Design and Control of a Reactive Distillation Process for Synthesizing Propylene Carbonate from Indirect Alcoholysis of Urea

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Abstract: Dimethyl carbonate is a green compound with a broad variety of application. In the study, the process design and control of synthesizing propylene carbonate (PC) for the dimethyl carbonate production by using CO₂ as a raw material is investigated by indirect alcoholysis of urea. This attractive reaction distillation route of urea shows many advantages such as environmentally friendly chemicals, cheap raw materials, and mild and safe operation condition. Some reaction distillation (RD)-based processes for PC synthesis by this route are proposed, designed, and optimized in this work. These processes consist of two operation configurations, near neat operation and excess reactant operation. The intensified technologies of heat integration in addition to RD are used to design economic PC synthesis processes. Steady-state simulation results indicate that the novel intensified process containing a RD column and a conventional distillation column with internal vapor compression provides the most economical design. This process is operated under excess reactant and fully utilizes the special azeotrope characteristic of propylene carbonate and propylene glycol pair. This pair forms a homogeneous minimum-boiling azeotrope near the pure PG end under low pressure. However, this azeotrope vanishes under high pressure. Furthermore, steady-state analysis is used to design a simple temperature control strategy. Different desired temperature profiles can be found in the RD column under various feed flow rates. Set point of the temperature loop for maintaining bottom product purity of the RD column is then reset when throughput rate changes. Dynamic simulation results reveal that the proposed temperature control can maintain product purities at their desired values in face of feed flow disturbances.

Keywords: Design, control, propylene carbonate, plant-wide, urea.

1. INTRODUCTION
Carbon dioxide (CO₂) emission has recently become a global issue due to the significant and continuous rise of atmospheric CO₂ concentration. CO₂ utilization and chemical conversion into high value-added products play a key role in minimizing CO₂ emission. Dimethyl carbonate (DMC) is an important organic compound and chemical intermediate with the label of ‘‘green chemical’’. There are several reaction paths to manufacture DMC. Among these paths, DMC production utilizing CO₂ as a raw material attracts much attention because it supplies direct environment benefits. The CO₂-based methods to produce DMC include direct synthesis from urea and propylene glycol (PG) or ethylene glycol to synthesize ammonia and PC or ethylene carbonate. This reaction route provides many benefits, such as cheap and easily available raw materials, mild reaction conditions, safe operations, environmentally friendly chemicals, etc. Fig. 1 shows the concept of the plant-wide process for the DMC production by indirect alcoholysis of urea. Urea, PC, and DMC are sequentially synthesized from the plant-wide process. The most important characteristic in this plant-wide process is that PG, a byproduct in the transesterification reaction for DMC synthesis, can be used as the reactant for PC synthesis and the released ammonia from PC synthesis can be recycled back to produce urea by reacting with CO₂. The overall process forms a green chemical cycle, which increases the utilization of raw materials for the DMC production. Some reports (Hamidipour et al., 2005; Zhang et al., 2005; Holtbruegge et al., 2013; Holtbruegge et al., 2014) can be found in discussing about the process design of urea synthesis and DMC synthesis. However, nowadays, very few literatures investigate the process design and control for PC synthesis. In this work, some processes, classified in terms of two operation configurations, near neat operation and excess reactant operation, for PC synthesis by reacting urea and PG are proposed, designed, and optimized by minimizing total annual cost (TAC). Reactive distillation (RD) and internal vapor compression technologies are used to intensify the plant-wide PC synthesis processes. In addition, the strategy of temperature control instead of composition control is proposed to maintain product purities by steady-state analysis for the most economical plant-wide process.
Fig. 1. Concept of the plant-wide process for DMC production by indirect alcoholysis of urea.

2. KINETIC AND THERMODYNAMIC MODELS

Three reaction steps given below are proceeded for DMC production using CO₂ as the raw material by indirect alcoholysis of urea.

\[
\begin{align*}
\text{CO}_2 + 2 \text{NH}_3 &= \text{Urea} + \text{H}_2\text{O} \quad (1) \\
\text{Urea} + \text{PG} &\rightarrow \text{PC} + 2 \text{NH}_3 \quad (2) \\
\text{PC} + 2 \text{MeOH} &= \text{DMC} + \text{PG} \quad (3)
\end{align*}
\]

In the first step, urea is produced by reacting CO₂ and ammonia. Next, urea is reacted with PG to coproduce PC and ammonia. DMC is synthesized in the final step by the transformation reaction of PC and methanol (MeOH). The byproducts, ammonia and PG produced from steps 2 and 3, respectively, are recycled back to steps 1 and 2, respectively, as reactants. The overall reaction is the one of CO₂ and MeOH to produce DMC and water. Ammonia and PG are the intermediates. In this work, we first explore the design of different PC synthesis processes. Some possible RD-based configurations are proposed to synthesize PC. Finally, the control of the most economical process is investigated.

