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Plant-Wide Control of Thermally Coupled Reactive Distillation to Co-Produce Diethyl Carbonate and Propylene Glycol

San-Jang Wang, Shueh-Hen Cheng, and Pin-Hao Chiu

***Abstract*—Diethyl carbonate is recognized as an environmentally benign chemical because of its negligible ecotoxicity and low bioaccumulation and persistence. There are several synthetic methods developed for producing diethyl carbonate. However, the major drawback of these methods was either a low yield of diethyl carbonate or the use of poisonous gas. Recently, a hopeful path supplying an excellent green chemical process to produce diethyl carbonate was developed by the transesterification of propylene carbonate with ethanol, coproducing useful propylene glycol. However, the transesterification reaction has an unfavorable reaction kinetic. Reactive distillation with excess ethanol reactant is selected in the study to increase reaction conversion and gain high-purity products. A conventional process, containing a reactive distillation column and a separation column for the purification of diethyl carbonate and ethanol is designed and optimized by minimizing the total annual cost. A thermally coupled reactive distillation process substantially reducing energy consumption is also developed. Furthermore, the temperature control strategies of the thermally coupled reactive distillation process are designed by a steady-state analysis for control purposes. Dynamic simulation results reveal that the proposed temperature control scheme can maintain not only reactant inventory but also product purities almost around their designed values.**

I. INTRODUCTION

Diethyl carbonate (DEC) is a versatile material because of its excellent chemical and physical properties. There are several synthetic methods developed to produce DEC. However, the major drawback of these methods was either a low yield of DEC or the use of poisonous gas. Recently, a promising method was developed to synthesize DEC and co-producing useful propylene glycol (PG) by the transesterification of ethanol (EtOH) and propylene carbonate (PC), produced by the reaction of carbon dioxide and propylene epoxide. The transesterification reaction provides an excellent green chemical process which changes the waste greenhouse gas (carbon dioxide) into the valuable chemical with a zero-discharge and a 100% atom economy. Therefore, this transesterification reaction is selected in the study to synthesize DEC.

Process intensification is a design philosophy that deliberately integrates different processes into a single operation to reduce energy consumption and capital investment, as well as achieve environmental and safety benefit. It represents an important trend in chemical engineering and process technology and has attracted increasing attention in the industry and research community. Reactive distillation (RD) and thermally coupled distillation are two promising technologies achieving substantial economical benefits from process intensification. The transesterification reaction of PC and EtOH is a typically equilibrium-limited one. RD with an excess reactant is adopted in the study to increase reaction conversion and gain high-purity products. A conventional separation column following the RD column is necessary to purify DEC and excess reactant, which is then recycled back to the RD column. Thermally coupled RD technology is then utilized between the RD column and the conventional separation column to design the plant-wide RD process for the DEC synthesis. Finally, the control strategy of the thermally coupled RD process will also be explored.

II. PLANT-WIDE DESIGN OF THE CONVENTIONAL RD PROCESS

The transesterification reaction of PC and EtOH is proceeded as follows:

$$\mathrm{PC} + 2\mathrm{EtOH} \rightleftharpoons \mathrm{DEC} + \mathrm{PG} \tag{1}$$

The yield for the transesterification reaction is strongly limited by the equilibrium conversion and can be catalyzed by a homogeneous catalyst, sodium ethoxide. The kinetic equation can be expressed as,[1]

$$r_{PC} = 1.9689 \cdot 10^4 \cdot \exp\left(\frac{-31293}{RT}\right) \cdot C_{PC} - 9.7868 \cdot 10^8 \cdot \exp\left(\frac{-48156}{RT}\right) \cdot \frac{C_{DEC} \cdot C_{PG}}{C_{EtOH}{}^2} \tag{2}$$

where r_{PC} is the reaction rate of PC (mol $\mathrm{L^{-1} \cdot min^{-1}}$) and C_i is the concentration of the i component (mol $\mathrm{L^{-1}}$). The concentration of the homogeneous catalyst is assumed to be 1 wt%.

