Design and control of diphenyl carbonate reactive distillation processes using arrangements with heat-integrated stages

J. Rafael Alcántara-Avila*, Masataka Terasaki, Hao-Yeh Lee*, Jun-Lin Chen, Julián Cabrera-Ruiz, Ken-Ichiro Sotowa, Toshihide Horikawa

Abstract— Diphenyl carbonate is a very important precursor of polycarbonate. Therefore, environmental friendly chemical routes and low-cost processes are necessary to cope with its demand. In this study, a new green route to produce diphenyl carbonate and methyl acetate from the reaction between phenyl acetate and dimethyl carbonate was adopted. Also, reactive distillation (RD) is the adopted process to do the reaction and separation simultaneously because this process can overcome chemical equilibrium limitations, obtain high selectivity, and can use the heat of reaction in distillation. The advantages of RD can increase the process efficiency and reduction of investments and operational costs. This study aims to design an RD process with heat-integrated stages that can further reduce the energy consumption in comparison with conventional RD technology. At the steady state, simulation and optimization techniques were combined to find the best design while at the dynamic state, the theoretical control properties at the open loop and the close loop performance were done to find the best control scheme and controller parameters.

I. INTRODUCTION

Diphenyl carbonate is an important precursor in the production of polycarbonate, which is an important thermoplastic with excellent mechanical, optical, electrical, and heat resistance properties. Most polycarbonates are manufactured by the phosgene process, which uses carbon monoxide and chlorine as raw materials. However, phosgene is highly toxic, needs a large amount of methylene chloride, and uses a large amount of water to separate the phosgene and chlorine from the produced polycarbonate. Therefore, a new green route has been proposed to produce diphenyl carbonate (DPC) and methyl acetate (MA) from the reaction between phenyl acetate (PA) and dimethyl carbonate (DMC) [1]. In addition, the DPC synthesis method is favorable because it has high equilibrium constants, no azeotropes, and no side reactions [2].

Reactive distillation (RD) is a combination of simultaneous separation and reaction in a single device. Through this integrative strategy, chemical equilibrium limitations can be overcome; higher selectivities can be achieved, and heat of reaction can be directly used for distillation. Thus, the advantages of RD are the increased process efficiency and reduction of investments and operational costs [3]. RD is attractive in systems that remove the products from the reactants by distillation, which implies that the products should be lighter and heavier than the reactants [4]. In terms of boiling point temperature, the previous situation is valid for the transesterification reaction of DMC and PA.

This work aims to design new RD processes that can further reduce the energy consumption in comparison with typical RD through the enforcement of heat integrations between the RD column at high pressure and the separation distillation (SD) column at low pressure. The typical heat integration takes place between the condenser at high pressure and the reboiler at low pressure. However, this situation is unfavorable because the RD operates at the highest pressure, and thus its reboiler is at the worst thermal condition. Thus, heat integration at lower pressure difference between RD and SD can be attained by enforcing heat integration between the stages in the rectifying section of RD and the stages in the stripping section of SD.

This study combines simulation and optimization techniques to find new heat-integrated RD processes with further reduction of energy consumption and cost. Also, analyses at the open loop and the close loop are done to assess the controllability of the proposed processes.

II. PROCESS MODELING

A. Kinetic model

The synthesis of DPC from DMC and PA is a two-step reaction that takes place through the formation of the intermediate methyl phenyl carbonate (MPC). Equation (1) shows the transesterification of DMC and PA to generate MPC and MA while (2) and (3) show the transesterification of MPC and PA to DPC and MA or the disproportionation of MPC to DPC and DMC [1].

\[ \text{DMC} + \text{PA} \xrightarrow{\text{Catalyst}} \text{MPC} + \text{MA} \]  

\[ \text{MPC} + \text{PA} \xrightarrow{\text{Catalyst}} \text{DPC} + \text{MA} \]  

\[ 2\text{MPC} \xrightarrow{\text{Catalyst}} \text{DPC} + \text{DMC} \]
The reaction rate expressions for (1)-(3) are shown in (4)-(6)

\[ r_1 = k_{f_1}C_{DMC}C_{PA} - k_{b_1}C_{MPC}C_{MA} \]  
\[ r_2 = k_{f_2}C_{MPC}C_{PA} - k_{b_2}C_{DPC}C_{MA} \]  
\[ r_3 = k_{f_3}C_{MPC}^2 - k_{b_3}C_{DPC}C_{DMC} \]

where \( r_i \) is the reaction rate of the \( i \)-th reaction (kmol/m³ s). \( k_{f_i} \) and \( k_{b_i} \) are the forward and backward reaction rate coefficients, respectively. \( C_j \) is the concentration of each component \( j \) (kmol/m³).

