



Optimization and control of a reactive distillation process for the synthesis of dimethyl carbonate☆



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ABSTRACT

Dimethyl carbonate is an environmentally benign and biodegradable chemical. Based on integration of reactive distillation and pressure-swing distillation technologies, a novel process for synthesis of dimethyl carbonate through transesterification with propylene carbonate and methanol has been developed by Huang *et al.* In this work, the optimization of this process was performed by minimizing the total TAC. The results show that the optimal design flowsheet can save energy consumption by 18.6% with the propylene carbonate conversion of 99.9%. Then, an effective plant-wide control structure for the process was developed. Dynamic simulation results demonstrate that the temperature/flow rate cascade control plus with simple temperature control can keep not only product purity but also the conversion of the reactant at their desired values in the face of the disturbance in reactant feed flow rate and feed composition.

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1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign and biodegradable chemical, and it has been widely used in the chemistry industry as a substitute to replace dimethyl sulfate and methyl halides in methylation reactions, or as a carbonylation agent in carbonylation reactions [1]. In addition, DMC also has been used an additive to fuel because of its high oxygen content and octane number [2]. So DMC has attracted substantial research efforts in recent years. There are several ways to prepare DMC, such as the methanolysis of urea [3] and direct synthesis of DMC from propylene carbonate (PC) and methanol (MeOH) [4]. However, urea methanolysis to DMC suffers from some problems including low production selectivity and high molar ratio of methanol to urea [5]. Although the direct production of DMC by reacting PC and MeOH is limited by the unfavorable equilibrium constant, a high conversion of PC still can be achieved by using reactive distillation method, because reaction products can be removed continuously from the reactive zone and thus conversion can be increased far beyond what is expected by the equilibrium. In the transesterification reaction of ethyl carbonate and methanol, the recent papers by Fang and Xiao [6] and Hsu *et al.* [7] reported that the completion conversion of the limiting reactant could be achieved by using reactive distillation.

But in the transesterification reaction of PC and MeOH, the products are DMC and propylene glycol (PG). The former can form a homogeneous azeotrope with the reactant MeOH, so the overhead of the

reactive distillation column will be a dimethyl carbonate and methanol mixture that is a challenge for the purification of dimethyl carbonate. Therefore, further separation of the mixture DMC and MeOH is needed. In order to break the dimethyl carbonate and methanol azeotrope, several techniques have been proposed, such as adsorption separation [8], extractive distillation [5,7,9], low temperature crystallization [10], pressure swing distillation [11,12], and membrane pervaporation [13,14]. Among these methods, pressure swing distillation is considered as one of the most effective and environmental friendly processes. The dynamic simulation and control of pressure swing distillation systems for separating azeotropes have been investigated and evaluated in a lot of research papers [15–19]. Wei *et al.* explored the pressure swing distillation systems for separation of DMC/MeOH and proposed an optimized separation configuration based on the global economic analysis [12]. Li *et al.* simulated and analyzed the process of separation of DMC and MeOH, including a high-pressure distillation column and an atmospheric distillation column in series [20].

In our previous works, the integration of the reactive distillation and the separation of the DMC/MeOH mixture were investigated, and a novel energy saving process for the synthesis of DMC was proposed [21]. This new process with a reactive distillation column and a high-pressure distillation column can save energy by 29.50% compared with the traditional process. However, the feed molar ratio of MeOH to PC is much higher than that of stoichiometric ratio in the transesterification reaction, which means that more energy is required to recover excess methanol. Furthermore, the dynamic characteristic of this process hasn't been investigated.

In this paper, optimization and control of the procedure for the synthesis of dimethyl carbonate by reactive distillation were carried out. First, the optimal flowsheet was obtained by minimizing the total annual cost (TAC) of the system. Then, the control strategy of this process with

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heat integrated was explored and its required control performance was discussed through varying feed flow rate and feed composition.

2. Reaction Kinetic and Thermodynamic Model

2.1. Reaction kinetic

The transesterification of PC with MeOH, using homogeneous or heterogeneous catalysts, has already been investigated [6,22,23]. Even though many catalysts are suitable for this reaction, sodium methoxide is still a promising candidate in the current industrial application since it possesses higher activity compared with other catalysts. Moreover, its reaction temperature is relatively mild. The liquid-phase reversible transesterification reaction considered is.



The kinetics for the forward and reverse reactions catalyzed by sodium methoxide are based on those given by Zhang [22].

$$r = k_F C_{\text{PC}} C_{\text{MeOH}} - k_R \frac{C_{\text{DMC}} C_{\text{PG}}}{C_{\text{MeOH}}}$$

$$k_F = 16551.8 \exp\left(\frac{41373.5}{RT}\right)$$

$$k_R = 19254.75 \exp\left(\frac{28285.5}{RT}\right)$$

where r is the reaction rate of PC ($\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$), C_i is the concentration of the i component ($\text{mol} \cdot \text{L}^{-1}$), R is gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is temperature (K).

2.2. Thermodynamic model

The phase equilibrium of this reaction system is complex due to the existence of a binary azeotrope mixture of DMC and MeOH. In order to accurately describe the phase equilibriums of the system, UNIQUAC model is used and its parameters are obtained to fit the vapor–liquid data. The experimental data for the pair of MeOH/DMC were obtained from literatures [24]. The vapor–liquid equilibrium data for the pairs of DMC/PC and DMC/PG were obtained from literature [25]. The model parameters of MEOH/PG and all other physical properties were obtained directly from Aspen Plus. Table 1 summarizes the UNIQUAC binary interaction parameters used in the simulation. The calculated boiling points of pure components and azeotropic compositions by using UNIQUAC model are presented in Tables 2 and 3, respectively, which indicates that the UNIQUAC model is suitable for this system.