The simulation of the transesterification distillation is carried out using the rigorous distillation model provided by ChemCad software. To account for the nonideality in the vapor-liquid equilibrium relationship, UNIQUAC model is used for activity coefficients. There are six binary pairs in the reaction system. The UNIQUAC parameters for EtOH-PG pair are given from the ChemCad data bank. The UNIQUAC parameters for PC-PG and EtOH-DEC pairs are calculated by

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regressing the vapor-liquid equilibrium data in Mathuni et al.[2] and Rodriguez et al.,[3] respectively. The phase equilibrium data of the other missing pairs (PC-EtOH, PC-DEC, and DEC-PG) in literature are determined experimentally in the present study. The UNIQUAC parameters for these three pairs are regressed from the experimental vapor-liquid equilibrium data. The chemical kinetic and thermodynamic models are used to design the RD process for DEC synthesis.

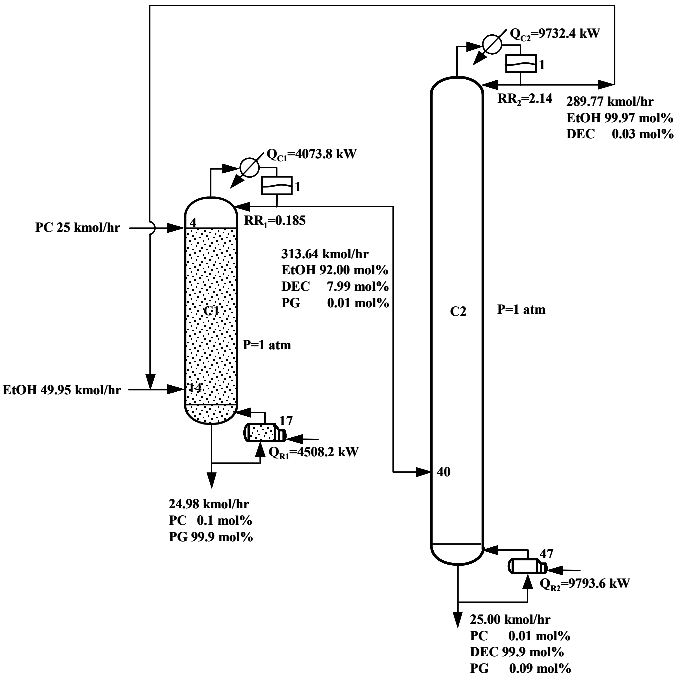


Figure 1. Flowsheet of a conventional RD process for DEC synthesis by the transesterification of PC and EtOH.

In the design of the RD process, the objective is to minimize the TAC by adjusting the design parameters in the distillation column. The TAC is defined as:

$$\text{TAC} = \text{operating cost} + \frac{\text{capital cost}}{\text{payback year}} \tag{3}$$

Here, a payback of three years is used. Fig. 1 shows the flowsheet of the conventional RD process with a RD column and a separation column. There are only rectification and reaction zones in the RD column. The high-boiling reactant, PC, and the homogeneous catalyst (sodium ethoxide) are fed into the top of reaction zone and the low-boiling reactant, EtOH, is fed into a tray below the PC feed tray in order to enhance their contact. The column trays below the PC feed location are all reactive trays. The feed rate of the reactant PC is set at 25 kmol/hr. The reactant EtOH with 49.953 kmol/hr is initially fed into the RD column in a near stoichiometric ratio. DEC and PG are produced in the reaction zone. However, a low reaction conversion is observed and high-purity PG can not be obtained at the column bottom. In the reaction system, two reactants are the lightest and heaviest components, respectively. This means that the reaction system has the least favorable relative volatility ranking (products are intermediate keys) for a RD column and the reactants are much more easily removed from the reaction zone in the RD column than the products. To increase the reaction conversion of PC and prevent PC from being withdrawn from the column bottom, excess EtOH is fed into the column to react away almost the PC toward the column bottom. High-purity PG with 99.9 mol% can then be obtained at the column bottom. The distillate product is a mixture containing mostly DEC and un-reacted EtOH. The DEC/EtOH mixture is then fed to a separation column. High-purity EtOH (99.97 mol%) and DEC (99.9 mol%) are produced in the column distillate and the column bottom, respectively. The overhead EtOH is recycled back to the RD column. The RD column and separation column are both operated at 1 atm.

