

# Dynamic Simulation, Parameter Optimization, and Control of a Reactive Distillation Column for Production of Isopropanol via Propylene Hydration



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In this study, a reactive distillation column for production of isopropanol was investigated. Firstly, a dynamic model was developed for the process. The model of the process was then programmed, and the process simulated using a base case obtained from the literature. Results showed that distillate contained more than 58 mol% propylene-free isopropanol. In the next step, optimization of some operating variables was performed to maximize concentration of isopropanol in distillate with condenser temperature as constraint, which was considered to be above the freezing point of water. Several simulations were performed by changing operating parameters, and finally optimum isopropanol content in distillate was obtained above 58 mol%. Results of using classic controllers showed that PID controller had the best performance for both condenser temperature set-point tracking and disturbance rejection.

## Keywords

reactive distillation, isopropanol, process modeling, dynamic simulation, process optimization, process control

## Introduction

Distillation is one of the important separation processes in chemical industry. Any improvement in this process can have great economic benefits. Reactive distillation (RD) is one of the major steps in separation history to achieve this goal. It is a combination of chemical reaction and physical separation within a single unit operation. Some of its benefits include increasing of reactants conversion and product selectively, heat integration, and reduction of fixed and operating costs<sup>1</sup>. The most important applications of RD include esterification<sup>2,3</sup>, hydration<sup>4-6</sup>, crude oil residue conversion<sup>7</sup>, etc. Reactive distillation was firstly considered by Smith<sup>8</sup> in 1980 for production of methyl tert-butyl ether (MTBE), and its first industrial application was introduced for production of MTBE in 1981<sup>9</sup>. Since then, RD has been used theoretically and experimentally for production of many components.

Isopropanol is an important chemical component with many applications in coatings for metals, painting, preparation of pesticides, pharmaceuticals, production of acetone, etc.<sup>10</sup> Isopropyl alcohol (IPA) industrial production methods include indirect hydration of propylene in the presence of homogeneous

acidic catalysts<sup>11</sup>, and direct hydration of propene in the vicinity of a heterogeneous acidic catalyst<sup>12,13</sup>. In indirect hydration of propene, firstly propene is reacted with 60 % sulfuric acid and converted to isopropyl hydrogensulphate ( $\text{CH}_3\text{CHCH}_3\text{OSO}_2\text{OH}$ ). In the next step, the produced intermediate is hydrated by water to produce IPA and  $\text{H}_2\text{SO}_4$ <sup>11</sup>. In direct method, propene directly reacts with water in the presence of solid acidic catalysts<sup>12,13</sup>. Indirect method needs more equipment than the direct method for producing IPA, and due to high corrosivity of sulfuric acid, currently it is replaced by the direct method. Direct method has higher efficiency and lower energy consumption. Catalysts of direct method include solid phosphoric acid<sup>14</sup>, synthetic zeolites<sup>12</sup>, and tungsten-based hetero-poly-acid<sup>15</sup>. Synthetic zeolites have advantages such as higher propylene conversion and lower energy consumption compared to other methods<sup>13</sup>.

In recent years, a new technology for production and separation of IPA using direct hydration of propene in a single catalytic distillation column has been investigated by some authors. Xu *et al.*<sup>14</sup> investigated production of IPA within a RD column using a zeolite catalyst. They developed their steady-state model in Aspen Plus<sup>TM</sup> and assumed reactions in chemical equilibrium. Wang and Wong<sup>4</sup> investigated the control of reactive distillation of IPA. The column had 26 ideal plates, and a reaction

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zone near condenser. They claimed that high conversions of propene were achieved and high-purity IPA exited from the reboiler as product. Niu and Rangaiah<sup>16</sup> investigated retrofitting of RD unit with acidic proton-exchange resin as catalyst, as well as the issue of excess propene in product and proposed two designs. In the first design, they used two RD columns where excess water entered the second column. In the second design, two RD columns received same feeds but with different flow rates. Their bottom products were then mixed, and entered an extractive distillation (ED) column. They used catalyst information only for economic calculations. Their results showed that the first design was more economic than the second one, with 14 % reduction in capital costs compared to a base case. Chua *et al.*<sup>5</sup> investigated the design and optimization of RD of isopropanol and proposed two designs. In the first design, they used propene in excess to consume water completely to avoid azeotropic conditions. In the second design, they used water in excess to consume propene and avoid its loss. Azeotropic mixture from the bottom of RD column was entered into an ED column. For economic calculations, they considered Amberlyst 36 as catalyst in the reaction zone of RD columns. Their results showed that the second design was more economic than the first one.