The Arrhenius equation was adopted to consider the temperature dependence of the reaction rate coefficients. Table I shows the pre-exponential factor \( k_0 \) and the activation energy \( E_a \) of each reaction rate coefficient in (4)-(6). These parameters were taken from the experimental work of Shen et al. [5]

### B. Thermodynamic model

For the reaction system in the previous subsection, azeotropes do not exist, and there are large boiling-point temperature differences between the components. The order of normal boiling point temperature for pure components is: DPC (302 °C) > MPC (234.7 °C) > PA (195.7 °C) > DMC (90.2 °C) > MA (57.1 °C). Yao et al. [6] experimentally demonstrated that the ideal solution model provided a satisfactory fit to the vapor-liquid equilibrium data in the system. Therefore, the ideal thermodynamic model was used to represent the vapor-liquid relationships in the reaction system [1].

### III. DESIGN OF HEAT-INTEGRATED REACTIVE DISTILLATION

Heat integration between columns has been widely used to reduce the energy consumption in distillation processes. This energy conservation method can be extended to a process in which one of the reactants is fed in excess to the RD column, and then separate it and recycle it in the SD column. Thus, heat integration between columns is possible by adjusting the operating pressure in the columns.

Nevertheless, when the condenser in the high-pressure RD column and the reboiler in the low-pressure SD column are the only places subject to heat integration, the pressure difference between columns is at its maximum value. It is not beneficial from the reaction and the vapor-liquid equilibrium viewpoints because the catalyst can deactivate at high temperatures and the relative volatility between components decreases as pressure increases. Thus, more expensive steam cost and energy consumption are necessary for the reboiler of the high-pressure RD column.

Fig. 1 shows the RD sequence that was taken as the base case [1]. This process does not have heat integration. The structural variables are the number of stages in the reactive and separation columns \( (N_{RD} \) and \( N_{SD} \), respectively), the feed stages of the reactants \( (f_{PA} \) and \( f_{DMC} \), and the feed stage in the separation column \( f_{SC} \). The operation variables can be the reflux ratios \( (RR_{RD} \) and \( RR_{SD} \), distillate or bottoms flow rates, and the reboiler duties \( (Q_{bRD}^0 \) and \( Q_{bSD}^0 \).

For heat-integrated sequences, the additional structural variables are the number and location of intermediate heat exchangers and the additional operation variables are the heat transfer amount at each heat exchanger. By looking at the boiling point of each component involved in the reaction system, the temperature in RD will be higher than that in SD. Therefore heat integration between the rectifying section in RD and the stripping section in SD will be subject to study.

<table>
<thead>
<tr>
<th>TABLE I. REACTION RATE PARAMETERS</th>
<th>( k_0 ) (m³/kmol s)</th>
<th>( E_a ) (kJ/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{f_1} )</td>
<td>135</td>
<td>54200</td>
</tr>
<tr>
<td>( k_{b_1} )</td>
<td>52</td>
<td>54900</td>
</tr>
<tr>
<td>( k_{f_2} )</td>
<td>1210</td>
<td>61500</td>
</tr>
<tr>
<td>( k_{b_2} )</td>
<td>611</td>
<td>56200</td>
</tr>
<tr>
<td>( k_{f_3} )</td>
<td>82000</td>
<td>76800</td>
</tr>
<tr>
<td>( k_{b_3} )</td>
<td>109000</td>
<td>70800</td>
</tr>
</tbody>
</table>

![Figure 1. Base case without heat integration.](image-url)
high-pressure RD column and low-pressure SD column. Therefore, in this study, the structural and operation variables related to the heat integration network are calculated in the optimization CPLEX optimization studio 12.6.