There are many design and operation variables in the RD column shown in Fig. 1. The design variables include the total number of trays and the PC and EtOH feed tray locations. Because the PC reactant and the homogeneous catalyst are fed to the same tray, the number of trays in the rectification and reaction zones in the RD column can be determined from the total number of trays of the RD column and PC feed tray location. The operation variables include the reflux ratio, the reboiler duty, and the EtOH recycled flow rate. Reaction conversion should be considered in the design of the RD column in order to obtain high-purity products from the RD process. The reflux ratio is varied to insure PC reaction conversion at 99.9%. The reboiler duty is adjusted to satisfy the PG product specification at the column bottom. Sufficient EtOH reactant is necessary to be fed into the RD column in order to satisfy the specifications of both reaction conversion and product purities. Therefore, three degrees of freedom (total number of trays, PC and EtOH feed tray locations) in the RD column are available for minimizing the TAC. In the separation column, the design variables include the total number of trays and the feed tray location. The operation variables include the reflux ratio and the reboiler duty. The reflux ratio and reboiler duty are changed to satisfy the overhead and bottom product specifications, respectively. Therefore, two degrees of freedom (total number of trays and feed tray location) in the separation column are available for minimizing the TAC. Thus a total of five variables can be changed to find the optimal design. The total TAC of the RD process is at the minimum (\$$2.645\times10^6$ per year) when NT_1, $NF_{1,PC}$, and $NF_{1,EtOH}$ in the RD column are 17, 4, and 14, respectively, and when NT_2 and NF_2 in the separation column are 47 and 40, respectively. The corresponding TACs of the RD column and separation column are \$$9.208\times10^5$ per year and \$$1.724\times10^6$ per year, respectively. The reboiler duties of the RD column and separation column are 4508.2 kW and 9793.6 kW, respectively, under the optimal condition. The corresponding reflux ratios of the RD column and separation column are 0.185 and 2.14, respectively. Fig. 1 also gives the stream information and optimal condition for the conventional RD process.

III. DESIGN OF THE THERMALLY COUPLED RD PROCESS

In order to reduce energy consumption, thermal coupling of the RD column and the separation column is explored. Without loss of generality, the same numbers of trays are used for the processes without and with thermal coupling. Liquids and vapors are directly interchanged between the RD column and the separation column. One condenser can be reduced by implementing thermal coupling. The thermodynamically equivalent configuration of the thermally coupled RD process is given in Fig. 2. It consists of a RD column and a side stripper column. The high-boiling product, PG with a purity 99.9 mol%, is withdrawn from the bottoms of the RD column. High purity EtOH (99.97 mol%) is distilled from the top of the RD column and recycled back to the fresh EtOH feed location in the RD column. Part of the liquid from the RD column is fed to the side stripper column for the purification of the DEC. Vapor from the top of the side stripper column is totally fed to the RD column. High purity DEC with 99.9 mol% is obtained from the bottom of the side stripper column.