In this study, the dynamic model of the reactive distillation column of IPA production by direct hydration of propene on HZSM5 was created. The simulation was then run using a base case to reveal model performance. After validation of the results, optimization of some operating variables was performed by changing their values within predefined ranges. Finally, parameters of classic controllers were tuned using the dynamic response of the IPA composition in order to maintain IPA composition in distillate at its desired and optimum value.

To the best of our knowledge, no work has been done yet considering reaction kinetics in the reaction zone. In addition, all authors used commercial simulation software of Aspen Plus for process simulations, while we coded all the model equations, phase equilibrium calculations, and reaction kinetics in dynamic conditions, from scratch. Only Wang and Wong<sup>4</sup> performed process simulation dynamically, but they also only applied chemical equilibrium for the reaction zone. Another novelty of this study is the optimization of controller parameters, which has not been done by other authors.

## Material and methods

Fig. 1(a) shows the RD column used in this study for process modeling. Feed streams of pure

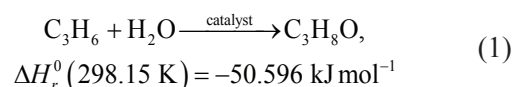
water and propylene entered the rectifying section of the column at pressure of 20 bar and temperature of 380 K. The reaction zone was located between feed streams, and contained HZSM5 zeolite catalyst. Gas phase reaction was taking place between water and propylene in this zone to produce IPA. The rest of column was used for the separation of components as a normal distillation column. The reaction zone was assumed to be equivalent to three ideal plates.

## Process modeling

For process modeling in dynamic mode, stages were numbered from bottom to top of the column. The following assumptions were used for process modeling:

- Pressure is constant at 20 bar within the column with no pressure drop,
- Liquid and gas phases on stages are at thermodynamic equilibrium,
- Gas phase on all stages is ideal,
- All stages are adiabatic except for condenser and reboiler,
- Holdups on stages are constant,
- Reaction only occurs in gas phase in reaction zone,
- Accumulation terms in total mass and energy balance equations are zero,
- Accumulation of components in gas phase is negligible compared to liquid phase,
- Condenser is partial.

The following reaction was considered to take place in the reaction zone:



In this study, kinetic model of the work of Sonnemans<sup>17</sup> was used:

$$r = k_{LH} C_{\text{C}_3\text{H}_6} C_{\text{H}_2\text{O}} / (K_{PR} C_{\text{C}_3\text{H}_6} + C_{\text{H}_2\text{O}})^2 \quad (2)$$

$$k_{LH} = 3.9906 \cdot 10^{13} \exp(-14613/T(K)) \text{ s}^{-1}, \quad (3)$$

$$K_{PR} = 0.0369$$

All parameters and variables are introduced in Symbols section. For process modeling, a system with one ideal stage of the column was considered, as shown in Fig. 1(b), and model equations were developed. The model was then used for all stages of the column, including condenser and reboiler.