Table 1
UNIQUAC model parameters for the DMC process

i	MeOH	DMC	DMC	PG	MeOH	MeOH
j	DMC	PC	PG	PC	PG	PC
a_{ij}	−0.201	0	0	0	0	0
a_{ji}	0.273	0	0	0	0	0
b_{ij}	14.87	172.470	−209.529	−301.778	−278.494	49.94
b_{ji}	−306.55	−216.199	−9.027	142.266	143.444	−244.595

Table 2
Boiling points of pure components at atmospheric pressure

Component ID	Component name	Temperature/K
MeOH	Methanol	337.68
DMC	Dimethyl carbonate	363.37
PC	Propylene carbonate	514.97
PG	Propylene glycol	460.87

Table 3

Comparisons of predicted and experimental azeotrope for MeOH/DMC at different pressures

Pressure/kPa	Predicted value		Experimental value [24]	
	T_b/K	Mass fraction	T_b/K	Mass fraction
101.3	336.80	(0.7007, 0.2993)	337.35	(0.7000, 0.3000)
405.2	377.18	(0.7910, 0.2090)	377.15	(0.7929, 0.2071)
607.8	391.10	(0.8240, 0.1760)	391.15	(0.8249, 0.1751)
1013.0	410.28	(0.8713, 0.1287)	411.15	(0.8761, 0.1239)
1519.5	426.94	(0.9677, 0.0323)	428.15	(0.9300, 0.0700)

3. Steady-state Optimization

3.1. Reactive distillation process

The process for the production of DMC by reactive distillation is shown in Fig. 1. In this flowsheet, the reactant PC (stream F1) is fed into the top part of the reaction section, and the fresh MeOH (stream F2) and a recycled stream rich in MeOH are fed into the bottom and middle of the reaction section, respectively. The top product of the reactive distillation (RD) column is a mixture of product DMC and unreacted MeOH, while co-product propylene glycol leaves out the bottom of the RD column. The distillate of the RD column is fed into the high pressure (HP) column, which produces high-purity DMC in the bottoms and a distillate stream whose composition is near that of the azeotrope. The distillate (stream R1) is recycled back to the RD column. Due to the very low catalyst concentration (about 0.15 wt%), the catalyst component was ignored in the simulation for simplification.

Based on the industrial data provided by Feiyang Chemical Co., Ltd. (in China), a detail simulation was performed in our previous study [21]. The results indicate that the proposed process is feasible for the synthesis of DMC. However, the feed molar ratio of MeOH to PC ($\approx 5.6:1$) is much higher than that of stoichiometric ratio in the transesterification reaction and the PC conversion is not very high (about 96.5%), which means that more energy is required to further purify the co-product PG and recover excess methanol. Hence, in this study the feed molar ratio will be optimized while ensuring the desired PC conversion rate of 99.9% and the desired DMC purity of 99.5 mass%. Since the solubility of sodium methylate in the PC or PG is relative low, sodium methylate is dissolved in the methanol firstly and then is introduced into the RD column with PC. To avoid clogging pipes or internals in the RD column due to the crystallization of the sodium methylate, the mass concentration of MeOH in the fresh PC feed is another constrain.

There are many design variables needed to be optimized in this process. In the RD column, such design variables involve the total number of trays (N_{RD}), PC feed location (NF_1), MeOH feed location (NF_2), and recycle stream feed location (NF_R). For the HP column, the total number of trays (N_{HP}) and the feed location (NF_{HP}) also need to be optimized. Moreover, the operating pressure is an important process parameter for the distillation system. Zhang *et al.* found that the transesterification of PC and MeOH is an exothermic reaction and the optimum reaction temperature ranges from 333.2 to 341.2 K [22]. And the transesterification reaction mainly takes place on the 5th stage (as shown in Fig. 4). When the RD column is operating at atmospheric pressure, the temperature on the 5th stage is 339.2 K. So the RD column is operating at atmospheric pressure in this work. Note that all produced dimethyl carbonate that leaves the reactive section zone goes at the top of the RD column with the methanol. And the HP column that is used to separate dimethyl carbonate from methanol produces high-purity dimethyl carbonate in the bottom and produces a distillate that has a composition near the azeotropic composition. The composition of the azeotrope (DMC/MeOH) varies with the change of pressure. If the HP column is operating at high pressure, the methanol recycled

In the same way, $D_{2, \text{DMC}}$ is estimated by Eq. (5).

$$D_{2, \text{DMC}} = \frac{D_{1, \text{MeOH}}}{m_2} \times (1 - m_2) \quad (5)$$

where m_2 is the mass composition of MeOH in the recycle stream.

Thus, the procedure to estimate the flow rate of the recycle stream between the RD and HP columns is described as follows:

- (1) Give the mass composition of MeOH in the recycle stream (m_2) and suppose $D_{2, \text{DMC}}$ is equal to 0.
- (2) The amount of DMC in the distillate of the RD column is computed with Eq. (2).
- (3) The amount of MeOH in the distillate of the RD column is calculated using Eq. (3).
- (4) The mass flow rate of the recycle stream is calculated with Eqs. (4) and (5).
- (5) Go back to the step 2, repeat steps (2)–(4) until the calculated values ($D_{2, \text{DMC}}$ or $D_{2, \text{MeOH}}$) remain unchanged.

Once the values of $D_{1, \text{DMC}}$, $D_{2, \text{DMC}}$, $D_{2, \text{DMC}}$, and $D_{2, \text{MeOH}}$ are determined, the distillates of the RD column and the HP column (D_1 and D_2) are easy to be obtained.

3.3. Optimization

Note that the variable m_2 is the most sensitive design variable in terms of TAC optimization, because it determines the amount of the recycle stream and the difficulty of separating in the HP column and thus affects the energy consumption of the entire system. So, the optimization of m_2 was set at the outmost iterative loop. Another issue that needs to be addressed is that during each simulation run the holdup in the reactive tray must be iteratively estimated to consist with the one obtained from the tray sizing calculation. The detail optimization procedure is presented in Fig. 2.

By using above iterative optimization procedure, the values of the design variables were found: feed location of the RD column, total stages of the RD column, feed location of the HP column, and total stages

of the HP column. The effects of variables on TAC are displayed in Figs. 3 and 4. Because the overhead vapor at the top of the HP column can be used as the heat source of the reboiler of the RD column, the TAC of the RD column does not include energy cost and reboiler cost and thus is significantly lower than the TAC of the HP column (Table 5). The resulting optimal flow sheet with flow and composition is shown in Figs. 1 and 5 shows component generation amounts profile in the RD column, and the corresponding temperature and vapor composition profiles are presented in Fig. 6. Note that the feed molar ratio of MeOH to PC is 2.61:1 and close to stoichiometric ratio in the transesterification reaction. The conversion of PC under optimal conditions reached as high as 99.9% and energy saving of 18.6% was achieved compared to the result given in the literature [21].

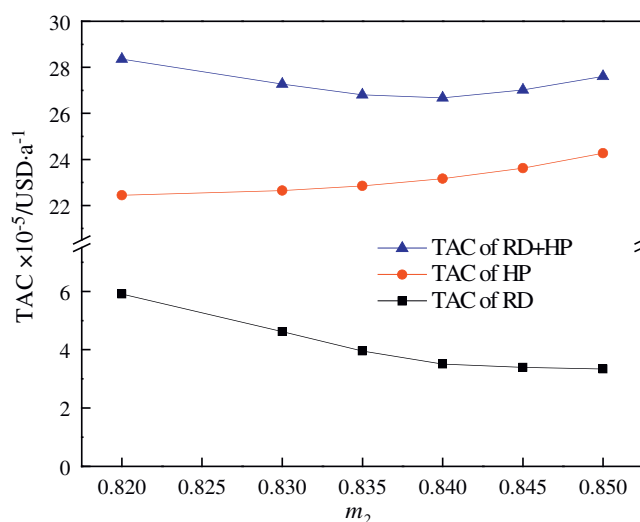


Fig. 3. Effect of the MeOH composition (m_2) in the recycle stream on the TAC.