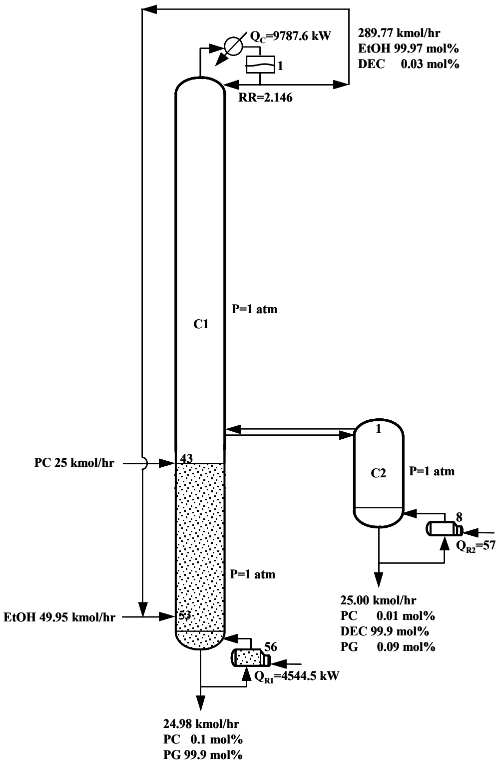
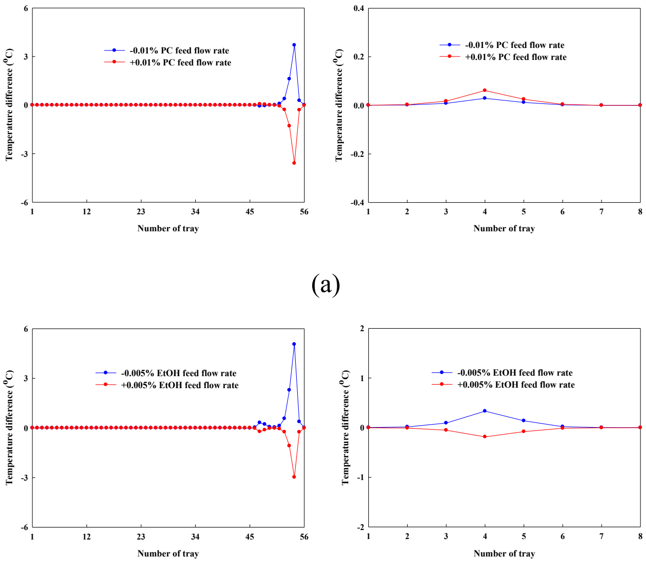


Figure 2. Configuration of the thermally coupled RD process.

There are four design degrees of freedom in the thermally coupled RD process shown in Fig. 2: two reboiler duties, the reflux ratio of the RD column, and the liquid split ratio (LSR). The LSR is specified as the ratio of the liquid flow directed to the RD column to the liquid flow directed to the side stripper column. The two reboiler duties and the reflux ratio are adjusted to satisfy the product specifications of PG, DEC, and EtOH from the three outlet streams. The LSR is used to minimize the total reboiler duty of the process. The reboiler duties of the RD column and side stripper column are 4544.5 kW and 5738.5 kW, respectively, under the optimal condition of a LSR of 9.12. The reflux ratio of the RD column is 2.146. The reboiler duty (9793.6 kW) of the separation column in the conventional RD process can be substantially reduced by implementing the thermal coupling between the RD column and the separation column while there are only small variations in the reboiler duty of the RD column. The thermally coupled RD process could save about 28.1% of the total reboiler duty of the RD process without thermal coupling. Fig. 2 also gives the stream information and operating condition for the thermally coupled RD process.

IV. PLANT-WIDE CONTROL OF THE THERMALLY COUPLED RD PROCESS

There are three keys to controlling a RD column: (1) to maintain the correct ratio between the reactant feeds, (2) to maintain the product quality, (3) to account for possible changes in control objective when throughput changes. The ratio between the reactant feeds must be maintained when operating a RD column. Feed ratio control is the simplest way to maintain the balance. However, the feed-ratio control scheme will not be able to keep the desired feed ratio when there is a measurement bias in feed flow rate. To overcome this problem, Al-Arfaj and Luyben[4] suggested that the reactant composition of some column tray be controlled by the reactant feed flow. However, most product analyzers, such as gas chromatographs, suffer from large measurement delays and high investment and maintenance cost. Temperature control is usually used instead of composition control in industrial applications. Hence, the internal composition loop is replaced in the study by an internal temperature loop. PC and EtOH feed flows are two candidates for the manipulated variable of the internal temperature control to maintain feed ratio control.