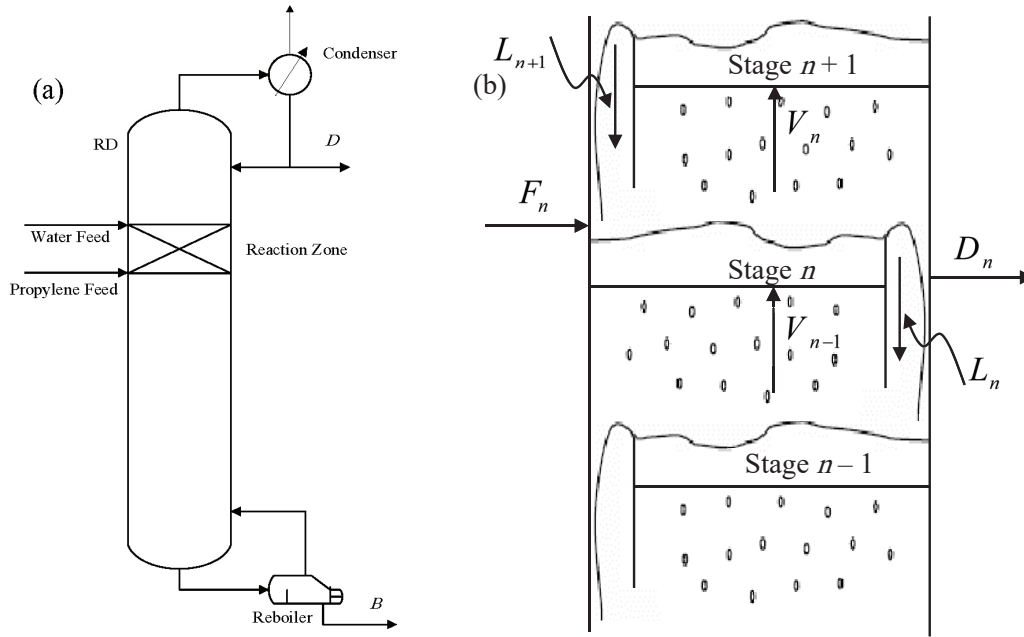


Fig. 1 – a) Schematic of RD column in this study, b) input and output mass streams for stage  $n$

Total mole balance for stage  $n$  assuming steady-state condition:

$$L_{n+1} - L_n - D_n + V_{n-1} - V_n + F_n + I_n v_{L,n} \sum_{i=1}^c v_i r_n = 0 \quad (4)$$

$$I_n = \begin{cases} 1 & n = 23, 24, 25 \\ 0 & \text{otherwise} \end{cases}, D_n = \begin{cases} 0 & n \neq N + 2 \\ L_n / R & n = N + 2 \end{cases} \quad (5)$$

where  $N+2$  refers to the condenser.

Energy balance for stage  $n$ :

$$L_{n+1} H_{n+1} - (L_n + D_n) H_n + V_{n-1} h_{n-1} - V_n h_n + F_n H_{F,n} + Q_n = 0,$$

$$Q_n = \begin{cases} Q_R & n = 1 \\ -Q_C & n = N + 2 \\ 0 & \text{otherwise} \end{cases} \quad (6)$$

Mole balance for component  $i$  in stage  $n$ :

$$v_{L,n} \frac{d}{dt} (\rho_{L,n} x_{i,n}) = L_{n+1} x_{i,n+1} - (L_n + D_n) x_{i,n} + V_{n-1} y_{i,n-1} - V_n y_{i,n} + F_n x_{F,i,n} + I_n v_{L,n} v_i r_n, \quad i = 1, \dots, c - 1 \quad (7)$$

As mentioned previously, holdups were assumed to be constant. They were calculated using

column internal diameter and weir height. Calculated holdups for trays were  $0.141 \text{ m}^3$  assuming  $2 \text{ m}$  for column ID and  $5 \text{ cm}$  for weir height, and excluding  $10 \%$  of the tray cross-sectional area for downcomers<sup>18</sup>. Holdups for condenser and reboiler were considered to be three-fold of those for trays, i.e.,  $0.424 \text{ m}^3$ .

For calculating  $K$ -values, gas phase was assumed to be ideal, and activity coefficients of the components in the liquid phase were calculated using UNIFAC method.

$$K_i = \gamma_i P_i^* / P \quad (8)$$

Due to low critical temperature of propylene, generally, temperature in stripping section of the column and especially in the reboiler is above the critical temperature of propylene. For these conditions, Henry's law was applied for phase equilibrium calculations of propylene. Henry's law constant was calculated using method of Campanella *et al.*<sup>19</sup>

To determine temperature changes in stages with time, the derivative of equation (8) was taken with respect to time. It was assumed that  $K$ -values are functions of temperature and liquid composition only. After simplification, the following equation was obtained:

$$\frac{dT_n}{dt} = \frac{\sum_{i=1}^c K_i (dx_{i,n}/dt) + \rho_{L,n} v_{L,n} \sum_{i=1}^c x_{i,n} \sum_{j=1}^c (\partial K_i / \partial n_j) (dx_{j,n}/dt)}{\sum_{i=1}^c x_{i,n} (\partial K_i / \partial T)} \quad (9)$$