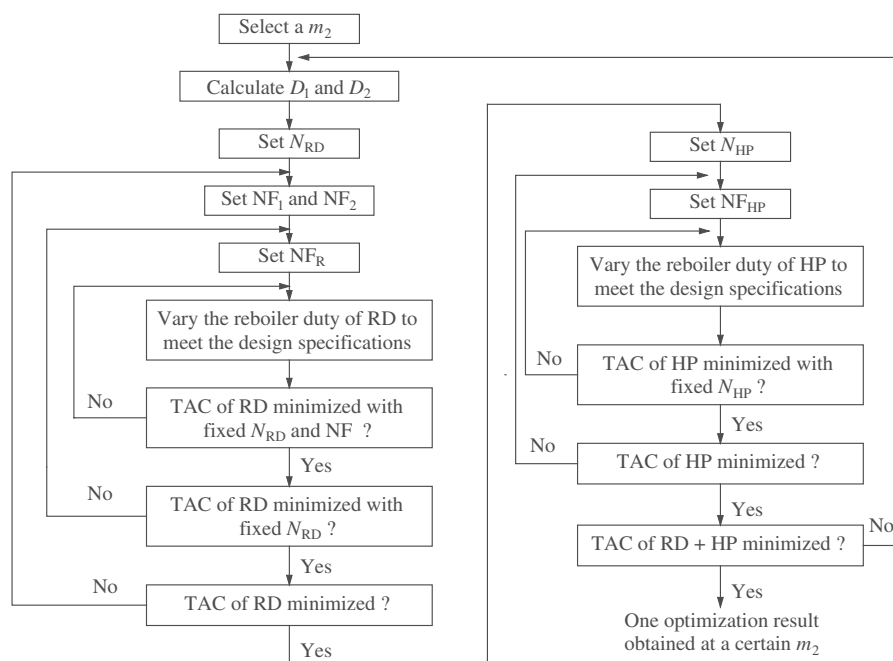


Fig. 2. Sequential iterative optimization procedure.

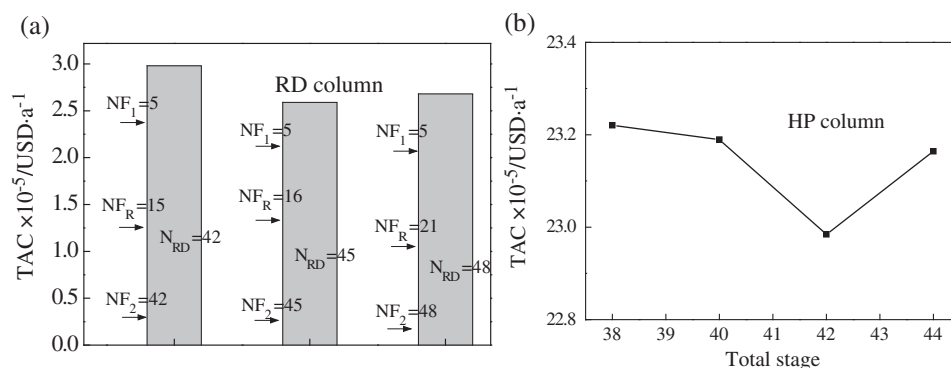


Fig. 4. Relationship between TAC and design variables: (a) RD and (b) HP column.

Table 5
Column specifications for original and optimal designs

	Original design [21]		Optimized design (This work)	
	RD	HP	RD	HP
Total stage	35	23	45	42
Pressure/MPa	0.1	1.1	0.1	1.1
Feed stage	$NF_1 = 10$ $NF_2 = 30$ $NF_R = 30$	$NF = 10$	$NF_1 = 5$ $NF_2 = 45$ $NF_R = 16$	$NF = 33$
Reflux ratio	2.34	2.5	0.87	1.37
Condense duty/MW	8.03	(5.99)	6.12	(5.57) + 0.38
Reboiler duty/MW	(5.99) + 2.28	6.30	(5.57)	6.98

Note: The data in parentheses denote energy saving.

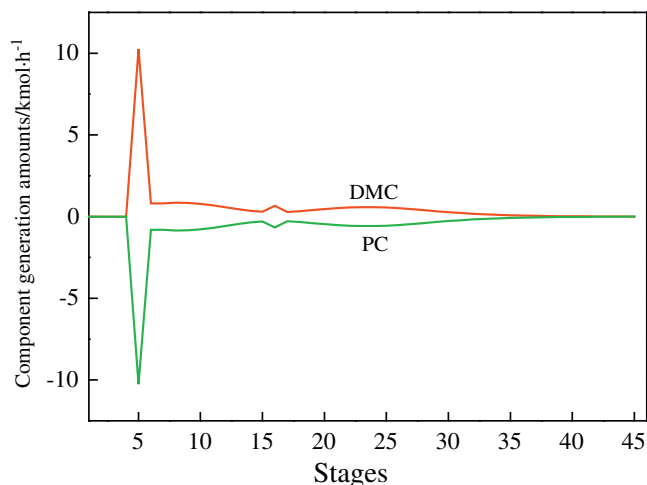


Fig. 5. Component generation amount profile in the RD column.

4. Overall Control Strategies

In the following, the proper overall control strategy of the process for the production of DMC will be investigated. Aspen Dynamics was used for the control study. Before the Aspen Plus steady state simulation was exported to Aspen Dynamics as a pressure-driven simulation, all the pumps and control valves needed in the process should be added and the volume of vessels should be determined. So, the tray-sizing function in Aspen Plus was used to calculate the size of the RD column and the HP column. The sizes of the reflux drum and the sump were determined by using heuristic methods recommended by Luyben [28]: all

are sized to provide 5 min of holdup when at 50% level. The pressure drops inside both the RD column and the HP column were automatically calculated in Aspen Dynamics to account for liquid hydraulics and vapor traffic.

The main control objective is to maintain the conversion of PC ($\geq 99.9\%$) and the DMC product specification ($\geq 99.5\%$ mass). The overall control strategies of this system will be developed in order to hold above specifications in spite of the fluctuations of feed flow and feed composition that frequently exist in the practical processes. Since temperature control is usually used instead of composition control in chemical industrial applications, temperature control is preferred in the control strategy development.