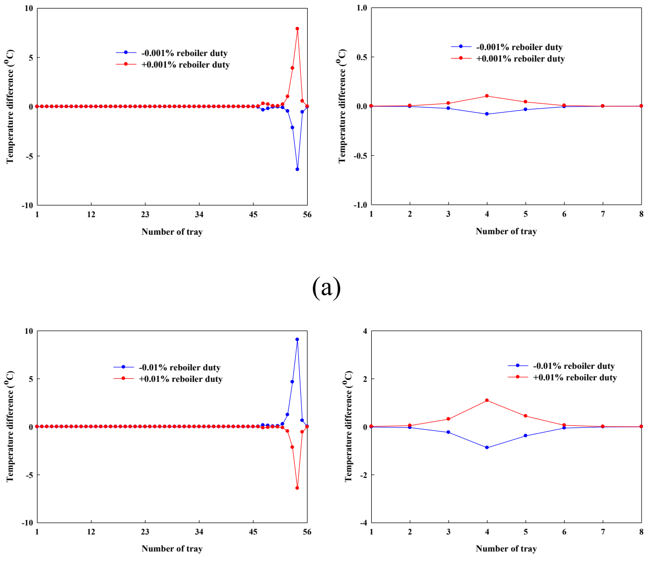


(a)

(b)

Figure 3. Open-loop sensitivity analysis between tray temperatures and feed flow rates of (a) PC reactant and (b) EtOH reactant, respectively, in the thermally coupled RD process.

RD often exhibits input multiplicities, which increases the difficulties of operation and control. Input multiplicity occurs when two or more sets of input variables produce the same output variable. With reference to control structures, input variables are those that can be manipulated by control valves or other actuating devices. Output variables are those that are either controlled or measured to describe the process conditions. Hence the internal tray temperature selected should have a near linear relationship without multiplicity and a sufficient sensitivity with respect to the feed flow rate. Fig. 3 shows the open-loop sensitivity analysis between tray temperatures and feed flow rates of PC reactant and EtOH reactant, respectively, in the thermally coupled RD process. Input multiplicity appears just around the nominal operating point between PC feed and temperatures of trays 3 to 5 in the side stripper column. However, there is no input multiplicity between EtOH and tray temperatures in the thermally coupled RD process. Wang et al.[5] showed that interaction multiplicity is one of the most important factors to be considered in selecting the manipulated variable. The tray temperatures with input multiplicity or interaction multiplicity with manipulated variables should not be used as controlled variables to avoid the problem of control stability. Therefore, EtOH feed flow is chosen as the manipulated variable in the temperature loop to maintain the correct feed ratio.

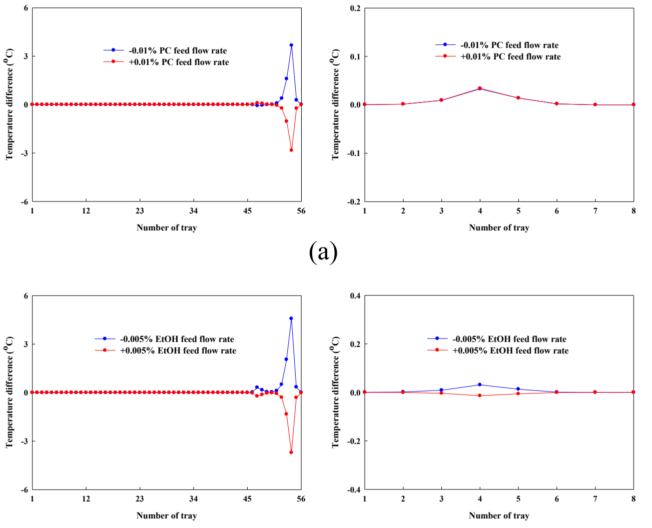


(a)

(b)

Figure 4. Open-loop sensitivity analysis between tray temperatures and reboiler duties of the (a) RD column and (b) side stripper column, respectively, in the thermally coupled RD process.