Wang (2012) presented a kinetic model given below for PC synthesis by using MgO as the heterogeneous catalyst.

\[
r_{PC} = 1.5888 \exp\left(-\frac{562.602}{T}\right) \cdot C_{\text{urea}} \cdot C_{\text{PC}}
\]

where \( r_{PC} \) represent the reaction rate of PC synthesis (mol·liter⁻¹·min⁻¹), \( T \) and \( C_i \) denote temperature (K) and concentration (mol·liter⁻¹) of component \( i \), respectively. The catalyst concentration is assumed to be 2 wt%, used in the experiment study.

In the study, the process simulation is conducted by a rigorous model provided by ChemCad software. The vapor-liquid equilibrium (VLE) relationship is described by UNIQUAC activity coefficient model. In the PC synthesis reaction system, only the thermodynamic data of urea-ammonia and PG-PC pairs are found in the literatures (Mathuni et al., 2011; Holtbruegge et al., 2013; Voskov and Voronin, 2016). The solubility of ammonia in the reaction mixture is represented by using Henry coefficients. The phase-equilibrium relationships for the other pairs are determined in the study by the ideal model from ChemCad software. Fig. 2 shows the VLE relationship for PG-PC pair. It indicates that homogeneous minimum-boiling azeotrope can be found for this pair under low pressure (0.12 atm) (Mathuni et al., 2011). However, there is no azeotrope under relatively high pressure (1 atm). This important characteristic is fully utilized to reduce energy consumption in the following process design for PC synthesis under excess reactant operation.

Fig. 2. VLE relationship for PG-PC pair under pressures (a) 0.12 atm and (b) 1 atm.

3. DESIGN OF PC SYNTHESIS PROCESSES

In the design of the process to synthesize PC, the objective is to minimize the TAC by adjusting design variables. TAC is calculated by the sum of operating cost and capital cost/payback year. The operating cost (OC) includes the costs of steam, cooling water, catalyst (replaced annually), and electricity. The capital cost (CC) comprises the costs of the column shell, stage, heat exchanger, and compressor. The formulas of these cost estimations are taken from Turton et al. (2012). Here, a payback of eight years is used. An annual operating time is assumed to be 8322 hours. The unit costs of medium pressure steam (at 10 barg and 184 °C), high pressure steam (at 41 barg and 254 °C), and cooling water (at 30 °C) are 14.19 US$/GJ, 17.70 US$/GJ, and 0.354 US$/GJ, respectively. The unit cost of electricity is 16.8 US$/GJ.

3.1 Near Neat Operation

RD is an intensification technology that integrates reaction and separation operations in a single vessel. The RD configuration for PC synthesis is shown in Fig. 3. The SCDS...
module in ChemCad is used to simulate a RD column. Two reactants (urea and PG) are fed into the first RD column for PC synthesis. Ammonia is removed from the partial condenser. PC is achieved from the column bottom and then fed into the second RD column to react with MeOH for DMC synthesis. In the second RD column, the overhead product mainly contains a mixture of DMC and MeOH. PG product is withdrawn from the column bottom and is recycled back to the first RD column for PC synthesis. PG is converted into the reactant for the PC synthesis by indirect alcoholysis of urea. Therefore, in addition to the first RD column for PC synthesis, the second RD column to synthesize DMC by reacting PC and MeOH is also optimally designed in the study.

Fig. 3. Process flowsheet of RD configuration for PC synthesis in conjunction with RD column for DMC synthesis.

In the PC synthesis, urea is fed with the flow rate of 40 kmol/h and its reaction conversion is designed to be greater than 99.98 mol% in the following different process configurations. The purity of vapor ammonia removed from the partial condenser is designed at 99 mol% while the PC purity of column bottom is set at 99.5 mol%. There are some design and operation variables in the PC synthesis column. The design variables include the feed ratio of PG and urea reactants, the pressure of the RD column, the number of total stages, the stage numbers of the rectifying and reaction sections, and the locations of urea and PG feed stage. The operation variables include the condenser duty and the reboiler duty. Reboiler duty is varied to satisfy the PC product specification (99.5 mol%) at column bottom while condenser duty is changed to maintain the product purity of vapor ammonia at 99 mol% from column top.