4.1. Inventory control

In this system, there are twelve control degrees of freedom: PC feed flow, MeOH feed flow, RD reboiler duty, RD bottom flow, RD distillate, RD reflux, RD condenser duty, HP bottom flow, HP reboiler duty, HP distillate, HP reflux, and HP condenser duty. In order to keep the total material balance, eight degrees of freedom are used for the inventory control loops. That is, the reflux drum levels of the RD column and the HP column are controlled by manipulating their distillate flows, while base levels of the columns are controlled by manipulating the corresponding bottom flow rates. The pressures of both condensers are controlled by manipulating the condenser duties. Fresh PC feed (stream F1) is flow controlled and used as a throughput manipulator to change its set point when production rate changes are needed. The total MeOH feed is flow controlled by manipulating a control valve at fresh feed stream while the set point of this flow control loop is adjusted to maintain suitable MeOH/PC feed ratio into the RD column. This set point can be reset by other controller, which will be discussed detail in next chapter. For the control loops of the flow rate, pressure, and liquid level, their controller parameters are configured by empirical values as shown in Table 6.

4.2. Quality control loops

The remaining manipulated variables include reflux flows and reboiler duties. In the HP column, the reflux flow rate is controlled by R/D ratio. It is important to select a sensitive tray location for temperature control. The steady state temperature profiles of both columns are presented in Fig. 6. In the HP column, the location where temperature changes rapidly from tray to tray is around tray 40, so the temperature on this tray is controlled by reboiler heat input. In order to improve the dynamic performance of the control loop, a “ $T_{40}C$ ” controller is on “cascade” with the “ Q_R/F ” ratio. The output value from the “ $T_{40}C$ ” controller is the ratio of reboiler heat input in the HP column to the distillate of the RD column. However, in the RD column there is a moderate change in temperatures from tray to tray. Therefore, a more

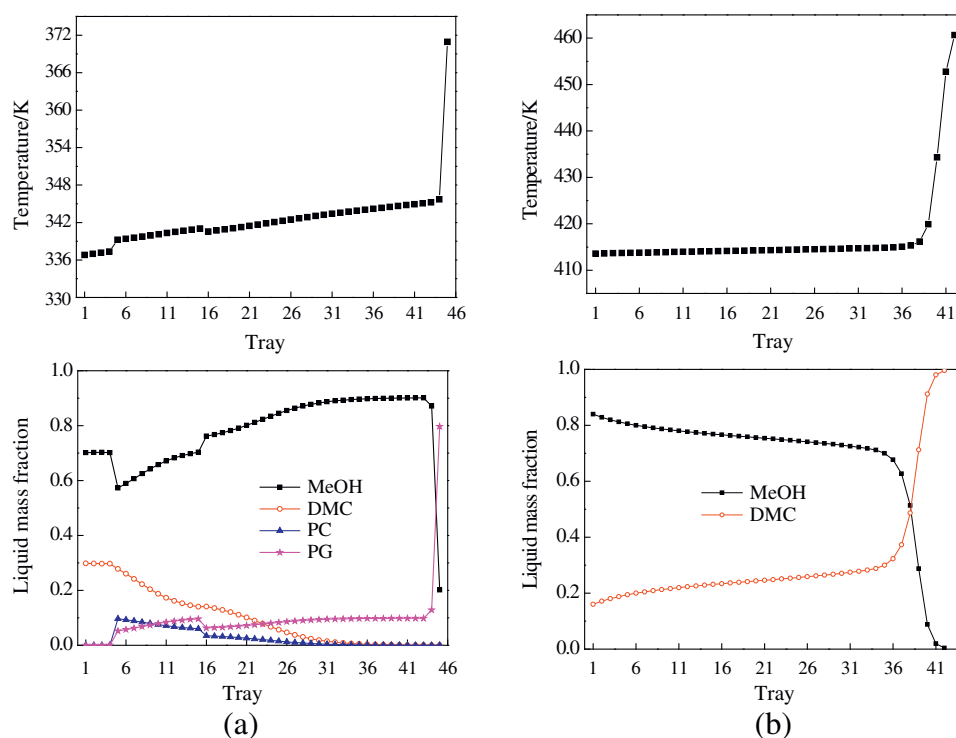


Fig. 6. Temperature and liquid composition profile in (a) the RD column and (b) the HP column.

Table 6

Conventional PI controller parameter

	Pressure	Level	Flow
Gain $K_c/\% \cdot \text{s}^{-1}$	20	2	0.3
Integral time τ/min	12	9999	0.5

sensitive tray temperature should be selected as controlled variable. In this work, sensitivity analyses were performed on the RD column. To determine the steady state gains of tray temperature in the linear region, small changes in the design value (PC feed flow rate $\pm 10\%$ and reboiler heat duty $\pm 0.5\%$) were carried out. Results are displayed in Fig. 7. For the disturbances of PC feed flow rate, there are two symmetrical peaks of temperature change on the 5th and 25th trays, while only one symmetrical peak of temperature change on the 5th tray when the disturbances of reboiler heat duty are introduced. So, the 5th tray was considered as a temperature control tray.

A suitable feed ratio between the reactants must be maintained when operating a reactive distillation column. Feed ratio control is the

simplest way to maintain stoichiometric balance. But PC feed (F1 stream) contains MeOH, so “Multiply” control model in Aspen Dynamic cannot be used directly in this case. Furthermore, MeOH feed must ensure that there is sufficient MeOH concentration in the bottom of the RD column. In order to satisfy the above requirements, a temperature/flow rate cascade control structure is explored, and the tray selected for temperature control is located in the bottom where the temperature changes quickly. Fig. 9(a) shows that the set point of the MeOH flow controller is adjusted by the output of the temperature controllers ($T_{45}\text{C}$) in the RD column.