To maintain high-purity PG and DEC at the bottoms of the RD column and side stripper column, respectively, two temperature loops can be used, in which two tray temperatures are maintained by manipulating the reboiler duties of the two columns. Fig. 4 shows the open-loop sensitivity analysis between tray temperatures and reboiler duties of the RD column and side stripper column, respectively, in the thermally coupled RD process. No input multiplicity is observed between tray temperatures and these two reboiler duties. In the RD column with thermal coupling, the specification of overhead EtOH purity also needs to be satisfied in addition to the bottom PG purity. Instead of controlling both product purities of the column by temperature loops, it may be possible in some processes to only control one product and over-purify the other product. Single-end control is simpler and easier to tune and gives faster response than double-end control because of the reduced interaction among the control loops. Hence simple constant reflux-ratio control may be sufficient to maintain top EtOH of the RD column.



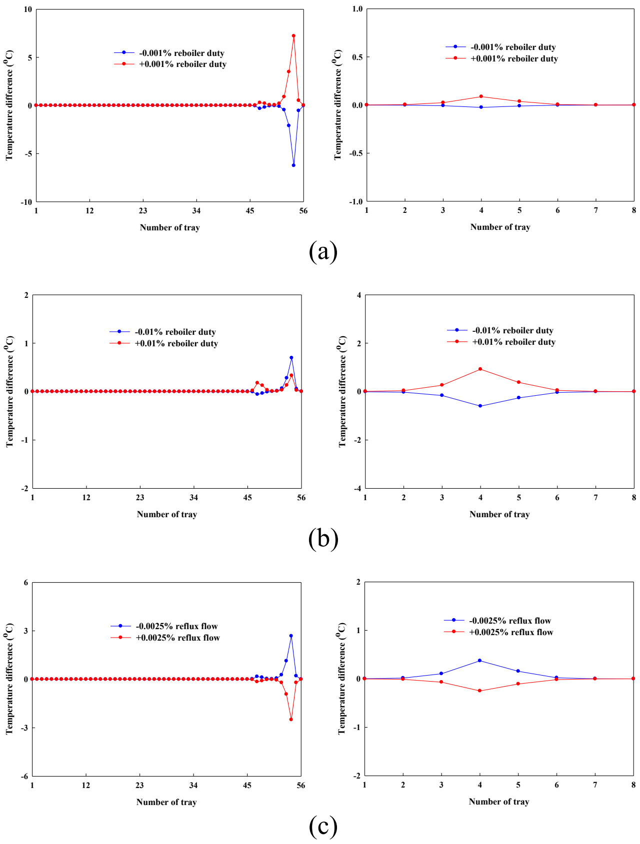
(a)

(b)

Figure 5. Open-loop sensitivity analysis between tray temperatures and feed flow rates of (a) PC reactant and (b) EtOH reactant, respectively, in the thermally coupled RD process.