Equation (7) shows the objective function that minimizes the energy consumption (ENC) in the RD process. It comprises the total amount of heating utilities (i.e., hot oil and steam) in the RD column and the SD column.

\[
ENC = \sum_{i \in HU} \sum_{j \in STR_{RD}} Q^{ex}_{ij} + \sum_{i \in HU} \sum_{j \in STR_{SD}} Q^{ex}_{ij} \quad (7)
\]

where \( Q^{ex}_{ij} \) is the heat exchanged between a hot stream \( i \) and a cold stream \( j \). \( HU \) is the set of heating utilities, and \( STR \) is the set of stages in the stripping section of each column.

More details about the optimization model can be found in one of our previous publications [7].

B. Solution procedure

After the minimization of (7), the economic analysis is done at a post-optimization step. The equipment cost was calculated using the Guthrie Method [8]. Equation (8) shows how the Total Annual Cost (TAC) was calculated. The necessary information to calculate the Equipment Cost (EC) is the heat exchangers area, column diameter, number of stages, and column height. The necessary information to calculate the operation cost (OC) is the cost of hot and cold utilities.

\[
TAC = \frac{EC}{\tau} + \theta \times OC \quad (8)
\]

where \( \tau \) and \( \theta \) are the payback time and the annual operation hours, respectively.

The solution procedure is as follows:
1. Simulate the base case in Fig. 1.
2. Set the operating pressure in the RD column, which must be higher than that in the SD column.
3. Obtain all the necessary data to perform the optimization so as to minimize (7).
4. Run the optimization problem and solve (7).
5. Input the optimization results into the simulation software and run the simulation.
6. Export the new temperature profile in each column to the optimization.
7. Repeat steps 4 to 6 until there are not changes in the temperature profile.
8. Calculate the TAC according to (8).
9. Exit the solution procedure.

C. Results and Discussion for the design at steady state

Fig. 2 shows the typical condenser-reboiler heat integration between stage 2 and the reboiler. Also, there is heat exchange between the condenser and cooling water. The latter type of heat integration is more advantageous than that in Fig. 2 to attain energy requirements and cost savings (25% and 11%, respectively) in comparison with the conventional process in Fig. 1 because as the pressure difference between columns becomes smaller, the energy requirement in the RD column decreases.

Another alternative to reduce energy is through thermal coupling between columns. In this approach, the condenser in the RD is replaced by two interconnecting streams: one liquid, and one vapor. Thus, about 24.5% energy savings can be obtained [1]. The results in this section show that thermal coupling and heat integration can attain similar energy savings when heat integration takes place at stages. Otherwise, thermal coupling will outperform typical condenser-reboiler heat integration. Therefore, the type of heat integration in Fig. 3 can be a realistic alternative to substitute the well-extended thermal coupling reactive distillation.
IV. CONTROL PROPERTIES

In this section, the control properties are evaluated at open-loop by analyzing the changes in the output variables (i.e., the purities of DPC (x_{DPC}), MA (x_{MA}), and DMC (x_{DMC})) after perturbing the input variables (i.e., \(Q_{RD}^0\), \(Q_{SD}^0\), and \(RR_{RD}^0\) ±1%). The singular value decomposition (SVD) was the used tool to evaluate the control properties. It is a factorization of a real or complex matrix into three matrices as shown in (9)

\[
M = W \Sigma V^T
\]

(9)

where \(M\) is a given matrix, \(W\) and \(V\) are orthogonal matrices and \(\Sigma\) is a diagonal matrix of singular values.

From the control point of view, the maximum and minimum singular values of \(\Sigma\), \(\sigma_{max}\) and \(\sigma_{min}\) respectively, are important since they denote the maximum and minimum gains of the output of the system as the input is varied [9].

The condition number (CN) in (10) is defined as the ratio of the maximum and minimum singular value

\[
CN = \sigma_{max}/\sigma_{min}
\]

(10)

and it represents the sensitivity of the system to input uncertainty.