In addition, note that the temperature difference (ΔT) between the condenser of the HP column and the base of the RD column is quite large ($413.6 - 370.9 = 42.7\text{ K}$) and the reboiler heat input of the RD column, $Q_R = 5.57\text{ MW}$, is lower than the condenser heat removal of the HP column, $Q_C = 5.95\text{ MW}$. Therefore, the overhead vapor in the HP column can be used as the heat source of the reboiler of the RD column, and the excess heat in the condenser in the HP column is removed by an auxiliary condenser. Here, assuming that the heat-transfer area of the condenser/reboiler is 229.8 m^2 and the overall heat-transfer coefficient U is $0.002045\text{ GJ} \cdot (\text{h} \cdot \text{m}^2 \cdot \text{K})^{-1}$, the heat duty of the auxiliary condenser,

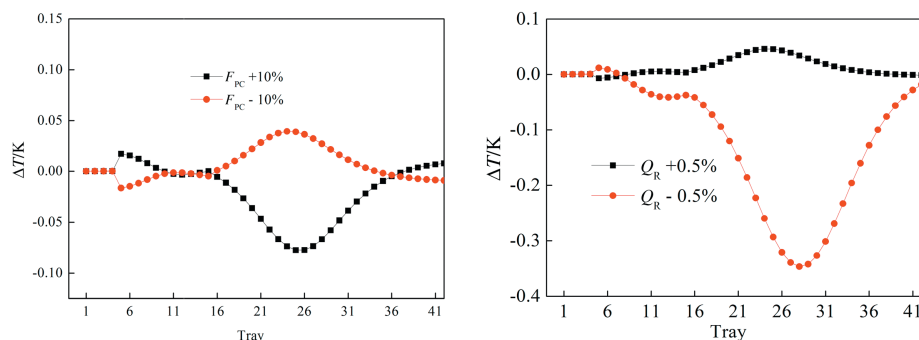


Fig. 7. Sensitivity analysis of the RD column.

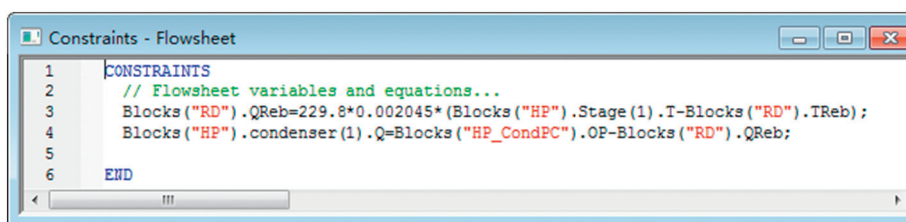


Fig. 8. Flowsheet equations.

0.38 MW, can be determined. In this way, the temperature on the 5th tray in the RD column is controlled by manipulating the reflux. The set point of this T_5 temperature controller is 339.2 K. Supposing there is a 1 min time delay in the temperature measurement, close loop relay-feedback testing and Tyreus–Luyben tuning yields the tuning parameters ($K_c = 28.08$, $\tau = 7.92$ min). And the auxiliary condenser duty can be manipulated to control the operating pressure of the HP column. Implementing this structure in Aspen Dynamics requires “flowsheet equations” as shown in Fig. 8. Fig. 9(a) gives the plant-wide control structure (CS1) and their set points are displayed in Fig. 9(b).

4.3. Closed-loop simulation results of CS1

The control performance is tested for feed flow disturbance. Fig. 10 gives dynamic response for the control structure under -10% PC feed flow rate disturbance. It is found the control structure performs nicely

in holding high purity of DMC product and conversion of the PC. However, when $+10\%$ PC feed flow disturbance is introduced at 2 h, the conversion of PC decreases sharply and the system goes wrong after running 4.5 h.

Usually when the feed rate is increased, the reboiler heat duty should increase. In this control system, however, increasing PC feed flow rate produces an immediate decrease in the distillate from the RD column as expected. The temperature on the 40th tray in the HP column will increase as the feed is decreased (as shown in Fig. 11). Because the temperature on the 40th tray is controlled by the reboiler heat input and the temperature controller is “reverse acting”, an increase in temperature should cause the controller to decrease the required heat duty of the reboiler. Since the heat duty of the condenser/reboiler depends on the product of ΔT , the heat transfer area, and the overall heat-transfer coefficient, decreasing the reboiler heat input in the HP column should produce a decrease in operating pressure in the HP column and thus overhead temperature, which in turn leads to a

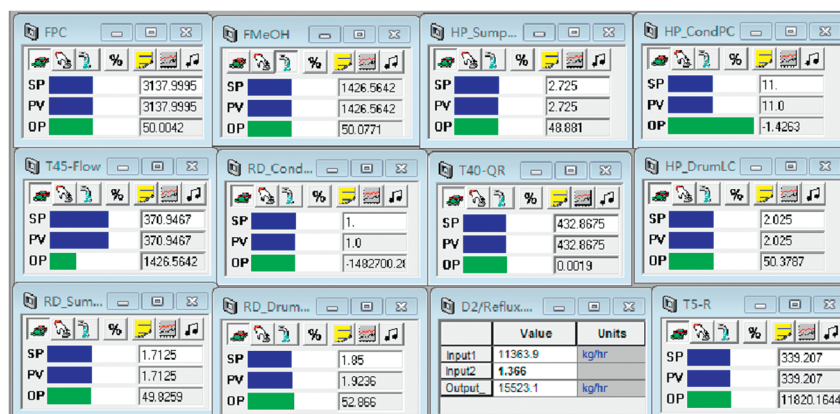
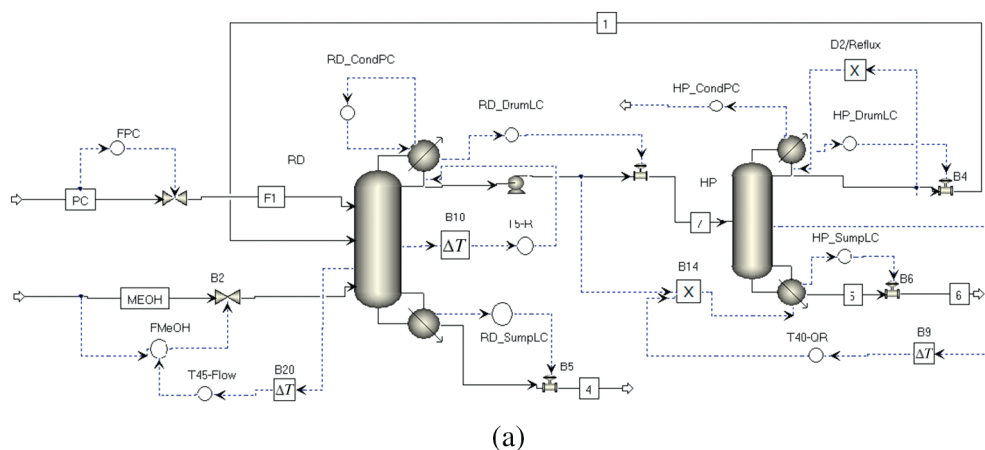


Fig. 9. (a) Control strategy (CS1) for partially heat-integrated process. (b) Controller faceplates.