In the DMC synthesis RD column, the product purity of bottom PG is set at 99.9 mol% while the reaction conversion of PC is set at 99.98 mol%. Design variables include feed ratio of MeOH and PC, number of total stages in the RD column, the feed stage of PC, and the feed stage of MeOH. The operation variables consist of reboiler duty and reflux ratio. Reboiler duty and reflux ratio are adjusted to satisfy the requirements of PG composition at column bottom and PC reaction conversion, respectively. The kinetic model and the thermodynamic model from Holtbrügge et al. (2013) are adopted in the RD column design for DMC synthesis. DMC and MeOH form a minimum-boiling homogeneous azeotrope. In the DMC synthesis reaction, sodium methoxide is used as a homogeneous catalyst to catalyze the reaction of PC and MeOH. Holtbrügge et al. (2013) specified that the homogeneous catalyst has a low solubility in the high-boiling reactant PC. In the study of Holtbrügge et al. (2014), PC reactant was fed above MeOH reactant into the RD column and this catalyst was fed along with MeOH stream. In the DMC synthesis column, there are large amounts of MeOH in the reflux stream. Therefore, in our study, this catalyst is selected to be fed into the reflux stream for mixing with MeOH and then returned to the RD column for catalyzing the reaction of PC and MeOH. DMC/MeOH mixture is recovered from the column top while high-purity PG with 99.9 mol% is withdrawn from the column bottom and recycled back to the PC synthesis column. DMC and MeOH can form an azoete trope and the azeotrope can be separated by extractive distillation or pressure swing distillation from our previous study (Wang et al., 2010) and some literatures (Wei et al., 2013; Zhang et al., 2017). Therefore, in the present study, the emphasis is not put on the separation of DMC and MeOH.

Fig. 3 also shows the optimal design with the minimal TAC by an optimization procedures. The optimal feed ratio of PG and urea is 1.02. High-purity (99.5 mol%) PC withdrawn from the bottom of the PC synthesis column is fed into the RD column for DMC synthesis. DMC/MeOH mixture is recovered from the top of DMC synthesis column while high-purity PG with 99.9 mol% is withdrawn from the column bottom and recycled back to the RD column for PC synthesis. The minimized TAC for the PC synthesis by the RD configuration, given in Table 1, is $973.4 \times 10^3$ US$/year. OC is almost ten times CC. Here CD denotes conventional distillation.

Table 1. TAC comparison of different configurations for PC synthesis

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Total CC</th>
<th>Total OC</th>
<th>TAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD</td>
<td>84.6</td>
<td>888.8</td>
<td>973.4</td>
</tr>
<tr>
<td>RD+CD HI1</td>
<td>220.2</td>
<td>835.3</td>
<td>1055.5</td>
</tr>
<tr>
<td>RD+CD HI2</td>
<td>196.6</td>
<td>674.2</td>
<td>870.8</td>
</tr>
<tr>
<td>RD+CD HI3</td>
<td>187.9</td>
<td>673.7</td>
<td>861.6</td>
</tr>
</tbody>
</table>

Cost unit = 10^3 US$/year

3.2 Excess Reactant Operation

In the above section, the optimal feed ratio of PG and urea is very close to one. In this section, we explore the process design with excess PG reactant in the RD column for PC synthesis. In this type of configuration, the bottom product, mainly containing PC and excess PG, of the RD column is introduced to a CD column for the separation of PC and PG. Heat integration between the RD and CD columns can then be implemented to reduce the energy consumption of the PC synthesis process by properly adjusting the pressures of RD and CD columns. In this study, three configurations of heat integrated RD+CD are proposed and their optimal designs are given below. Similar optimization procedures given in 3.1 section are also used in these heat integrated RD+CD configurations. Fig. 4 shows the first configuration of heat integrated RD+CD (named as RD+CD HI1). The overhead temperature of CD column is designed to be greater than the bottom temperature of the RD column. A minimum temperature difference of 10 K is ensured between the overhead vapor of the CD column and the bottom liquid of
the RD column. Then the latent heat of the overhead vapor from the CD column can be released to the reboiler of the RD column. In the RD column, design variables contain feed ratio of PG and urea, column pressure, number of total stages, stage numbers of the rectifying and reaction sections, and feed stages of urea and PG. Operation variables consist of condenser duty and reboiler duty in the column, used to satisfy the requirements of overhead ammonia product purity (99 mol%) and urea reaction conversion, respectively. In the CD column, design variables include column pressure, number of total stages and feed stage. Two operation variables, reflux ratio and reboiler duty, are varied to satisfy the product specifications of PG (98 mol%) and PC (99.5 mol%) at the column top and bottom, respectively.