To investigate the regulation effect of more temperatures in the RD column on control performance, the temperature control with reflux flow as a manipulated variable is used in place of constant reflux-ratio control in the RD column top. Open-loop sensitivity analysis is also used to search for suitable controlled variables in temperature loops. Fig. 5 shows this analysis between tray temperatures and feed flow rates of PC reactant and EtOH reactant, respectively, in the thermally coupled RD process. Input multiplicity appears just around the nominal operating point between PC feed flow rate and almost all the tray temperatures in the side stripper column. However, there is no input multiplicity between EtOH feed flow rate and tray temperatures in the thermally coupled RD process. Therefore, EtOH feed flow is chosen as the manipulated variable in the temperature loop to maintain the correct feed ratio. Fig. 6 shows the open-loop sensitivity analysis between tray temperatures and reboiler duty of the RD column, reboiler duty of the side stripper column, and reflux flow rate of the RD column, respectively, in the thermally coupled RD process. No input multiplicity is observed between tray temperatures and reboiler duty of the RD column or tray temperatures and reflux flow of the RD column. However, input multiplicity is observed between those tray temperatures near the RD column bottom and reboiler duty of the side stripper column. This phenomenon doesn't exist in Fig. 4b when reflux ratio is kept constant. Difficulties of operation and control are increased due to the input multiplicity when reflux flow rate is used as the manipulated variable in the temperature loop of the RD column top. In addition to input multiplicity, very low sensitivity is observed between those tray temperatures near the RD column top and reflux flow rate. High sensitivity but slow response speed is seen between the tray temperatures near the RD column bottom and reflux flow rate. These results reveal that top temperature loop in the RD column is improper to be used in the DEC synthesis process.

Hence simple constant reflux-ratio control was utilized in the study to maintain high-purity EtOH at the top of the RD column.



(a)

(b)

(c)

Figure 6. Open-loop sensitivity analysis between tray temperatures and (a) reboiler duty of the RD column, (b) reboiler duty of the side stripper column, and (c) reflux flow rate of the RD column, respectively, in the thermally coupled RD process.

TABLE I. RGA analysis for the thermally coupled process

	m_1	m_2	m_3
T_{47_1}	-5.16	0.55	**5.61**
T_{54_1}	**5.78**	-1.22	-3.56
T_{4_2}	0.38	**1.67**	-1.05

To select the most appropriate location for temperature control in the thermally coupled RD process, singular value decomposition (SVD) method[6] is used in the study. This method requires a steady-state gain matrix. These steady-state gains are calculated from the open-loop sensitivity analysis given in Figs. 3 and 4. The controlled temperatures are selected at trays 47 (T_{47_1}), 54 (T_{54_1}) of the RD column, and tray 4 (T_{4_2}) of the side stripper column by the SVD method. Table I shows the relative gain array (RGA) analysis of these controlled tray temperatures and manipulated variables. m_1, m_2, and m_3 represent the reboiler duty of RD column, reboiler duty of side stripper column, and EtOH feed flow respectively. The control loop pairing is that the temperatures at trays 47 and 54 in the RD column and tray 4 in the side stripper column are controlled by manipulating the EtOH feed flow, reboiler duty of the RD column, and reboiler duty of the side stripper column, respectively.

