1. The minimum TAC was determined if the product and byproduct specifications were satisfied. Figure 1(a) presents the optimal design with minimum TAC ($8.3 \times 10^5$). The formula of TAC shown in (7).

\[
TAC = TAC_{operating} + \frac{TAC_{capital}}{3}
\]

(7)

Figure 2(a) and 2(b) presents the RD1 and RD2 compositions. The remixing effect was observed at the bottom of RD1 and the top of RD2. This phenomenon can be eliminated using a thermally coupled configuration, which involves removing the reboiler of RD1 and the condenser of RD2. However, RD1 uses low-pressure steam and RD2 uses high-pressure steam. The total operating power would increase if RD1 energy is provided by RD2. Therefore, a thermally coupled configuration should be established between RD2 and C3.

As previously discussed, thermal coupling should be established between RD2 and C3. The flowsheet of a thermally coupled design is presented in Figure 1(b). The condenser duty of C3 increases because of the removal of the condenser of RD2. Figure 3(b) presents the thermally coupled composition profiles of RD1 and RD2. The thermally coupled design facilitates the elimination of the remixing effect from the top and bottom of RD2.

TABLE IV. THE ENERGY CONSUMPTION OF CONVENTIONAL AND THERMALLY COUPLED CONFIGURATION FOR EXCESS PA DESIGN

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Total Condenser Duty</th>
<th>Total Reboiler Duty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>-1386.09 kW</td>
<td>1226.11 kW</td>
</tr>
<tr>
<td>Thermally Coupled</td>
<td>-1239.24 kW</td>
<td>1095.08 kW</td>
</tr>
</tbody>
</table>

B. Excess DEC design for DPC synthesis

In the excess DEC design, RD1 consumes PA to produce DEC and EtAc. Therefore, PA clearly decreases at the top portion of RD1. Conversely, EtAc and DEC apparently increases at the higher stages of RD1. The products at the bottom of RD1 are DPC and intermediate EPC. In addition, a short second-step reaction is in progress below the column. Thus, intermediate EPC reacts with PA to generate DPC near the bottom of the column.

Because of the addition of PA stream, RD2 contains large amounts of PA, EPC, and EtAc. The reactive zone consumes PA and EPC to produce DPC. The proportion of DPC increase is consistent at higher stages. The top half of the reactive zone separates the byproduct EtAc. Therefore, the concentration of EtAc increase is consistent at the lower stages at the top of the reactive zone. The purpose of using the distillation column (C3) is to separate and recyle excess DEC. According to the boiling point, lighter components move to the top of the
column and heavier components move to the bottom. Hence, EtAc and DEC achieved their industrial specifications with change in stage.

Moreover, the side stream was fed back to RD1. This method can eliminate the remixing effect at the top portion of RD1. Similarly, the bottom portion of the reboiler was removed, and the bottom stream was fed to the upper portion of RD2. Simultaneously, the side stream was fed to the bottom RD1 to eliminate the remixing effect.

The minimum TAC was determined if the product and byproduct specifications are satisfied. The excess DEC design without a thermally coupled configuration also presents the optimal case with the minimum TAC ($8.9 \times 10^5$). Compared with the excess DEC configuration, the excess PA configuration can save $6 \times 10^4$. (Table V)

**IV. CONTROL STRUCTURE AND PROCESS DYNAMICS**

Workable control structures are required to overcome the disturbances that exist in realistic conditions. The feasibility of the control schemes was tested using the Aspen Plus Dynamics V8.4 simulator. As previously discussed, the excess PA configuration has minimal TAC compared with the excess DEC configuration. This section discusses the use of excess PA configuration for dynamic simulation and the dynamic behavior.

For dynamic simulation, two control loop level designs were employed: inventory control loop and quality control loop. To maintain the safety, the inventory control loop is required. To attain the product specifications, the quality control loop is required. Moreover, the quality control loop
scheme employs a temperature controller to meet the product specifications.

A. Inventory control loops

As discussed in the previous section, the thermally coupled design constituted two reactive columns and one distillation column. In an inventory control loop, a flow controller is employed to control the feed rate in the column. In addition, a pressure controller is required to control the pressure of the top column because of the temperature change and safety considerations. Furthermore, a level controller is required to control the reflux drum and the sump levels of the column.

The purpose of using C3 is to recycle the excess PA and feed it back to RD1 and RD2. However, this recycle process may exert a snowball effect if the level control loop design does not work as intended. To avoid this effect, Arifin and Chien (2008) presented the solution of using new inventory control loops. The bottom level of distillation column cascade with the flow rate of the fresh PA stream, avoiding the PA flow rate rise constantly.

B. Quality control loops

Before designing the quality control loop, the operating variables must be considered. For the RD column, reflux ratio, feed ratio, and reboiler duty are the three control degrees of freedom. The control degrees of freedom for the distillation column are reflux ratio and reboiler duty.

C. Control Performance

1. CS1

In the excess PA configuration, the recycled PA stream should be fed to RD1 and RD2. The flow rate controller become more complex for the flow rate of recycled PA stream to RD1 been limited by the recycled PA stream to RD2. To reduce the complexity of the process, the feed ratio of RD1 should be removed to control the sensitive stage.

The condenser reflux ratio was not an operating variable for RD2. Therefore, at least six temperature operating variables were considered for RD2. In Figure 4, the temperature control point was selected through open-loop sensitivity analysis.