The optimal design of RD+CD_HI1 configuration is also provided in Fig. 4. The overhead temperature of the high-pressure CD column and base temperature of the low-pressure RD column are 184.5 and 161.4 °C, respectively. The large temperature difference between these two temperatures insures that heat integration is a practical method to save energy consumption. The condenser duty of the CD column and the reboiler duty of the RD column are 1741.7 MJ/h and 5675.5 MJ/h, respectively. The condenser duty in the high-pressure CD column can be utilized to produce vapor in the RD column base, and an auxiliary steam-driven reboiler is needed with a duty of 3933.8 MJ/h. Similar DMC synthesis column to that in Fig. 3 is also given in Fig. 4. The minimized TAC of the RD+CD_HI1 configuration for PC synthesis, also given in Table 1, is 1055.5×10³ US$/year. In comparison with the RD configuration, the TAC is increased from 973.4×10³ US$/year for the RD configuration with almost neat operation to 1055.5×10³ US$/year for the RD+CD_HI1 configuration with excess reactant operation. The increased capital cost due to the addition of CD column is greater than the reduced operating cost due to the heat integration in the RD+CD_HI1 configuration.

![Fig. 4. Process flowsheet of RD+CD_HI1 configuration for PC synthesis in conjunction with RD column for DMC synthesis.](image)

Fig. 4. Process flowsheet of RD+CD_HI1 configuration for PC synthesis in conjunction with RD column for DMC synthesis.

In the CD column shown in Fig. 4, column top and bottom are all operated under high temperature. One of the methods to reduce energy consumption of the CD column is to operate it under low pressure. However, from the VLE relationship for PG-PC pair shown in Fig. 2, PC-PG pair can form a homogeneous minimum-boiling azeotrope near the pure PG end under low pressure. This indicates that using the CD column to separate these two components would require many stages or high energy consumption. Nevertheless, the azeotrope vanishes under high pressure. That is, much economical benefit can be achieved by operating bottom section of the CD column at low pressure and top section of the CD column at high pressure. This configuration is shown in Fig. 5 and is referred to as RD+CD_HI2. The CD column is divided into top and bottom sections. The overhead vapor of the bottom section is compressed by a compressor and used as a heating medium of the base of the top section. Therefore, the top section of the CD column can be operated under high pressure and temperature. The pressure of the top section can be manipulated such that overhead temperature of the CD column is greater than the base temperature of the CD column or the base temperature of the RD column. Therefore, heat integration can be implemented to save energy consumption by two different ways. The first way is to release the latent heat of overhead vapor to the reboiler in the CD column itself. If the condenser duty is greater than the reboiler duty, the additional latent heat can be released to the reboiler of the RD column. For the RD column in Fig. 5, the same design and operation variables as those in the RD+CD_HI1 configuration are used in the RD+CD_HI2 configuration. For the CD column, the pressure and stage number of top and bottom sections, respectively, are new design variables in the RD+CD_HI2 configuration.

![Fig. 5. Process flowsheet of RD+CD_HI2 configuration for PC synthesis in conjunction with RD column for DMC synthesis.](image)

Fig. 5. Process flowsheet of RD+CD_HI2 configuration for PC synthesis in conjunction with RD column for DMC synthesis.