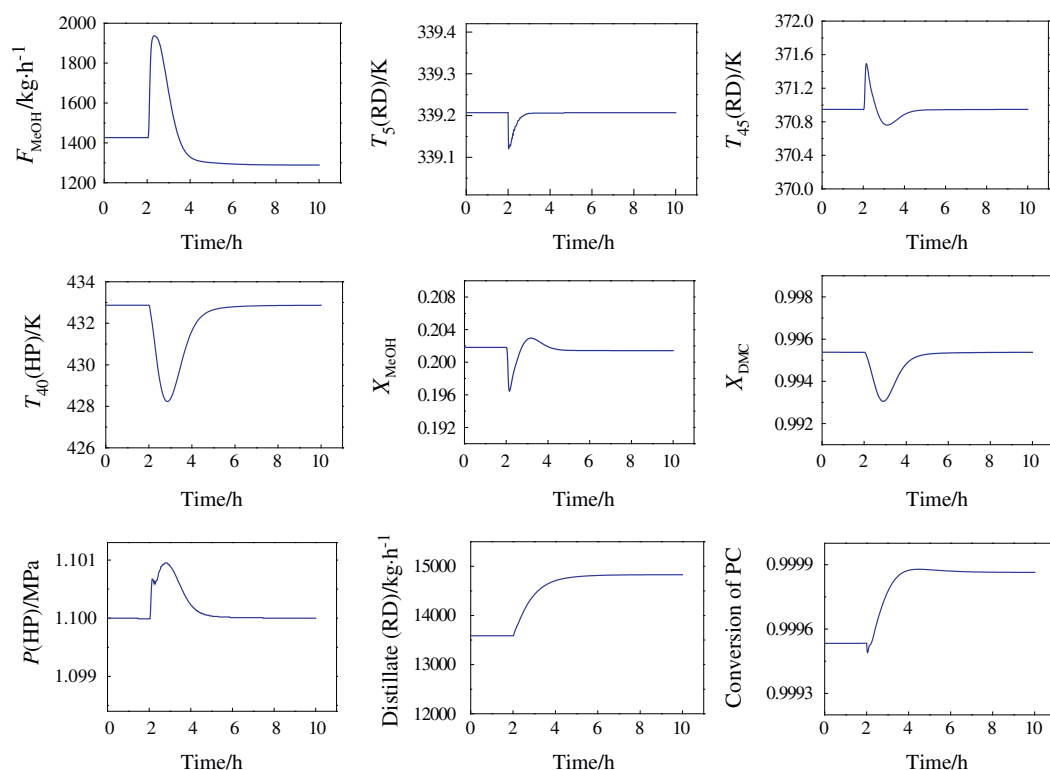


Fig. 10. Dynamic responses under -10% PC feed flow rate disturbances.

reduction in reboiler heat duty in the RD column. Therefore, the interaction among these factors makes the system gradually deviate from the normal operating state. So an improved control strategy is required to provide a correct adjustment in reboiler heat input.

4.4. Improved control structure

Fig. 12(a) displays the improved control structure CS2. It only differs from the CS1 structure in the following aspects: (1) the reflux flow rate

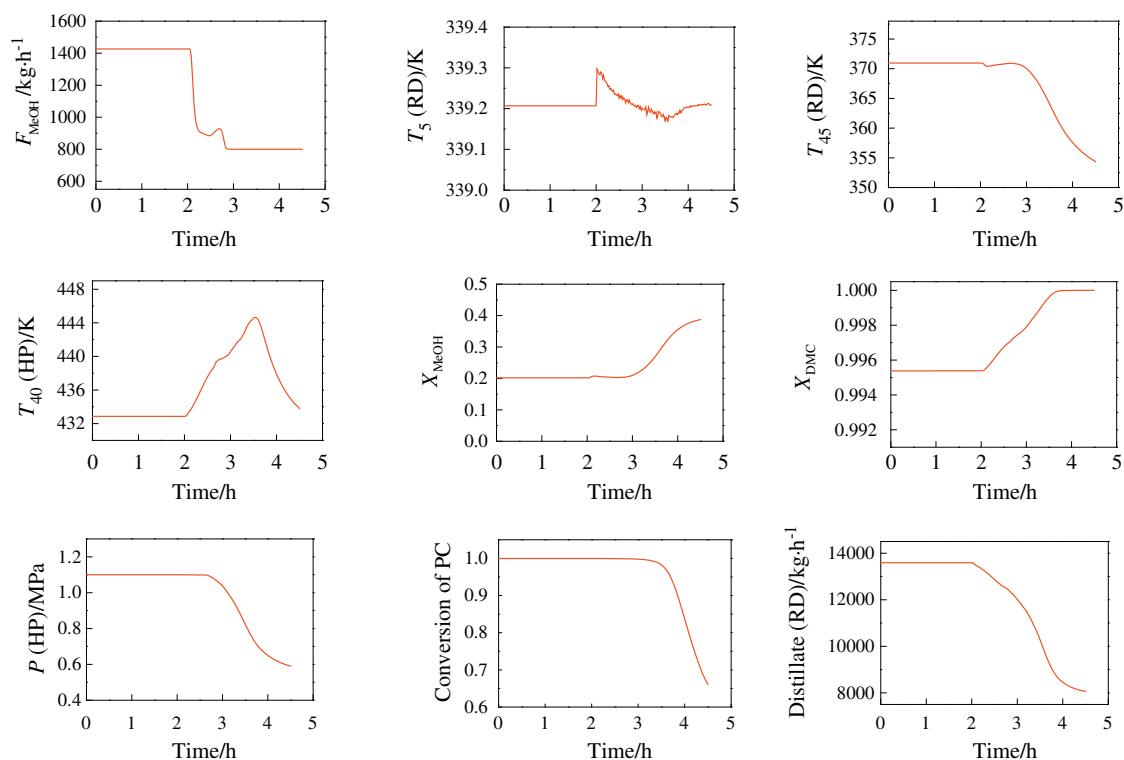


Fig. 11. Dynamic responses under $+10\%$ PC feed flow rate disturbances.