Large values of CN must be avoided because they imply that the system is ill-conditioned. If the system is almost singular, the computation of its inverse and its solution is susceptible to large numerical errors. A matrix that is not invertible has \(\sigma_{min}\) equal to zero. Therefore values of \(\sigma_{min}\) represent the system invertibility, and values close to zero must also be avoided [10]. Equation (11) shows the transfer function matrix \(M\) for the process in Fig. 3.

\[
\begin{align*}
\begin{array}{c|ccc}
\text{x}_{\text{out}} & Q_d^0 & Q_s^0 & RR_s^0 \\
\hline
1 & 0.08 & 0.94 & 1.14 \\
1+4.12x & -0.13 & -1.26 & -1.45 \\
1+7.47x & 0.34 & 0.61 & 0.41 \\
1+2.09x & 1+2.69x & 0.41 & 1+13.39x \\
\end{array}
\end{align*}
\]

(11)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure4.png}
\caption{Open-loop analysis in the frequency domain.}
\end{figure}

From the results in Fig. 4 it can be observed that the heat-integrated solution has better control properties for positive disturbances. For negative disturbances, the heat-integrated solution has better control properties at low frequencies less than 200 rad/s. Therefore, the natural dynamic in the heat-integrated solution shows good control properties.

V. PROCESS CONTROL

In this section, the process dynamics of the best configuration is investigated. Because there are some disturbances in the realistic operation, a workable control scheme is required. In this study, the Aspen Plus Dynamics simulator was used.

There are two levels in the design of control schemes. One is the inventory control loops, and the other is the quality control loops. The main purpose of inventory control loop is to maintain the safety of processes, and the main purpose of the quality control loops is to maintain the specifications of the products. In this study, the specifications of the product are controlled by the temperature controller which is used instead of composition controller.

A. Inventory control loops

Because this process contains a recycle stream from the bottom of SD, it may occur the snow ball effect if the recycle stream is used to control SD sump level [11]. There is a method to eliminate the snow ball effect by using a flow control in the recycle stream [12-13]. Therefore, the total flow rate of the DMC feed stream including fresh feed and recycle streams is a ratio to the PA feed stream in this inventory loops configuration. The fresh feed DMC is used to control the sump level of SD. This arrangement can avoid SD sump level rising continuously due to the snow ball effect.

There is a heat exchanger between the RD and the SD. Therefore, it needs to use the feature ‘Flowsheet Equations’ in Aspen Plus Dynamics to satisfy the relation between the heat duty and the temperature difference [14-15] according to (12)

\[
Q = U \times A \times \Delta T
\]

(12)

where \(U\) is the overall heat-transfer coefficient. Because there is a phase change in the heat exchanger, this \(U\) value can be set as 0.00306 (GJ h⁻¹ m⁻² °C⁻¹). \(A\) is the fixed heat-transfer area 52.15 (m²) which can be calculated under nominal operating condition. \(\Delta T\) is the temperature difference between the second stage of RD column and the reboiler of SD. In this study, the proportional-integral (PI) controllers are used for pressure control and flow control loops. The proportional (P) controllers are used for level control loops.

B. Quality control loops

There are four control degrees of freedom in this process which are: \(RR_{RD}\), \(Q_{SD}^0\), and feed ratio (\(FR_{RD}\)) of RD column, and \(RR_{SD}\). The open loop sensitivity analysis of these manipulating variables is used to find the temperature control points of column stages. By ± 0.01 % changes given of those
variables, the results are shown in Fig. 5. The results show that the most sensitivity temperature stage in the RD column is the 77th stage and in the SD column is the 7th stage, respectively. There are three manipulating variables in the RD column, thus more than one control scheme can be constructed. In this process, a fixed value of $RR_{RD}$ is considered. Therefore, the $FR_{RD}$ and the $Q^b_{SD}$ can be set as manipulating variables to control the 77th stage temperature of RD column.

The control performances of the two control schemes are evaluated and compared for throughput disturbance rejection. The variable $FR_{RD}$ is selected to control the 77th stage temperature of RD column, named CS1; and the other variable, $Q^b_{SD}$, is chosen to control the 77th stage temperature of RD column, named CS2. The selection of the control pairing is based on the RGA analysis. Both control schemes selected $RR_{SD}$ as the manipulating variable to control the 77th stage of SD. In this study, the proportional-integral (PI) controllers are used for temperature control loops. Furthermore, the autotune variation (ATV) method is applied to tune the controller parameters. And then the controller parameters are calculated by Tyreus-Luyben PI tuning rule. The sequential iterative tuning procedure is used to find the final controller settings. There are three time lags in which the time constant was set to 0.5 minutes and added in each temperature controller to simulate a more realistic process output delay. All parameters of quality control loops are summarized in Table II.