The optimal design of the RD+CD_HI2 configuration is also given in Fig. 5. The overhead temperature of the high-pressure top section and base temperature of the low-pressure bottom section in the CD column are 195.0 °C and 151.2 °C, respectively. The condenser duty of the top section and the reboiler duty of the bottom section are 1100.2 MJ/h and 676.5 MJ/h, respectively. Thus, the latent heat of the top section can not only be released 676.5 MJ/h to the reboiler of the bottom section in the CD column but also released 423.7 MJ/h to the reboiler of the RD column. An auxiliary steam-driven reboiler is required with a duty of 5266.1 MJ/h in the RD column. The TAC of the optimal RD+CD_HI2 configuration for PC synthesis, given in Table 1, is 870.8×10³ US$/year. In comparison with the RD configuration, a 10.5 % reduction of TAC can be obtained for the RD+CD_HI2 configuration. In comparison with the RD+CD_HI1 configuration, TAC can be reduced by 17.5 % for the RD+CD_HI2 configuration because it takes full advantage of the characteristic of PC-PG VLE relationship by adding an internal compressor between top and bottom sections of the CD column.
In addition to the heat integration shown in Fig. 5, the overhead vapor of the top section in the CD column can release total latent heat to the reboiler of the RD column. This configuration is named as RD+CD_HI3. The optimization procedures for this configuration are almost the same as those for the RD+CD_HI2 configuration. Heat integration is implemented between CD top and RD bottom in the RD+CD_HI3 configuration. Fig. 6 shows the optimal design of this configuration. The TAC of this configuration, given in Table 1, is $861.6\times10^3$ US$/year. In comparison with the RD configuration, TAC can be reduced by 11.5 % for the RD+CD_HI3 configuration. In comparison with the RD+CD_HI1 configuration, a 18.4 % reduction of TAC can be obtained for the RD+CD_HI3 configuration. This RD+CD_HI3 configuration provides the most economic design for the PC synthesis in the plant-wide process to produce the final product DMC. In the following section, the control strategy of this most economic optimal process is investigated under feed flow disturbances.

Fig. 6. Process flowsheet of RD+CD_HI3 configuration for PC synthesis in conjunction with RD column for DMC synthesis.

4. CONTROL OF A PC SYNTHESIS PROCESS

For a RD column in the kinetic regime, the desired steady-state temperature or composition profile changes when feed rate changes and product purities are kept at their designed values (Wang et al., 2003). Fig. 7 gives the desired temperature profiles of the RD column for PC synthesis in Fig. 6 under ±10% feed flow changes. The temperature profile between stages 2 and 11 at nominal state is located below the temperature profiles between stages 2 and 11 under ±10% feed flow changes. In industrial applications, temperature control is usually used instead of composition control. The reason is that most product analyzers, such as gas chromatographs, suffer from large measurement delays and high investment and maintenance cost. To improve the control performance and have a faster mean of measuring the changes occurring in column during transient conditions, the feasibility of temperature control is investigated in this work by adding disturbances of changes in reactant feed rates. Hence there are three keys to controlling such a process: (1) to maintain the correct stoichiometric balance between the reactant feeds, (2) to maintain the product quality, (3) to account for possible changes in control objective when throughput rate changes. The product purity and stoichiometric balance between the reactant feeds must be maintained when operating a RD column. Feed ratio control is the simplest way to maintain stoichiometric balance and is then used in the study. In the Fig. 7, different reflux ratios are necessary to be designed in order to maintain overhead ammonia and bottom PC product purities. However, the top temperature is almost unchanged under different feed flow rates. Therefore, the flow rate of cooling water is manipulated to control the temperature of vapor withdrawn from the partial condenser. Fig. 8 shows the open-loop sensitivity analysis for the RD column of PC synthesis under ±0.1% changes of reboiler duty. Temperature at stage 10 gives the most sensitivity except top temperature and is then chosen as the controlled variable. In the RD column, the temperatures located at stage 1 and stage 10 are then controlled by manipulating cooling water and reboiler duty. However, from Fig. 7, the set point of bottom temperature loop needs to be changed under feed flow changes if bottom PC product purity is wanted to be maintained at its desired value. In the inventory control loops, RD column pressure is controlled by changing the overhead vapor flow. The reflux drum level and bottom level are maintained by varying reflux flow and bottom flow rates, respectively. In the control of the CD column, reflux ratio is controlled by changing distillate flow rate to maintain the overhead PG product purity. Fig. 9 gives the open-loop sensitivity analysis for the CD column under ±1% changes of reboiler duty. To maintain the bottom PC product purity, the temperature located at stage 7 in the bottom section is chosen as the controlled variable because of its most sensitivity to reboiler duty. In addition, the reflux drum level and bottom level are maintained by changing reflux flow and bottom flow rates, respectively.

Fig. 7. The desired temperature profiles of the RD column under different feed rates.

Fig. 8. Open-loop sensitivity analysis for the RD column under ±0.1% changes of reboiler duty.
feed flow changes, respectively. Controlled stage temperature is quickly increased and can be settled at its new set point. Bottom PC product purity can be operated at its desired value under temperature control. In the CD column, only small variations of overhead temperature and PG composition are observed under constant reflux ratio control. In the bottom temperature loop, the set point of the controlled stage temperature is unnecessary to be reset. The controlled stage temperature returns to its set point and bottom PC purity can be maintained at its designed value.

REFERENCES