Table 1 – Values of operating variables used for optimization

| Factor   | Assessed values | Unit                 |
|--|-----------------|----------------------|
| Reflux ratio   | 18, 20, 24, 28  | –                    |
| Propylene feed flow rate                               | 36, 43.2, 54    | kmol h <sup>-1</sup> |
| Water to propylene feed ratio (mol mol <sup>-1</sup> ) | 1.2, 1.5        | –                    |
| Vapor fraction in condenser                            | 0.05, 0.07, 0.1 | –                    |

All required derivatives were obtained analytically.

### Process simulation and optimization

After the development of dynamic model of the process, model equations were coded in MATLAB®, and a base case was used for simulation. Initially, some reasonable values were assumed for liquid compositions and temperatures in all stages. Equations (4) and (6) were then solved analytically in each time step assuming steady-state condition in order to calculate liquid and vapor mole flow rates from the stages, as well as heat duties of condenser and reboiler. It was assumed that three parameters, including reflux ratio, distillate rate, and vapor fraction in condenser are known. In the next step, the system of component mole balance equations, (7), was solved numerically using an ordinary differential equation solver in each time step. Vapor mole fractions were calculated assuming thermodynamic equilibrium between phases in stages and using equation (10). As condenser was assumed to be partial, eq. (10) can also be applied to the condenser.

$$y_{i,n} = K_{i,n} x_{i,n}, \quad i = 1, 2, \dots, c, \quad n = 1, 2, \dots, N + 2 \quad (10)$$

In the reaction zone, generation and consumption of components were also included in calculations. Calculations were repeated until reaching final time determined for the simulation.

In this study, values of four factors with high impact on the performance of RD column, including reflux ratio, propene feed flow rate, water to propene feed ratio, and vapor fraction in condenser were examined and optimized by the method of one-factor-at-a-time<sup>20</sup>, and process simulation. Table 1 shows the parameters and their assessed values during optimization.

### Process control

Classic controllers were designed and applied for the control of RD column at optimum conditions. Condenser temperature was considered as controlled variable, and reflux ratio as manipulating variable. For controller design, firstly, the response of condenser temperature to a step-change in reflux ratio was obtained. A first-order model with time-de-

lay was then proposed for the response, and its parameters were estimated using process reaction curve<sup>21</sup> and curve fitting methods. The response of open-loop system to a step change in its input at  $t_0 = 0$  is called the reaction curve. The step response of the above system can be described as:

$$y(t) = AK_p \left[ 1 - \exp\left(-\bar{t}/\tau_p\right) \right], \quad \bar{t} = t - \tau_d \geq 0 \quad (11)$$

where  $A$  is the step-change amplitude. In the reaction curve method, a tangent line on reaction curve at inflection point is drawn. If intercept of straight line with horizontal axis is shown with  $t_1$  then the parameters of the above system can be obtained using the following equations<sup>21</sup>:

$$\tau_d = t_1 - t_0 = t_1 \quad (12)$$

$$K_p = \frac{y(t \rightarrow \infty) - y(t_0 = 0)}{A} \quad (13)$$

$$\tau_p = t_2 - t_1 \quad (14)$$

where  $t_2$  is the location of the intercept of the tangent line with the horizontal line drawn at ultimate value of the response,  $y(t \rightarrow \infty)$

In the curve fitting method,  $\tau_d$  is estimated just like in the reaction curve method. It can then be shown that  $\ln(dy/d\bar{t})$  is a straight line with respect to  $\bar{t}$ , where  $-1/\tau_p$  and  $\ln(AK_p/\tau_p)$  are the slope and y-intercept of the line, respectively. Thus,  $K_p$  and  $\tau_p$  can be found by linear regression. After system identification, the parameters of controllers were found using Ziegler-Nichols method<sup>22</sup>. Finally, the designed controllers were used for process control and their performances were compared.