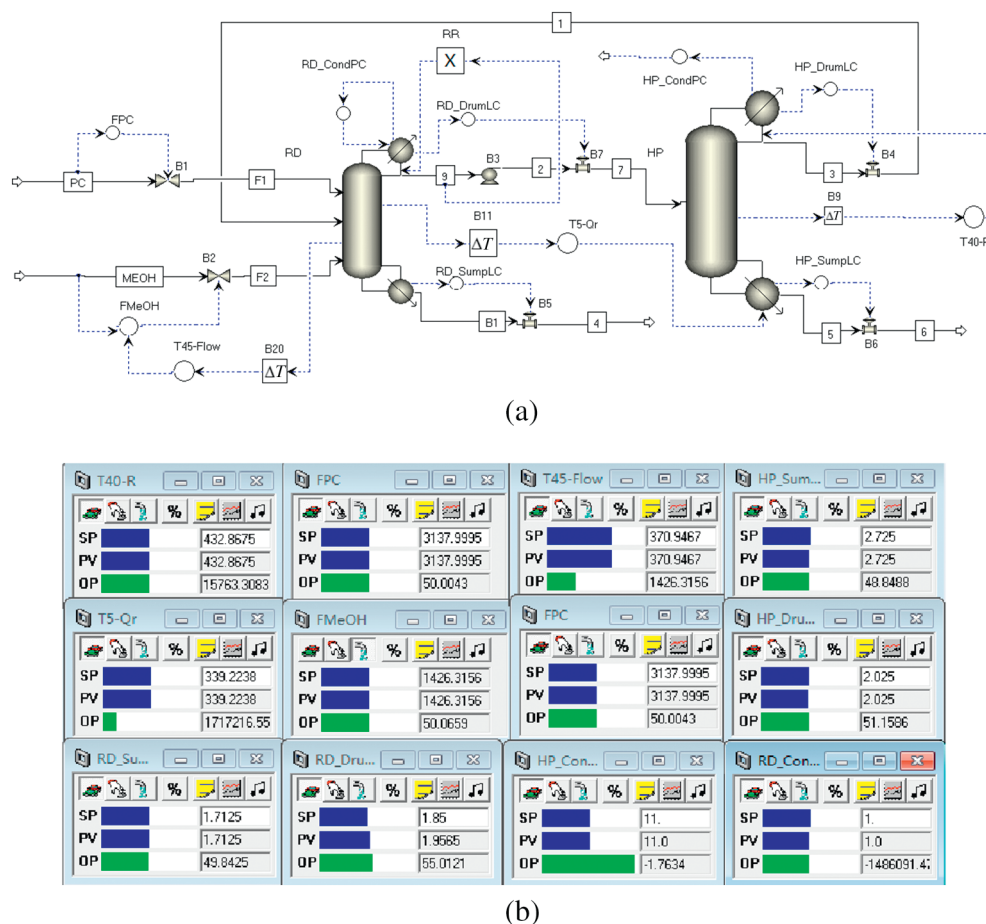


Fig. 12. (a) Control strategy (CS2) for partially heat-integrated process. (b) Controller faceplates.

in the RD column is controlled by R/D ratio; (2) the temperature on the 5th tray in the RD column is controlled by manipulating the reboiler heat input to the HP column; and (3) in the HP column the temperature on the 40th tray is controlled by manipulating the reflux flow rate. All the controllers are retuned and tuning parameters are presented in Table 7.

Table 7
Controller tuning parameters for control structure CS1 and CS2

	CS1	CS2
Controlled variable	T_{45} (RD)	T_{45} (RD)
Manipulated variable	F_{MeOH}	F_{MeOH}
Gain $K_c/\% \cdot \text{min}^{-1}$	43.65	43.65
Integral time τ/min	13.20	13.20
Controlled variable	T_5 (RD)	T_5 (RD)
Manipulated variable	RD.Reflux.Fm	HP.QReb
Gain $K_c/\% \cdot \text{min}^{-1}$	28.08	78.64
Integral time τ/min	7.92	42.24
Controlled variable	T_{40} (HP)	T_{40} (HP)
Manipulated variable	HP.QReb	HP.Reflux.Fm
Gain $K_c/\% \cdot \text{min}^{-1}$	43.89	1.20
Integral time τ/min	2.64	18.48

Fig. 13 gives dynamic responses for the control structure under $\pm 10\%$ PC feed flow rate disturbances, while Fig. 14 for $\pm 10\%$ PC feed composition disturbances. The solid blue line demonstrates the response for negative step changes, while the dashed red line shows the response for positive step changes. Both the disturbances are introduced at 2 h. It is observed that CS2 can adjust the MeOH feed to accommodate PC changes, as was desired. Except for T_5 in the RD column

which shows a small deviation from its base case value, both T_{45} in the RD column and T_{40} in the HP column returned to their set point values. The responses of PC conversion show asymmetric behavior for positive and negative PC feed composition disturbances but meet the design requirement. In addition, both DMC product composition in the HP column and MeOH composition in the bottom of the RD column also meet their corresponding specifications. The above results demonstrate that the proposed temperature controls can maintain product quality and provide a robust operation.

5. Conclusions

Dimethyl carbonate is an environmentally benign and biodegradable chemical. A novel process including a RD column with an excess of reactant MeOH and a high-pressure distillation column is used to obtain high PC reaction conversion and high purity dimethyl carbonate product. The optimal process is determined by minimizing the total TAC. To estimate the flow rate and composition of the recycle stream in a pressure-swing distillation system, a simple and effective method is proposed and adopted in the process optimization. The optimization results show that the feed molar ratio of MeOH to PC is 2.61:1 and close to stoichiometric ratio in the transesterification reaction, and the modification process can save energy consumption by 18.6% with the propylene carbonate conversion of 99.9%.

Dynamic simulation results illustrate that the temperature/flow rate cascade control plus with simple temperature control can keep not only product purity but also conversion of the reactant at their desired values in the face of the disturbances in reactant feed flow and feed composition.