RD1 had two operating variables: reflux ratio (RRD1) and reboiler duty (QRD1). As shown in Figure 4(a) and 4(b), RD1 had two sensitivity temperature stages: 4th stage and 68th stage. The relative gain array is presented in the equation below. The variable RRD1 was selected to control the 4th stage and QRD1 was selected to control the 68th stage.

\[
\begin{bmatrix}
    \frac{RRD1}{QRD1} \\
    -2.05 & 3.05
\end{bmatrix}
\begin{bmatrix}
    T_4 \\
    T_{68}
\end{bmatrix}
\]

RD2 had two control variables: feed ratio (FRD2) and reboiler duty (QRD2). As shown in Figure 4(c) and 4(d), RD2 had only one sensitivity temperature stage, the 23rd stage. Therefore, the control variable FRD2 was selected to control the 23rd stage.

C3 had two control variables: reflux ratio (RRC3) and reboiler duty (Qc3). According to Figure 4(e) and 4(f), the sensitivity temperature stage was the 3rd stage. Because RRC3 is closer to stage 3, RRC3 can be selected to control the 3rd stage, named CS1 in Figure 5(a). Notice that a well-known L-V control structure is applied in RD1 for CS1.

![Figure 4](image_url)

The ultimate gain and period are obtained through the relay feedback test. Subsequently, the test result was applied by Tyreus–Luyben tuning rule to calculate the controller parameters. In addition, to simulate the realistic situation, three lags (Time interval = 0.5 min) were added for each temperature controller. All calculated parameters of quality control loops are shown in Table V.

<table>
<thead>
<tr>
<th>TABLE VI. TUNING PARAMETERS OF CS1</th>
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</thead>
<tbody>
<tr>
<td>Controlled Variable</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>( T_{4, RD1} )</td>
</tr>
<tr>
<td>( T_{68, RD1} )</td>
</tr>
<tr>
<td>( T_{23, RD2} )</td>
</tr>
<tr>
<td>( T_{3, C3} )</td>
</tr>
</tbody>
</table>

![Figure 6](image_url)

Figure 6 presents the responses of ±10% DEC feed disturbance after 1 h. The black line represents +10% and the red line represents −10% disturbance. Consequently, the system can reach a steady state after 9 h. Because the temperature TC3 is limited by the C3 sump level, it requires a longer time to achieve steady state. Moreover, recycled PA stream through spilt to the bottom of RD2. The flow rate variation causes a change in FRD2, leading to the requirement of a longer time to achieve steady state.
Figure 6. CS1 responses of ±10% throughput disturbance

Figure 7 presents the responses of −5% and −10% DEC composition disturbance after 1 h. The black line represents −5% and the red line represents −10%. According to the composition disturbance analysis, DPC exhibited a 1 mol% deviation. The byproduct EtAc can almost achieve the industrial specification.

2. CS2

The control structure of CS2 is presented in Figure 5(b). The difference between CS1 and CS2 is the controller pairing of the second RD column. Because CS1 uses FRD2 to control the 23rd stage temperature, it requires a long time to achieve steady state. Hence, QRD2 was used in the CS2 quality control loop to control the temperature of the 23rd stage. The tuning parameters are presented in Table VI.
Table VII. Tuning Parameters of CS2

<table>
<thead>
<tr>
<th>Controlled Variable</th>
<th>Manipulating Variable</th>
<th>Kc (%/%)</th>
<th>τI (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{1, RD1}</td>
<td>RR_{RD1}</td>
<td>5.11</td>
<td>13.20</td>
</tr>
<tr>
<td>T_{10, RD2}</td>
<td>Q_{RD2}</td>
<td>11.3</td>
<td>10.56</td>
</tr>
<tr>
<td>T_{23, RD2}</td>
<td>Q_{RD2}</td>
<td>1.89</td>
<td>11.88</td>
</tr>
<tr>
<td>T_{3, C3}</td>
<td>RR_{C3}</td>
<td>1.38</td>
<td>7.92</td>
</tr>
</tbody>
</table>

Figure 8 presents the responses of ±10% DEC feed disturbance after 1 h. The black line represents +10% and the red line represents −10%. The system can achieve steady state in 8 h. When the system became stable, DPC exhibited a 0.1 mol% deviation and EtAc exhibited a 0.05 mol% deviation.

Figure 9 presents the responses of −5% and −10% composition disturbance. After the disturbance analysis, DPC exhibited a 0.11 mol% deviation and the byproduct EtAc could almost achieve the industry specification. Similarly, at the sensitivity temperature stage of RD2, CS2 had little effect on the composition disturbance than CS1. Therefore, CS2 has better control performance than CS1.

In this study, the reactive distillation design was investigated by studying the transesterification of PA and DEC to DPC and EtAc. The excess reactant design was observed to increase the conversion of the product and yield 99.5 mol% of the product for industrial uses. To reduce energy consumption, the remixing effect was eliminated using a thermally coupled design. Furthermore, the equipment and operating costs of the excess PA configuration and excess DEC configuration were compared to determine the minimum TAC. The results indicate that the excess PA design can save 6.71% TAC than the excess DEC design.

A dynamic simulation was performed using a thermally coupled excess PA configuration. The throughput and composition disturbance analyses were performed to investigate the possibility of the control structures. Both CS1 and CS2 exhibited a favorable behavior during the throughout and composition disturbances. However, CS1 requires a longer time to achieve steady state because the RD2 temperature is limited by the recycled flow rate. In conclusion, CS2 is the superior control scheme because it employs reboiler duty to control the sensitive stage.

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References