## Results and discussion

### Vapor-liquid equilibrium results

Fig. 2 shows  $T$ - $xy$  diagram for the binary system of IPA and water at total pressure of 20 bar obtained using phase-equilibria software package written in this work. As may be seen, IPA and water formed an azeotrope at about 65 mol% of IPA, with mixture boiling point of 451.9 K. Therefore, complete separation of these two components in a single RD column could not be achieved and another extractive distillation column was required for this purpose.

Fig. 3 shows triangular diagram for the ternary system of propene/IPA/water, which was obtained from Aspen Plus. As may be seen, this system only exhibited two-phase behavior, and the only azeotrope was at about 66 mol% of IPA and 34 mol% of water. Thus, the result validated the result of  $T$ - $xy$  diagram calculated by our phase-equilibria package.

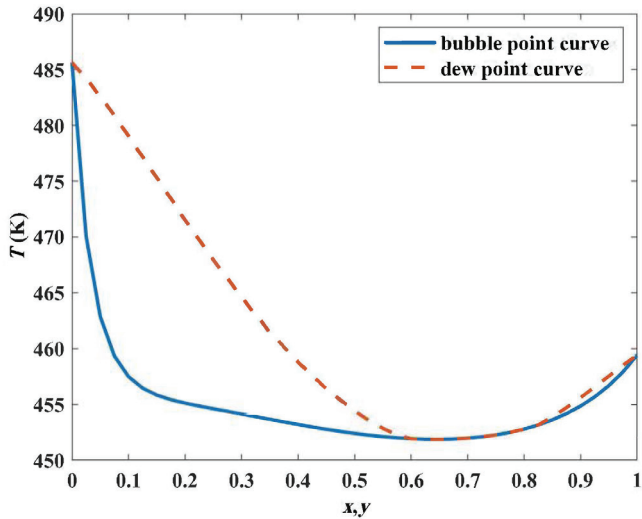


Fig. 2 –  $T$ - $xy$  diagram for the binary system of IPA (1) and Water (2) at pressure of 20 bar

**Base case simulation**

A base case was considered for simulation and validation of the proposed mathematical model of the RD column based on the data from the literature<sup>4</sup> as well as different runs of the written programs. The values of operating and design parameters for base case are shown in Table 2. Temperature

Table 2 – Values of design and operating parameters of RD system used in base case simulation

| Parameter                   | Value      | Unit                 |
|-----------------------------|------------|----------------------|
| Number of ideal stages      | 26         | –                    |
| Water feed flow rate        | 54         | kmol h <sup>-1</sup> |
| Propylene feed flow rate    | 36         | kmol h <sup>-1</sup> |
| Temperature of feed streams | 380        | K                    |
| Distillate rate             | 18         | kmol h <sup>-1</sup> |
| Reflux ratio                | 20         | –                    |
| Vapor fraction in condenser | 0.07       | –                    |
| Reaction zone stage numbers | 23, 24, 25 | –                    |

profiles for selected stages are shown in Fig. 4. Because the reaction is exothermic and the column was assumed to be adiabatic, the temperature in stage 25 was higher than the reboiler temperature. Minimum temperature was reported for condenser after 100 min, which was 257.6 K. Temperatures on other stages converged almost to a same value, except for stage 24, which was located in the reaction zone. As mentioned previously, the condenser was assumed to be partial for this process in order to avoid sharp decrease in temperature in the condenser.