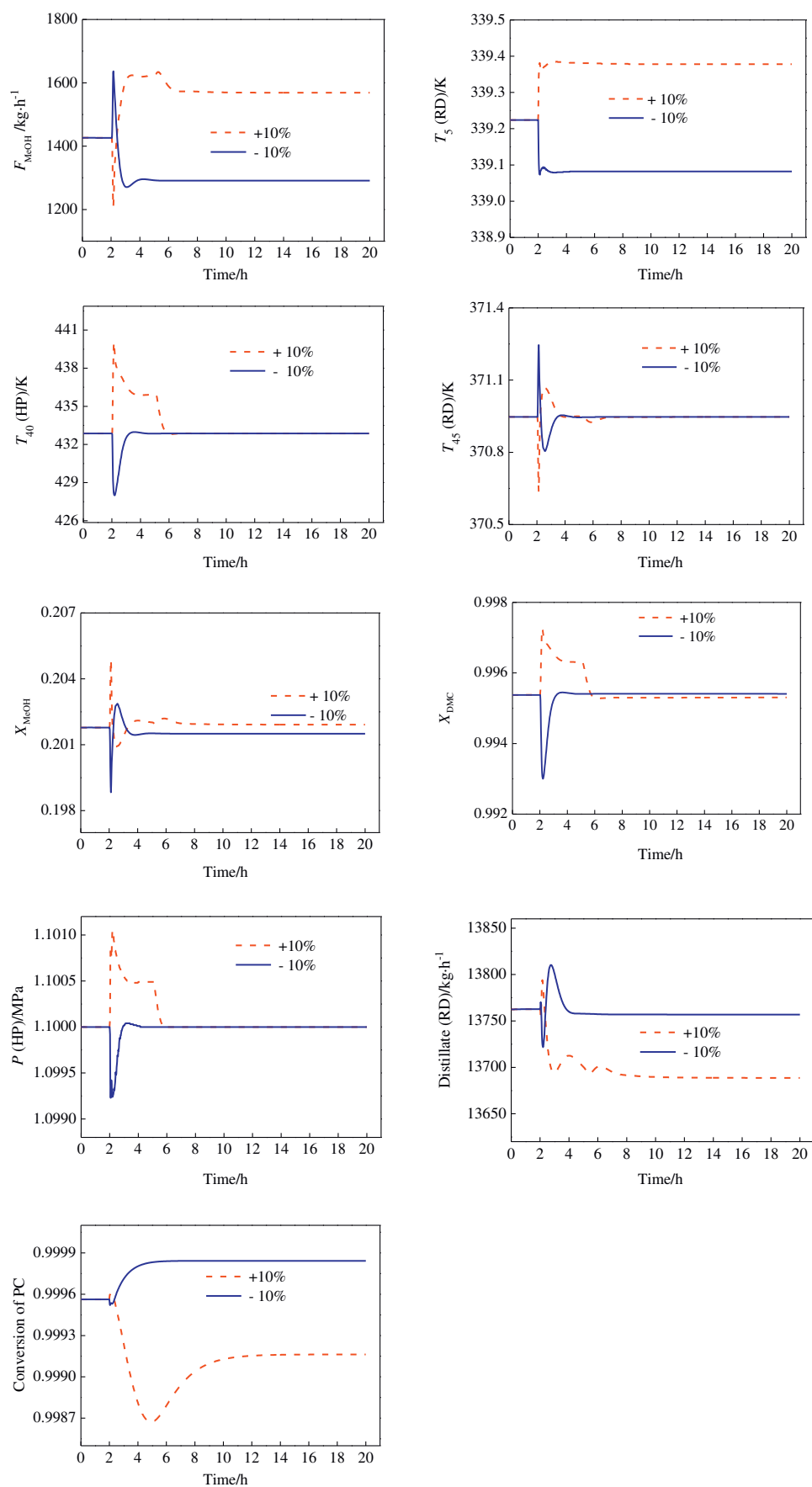
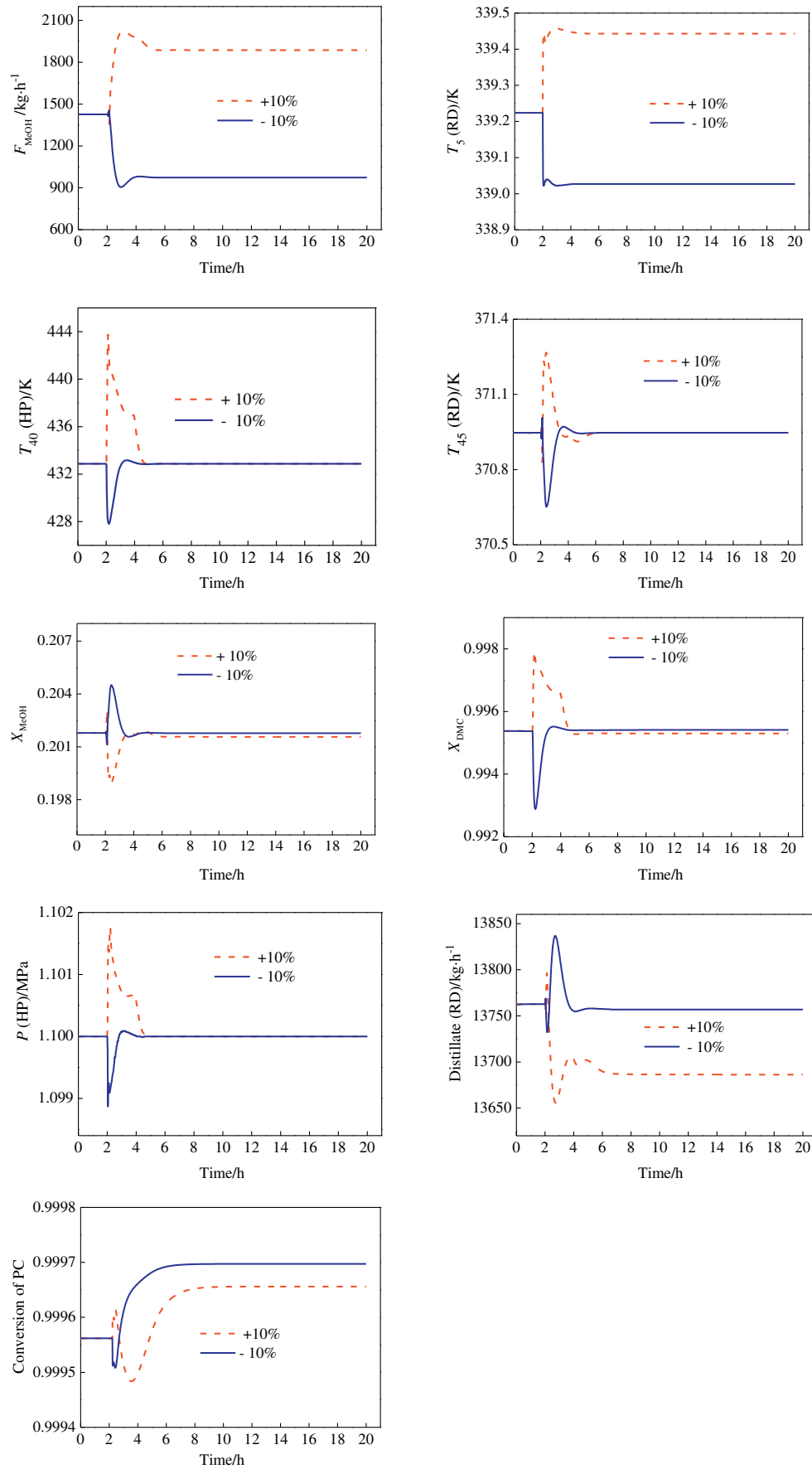


Fig. 13. Dynamic responses under $\pm 10\%$ PC feed flow rate disturbances.

**Fig. 14.** Dynamic responses under $\pm 10\%$ PC composition disturbances.

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