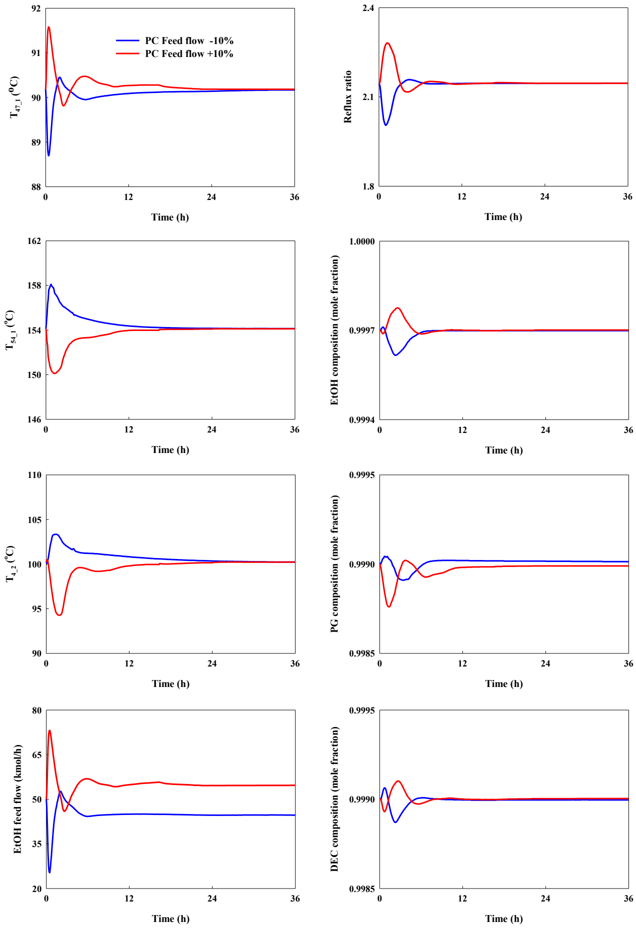


Figure 7. Dynamic responses of controlled tray temperatures, product purities, EtOH feed flow, and reflux ratio under temperature control + constant reflux-ratio control for ±10% changes in PC feed flow.

In the following discussions on control performance, the controllers are tuned using a sequential design approach[7] after the pairing is determined. For each controller, relay-feedback test[8] is performed to obtain ultimate gain and ultimate frequency. The following equations are used to calculate the tuning parameters of PI controllers:

$$K_C = K_{CU}/3 \tag{4}$$

$$T_I = P_U/0.5 \tag{5}$$

where K_C and T_I represent proportional gain and integral time, respectively, and K_{CU} and P_U are ultimate gain and ultimate period, respectively. In the control configuration of the thermally coupled RD process, three temperature control loops are designed by the above steady-state analysis. In the RD column, column pressure is controlled by manipulating coolant flow rate. Reflux-drum level and base level are maintained by changing reflux flow rate and bottom flow rate, respectively. Constant reflux ratio is controlled by manipulating distillate flow rate to maintain the overhead EtOH purity. Liquid split ratio is maintained by a liquid flow distributor. The PC feed is flow controlled. In the side stripper column, the base level is maintained by changing bottom flow rate. In the distillation control system, pressure, level, and flow control belong to inventory control maintaining the basic column operation. Thus in the following discussion, emphasis is placed on the response of temperature control + constant reflux-ratio control strategy used to maintain product quality and feed ratio.

Fig. 7 shows the dynamic responses of controlled tray temperatures, product purities, EtOH feed flow, and reflux ratio under temperature control + constant reflux-ratio control for ±10% changes in PC feed flow. The controlled tray temperatures are settled at their corresponding set points. Feed ratio and reflux ratio are also maintained at their corresponding designed values. Only very small steady-state offset is observed in the PG product composition at the bottoms of the RD column. EtOH and DEC product compositions can almost return to their desired operating values under the proposed control strategy.

V. CONCLUSIONS

In the study, a promising route is utilized to synthesize DEC by the transesterification of PC and EtOH. However, the transesterification reaction is a typically equilibrium-limited one and has the least favorable relative volatility ranking (products are intermediate keys) for a RD column. Therefore, a RD process consisting of a RD column with a large excess of reactant EtOH and a separation column is used to gain high PC reaction conversion and high-purity products. The optimal RD process is designed by minimizing the total TAC. A thermally coupled RD process is also derived by interchanging liquid and vapor between these two columns. Steady-state simulation results demonstrate that the process with thermal coupling provides a much more economical design than the process without thermal coupling.

In developing the control scheme, temperature control strategies are designed by using steady-state analysis for the thermally coupled RD process. EtOH feed having no input multiplicity with tray temperatures is used to maintain the reactant feed ratio in the RD column. The placement of temperature sensors is analyzed by the SVD method and the pairing of manipulated and controlled variables is done by using the RGA analysis. Dynamic simulation results reveal that the temperature control + constant reflux-ratio control scheme can maintain not only reactant feed ratio but also product purities at or around their desired values in face of the changes in reactant feed rate.

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