![Figure 5](image_url)

Figure 5. The open-loop sensitivity analysis for ±0.01 % changes (a) the reboiler duty in RD (b) the feed ratio in RD (c) the reflux ratio in RD (d) reflux ratio changes in SD.

<table>
<thead>
<tr>
<th>CONTROLLED VARIABLE</th>
<th>MANIPULATING VARIABLE</th>
<th>$K_C$</th>
<th>$\tau_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{77, RD}$</td>
<td>$FR_{RD}$</td>
<td>1.001</td>
<td>58.7</td>
</tr>
<tr>
<td>$T_{7, SD}$</td>
<td>$RR_{SD}$</td>
<td>2.93</td>
<td>19.79</td>
</tr>
<tr>
<td>$T_{77, RD}$</td>
<td>$Q^b_{SD}$</td>
<td>1.15</td>
<td>17.16</td>
</tr>
<tr>
<td>$T_{7, SD}$</td>
<td>$RR_{SD}$</td>
<td>2.93</td>
<td>19.8</td>
</tr>
</tbody>
</table>

### TABLE II. TUNING PARAMETERS OF TEMPERATURE CONTROLLERS

C. Control performance

1) CS1 for heat-integrated stages

The control scheme of the CS1 of this process is shown in Fig. 6. In CS1, $FR_{RD}$ and $RR_{SD}$ are used to control the temperatures of the 77th stage in the RD column and the 7th stage in the SD, respectively. The remaining variable, $Q^b_{SD}$, is ratio to PA fresh feed flow rate.

Fig. 7 shows that the dynamic responses under ± 20% throughput disturbances. In this study, the disturbance is entered into the system at the 2nd hour. It is found that it takes less than six hours to reach steady-state for throughput disturbances. However, the DPC mole fraction of the RD column bottom flow will drop down to 0.965 mole fraction at the beginning of disturbance entering the process and return 0.995 mole fraction after the 4th hour. Moreover, a large overshoot decrease around 50 ºC after the 2nd hour can be observed in the 77th stage temperature of RD column, but the temperature can go back to its setpoint after around four hours. The response of DMC composition in the SD bottom stream is not symmetrical under ±20% throughput disturbances. The DMC composition in the SD bottom stream goes down to around 0.915 mole fraction under ±20% throughput disturbance. Because there is no auxiliary reboiler in the bottom of SD, the bottom of DMC composition will be fluctuated by energy transfer in the side heat exchanger.

![Figure 6](image_url)

Figure 6. CS1 for heat-integrated stages DPC RD process.

![Figure 7](image_url)

Figure 7. The responses of ±20% throughput disturbance for CS1.
2) CS2 for heat-integrated stages

The control scheme of the CS2 of this process is shown in Fig. 8. In CS2, $Q_{RD}^0$ is used to control the temperature of the 77th stage in the RD column and $RR_{SD}$ is also used $RR_{SD}$ to control the temperature of the 7th stage of the SD. The remaining variable, $FR_{RD}$, is fixed in its nominal value under throughout disturbances.

Fig. 9 shows the dynamic responses under ±20 % throughput disturbances. It also takes about 6 hours to reach steady-state for throughput disturbances. Unlike the response of +20% throughput changes in CS1, the DPC mole fraction of RD column drops down a little to 0.987 mole fraction at the beginning of the disturbance entering the process, but its response is back to 0.995 mole fraction in less than one hour. Moreover, the temperature of the 77th stage in the RD column only decreases 30 °C. The same observation of the DMC composition can be found in the SD bottom stream. It also displays the non-symmetrical response under ±20 % throughput disturbances. However, the DMC composition in the SD bottom stream only decrease to 0.937 mole fraction. The CS2 control performance is better than CS1 because manipulating reboiler duty would rapidly and effectively control the variable when the disturbances entered.

VI. CONCLUSION

In this work, an iterative solution procedure combining simulation and optimization was adopted to find the heat-integrated distillation columns. The best result attained energy savings around 25% and cost savings around 12%. The control properties at open loop were better for the best heat-integrated solution. Finally, the two control schemes namely CS1 and CS2 were considered. Large variations in the throughput changes were investigated. Without using feed ratio in the CS2 control scheme, better control performance can be maintained at high-purity despite feed throughput disturbances.

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