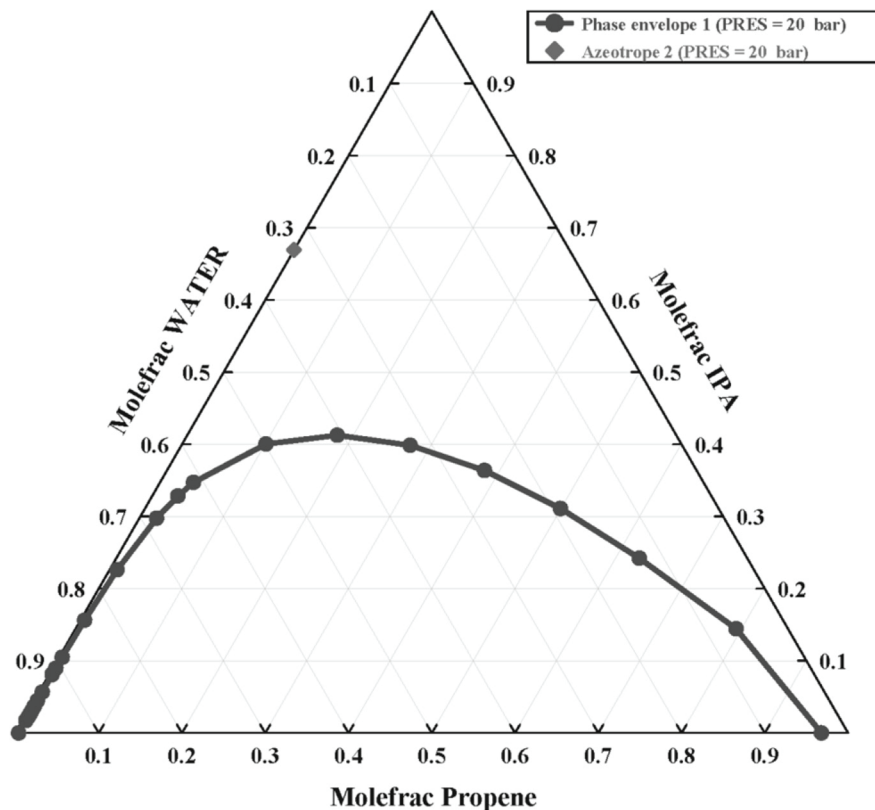


Fig. 3 – Triangular diagram for the ternary system of propylene/IPA/Water at pressure of 20 bar

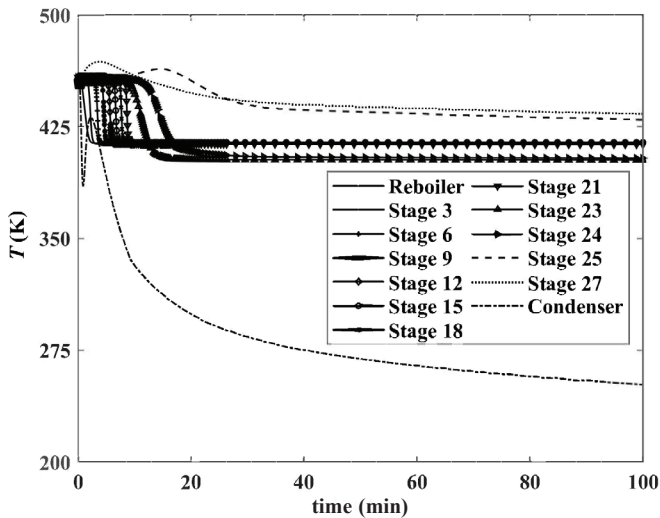


Fig. 4 – Temperature profiles of column stages with respect to time obtained for base case

Fig. 5 shows profiles of IPA compositions in selected stages of the RD column. As it is evident, IPA composition was near zero in the stripping section, but from reaction zone to the condenser it increased due to production by hydration reaction and separation by condenser. It seemed that IPA content in condenser was lower than in stage 27, which was due to the increase in propene content in cooling region, especially in the condenser (not shown here). However, since propene is a volatile component, it can be easily removed from IPA product outside of the column, and can be returned to the column. Obtained propene-free mole fraction of IPA in condenser was about 0.61, while it was 0.58 in stage 27 after 100 minutes of simulation.

Although good production and separation of IPA was achieved in the distillate, but due to the azeotropic condition of binary mixture of IPA and water, an additional extractive distillation column was required to obtain high purity IPA, which has also been investigated by Niu and Rangaiah<sup>16</sup> and Chua *et al.*<sup>5</sup> In addition, because condenser temperature is below the freezing point of water, the above result is not feasible, since coolant which is chilled water can't cool down the product to that temperature. To avoid this, condenser temperature has to be maintained above water freezing point. For this reason, and in order to obtain a good quality of output product, operating parameters of the process have to be optimized.

#### Optimization of IPA reactive distillation column

As mentioned previously, four operating variables were optimized. Column pressure was kept constant at 20 bar, based on the literature<sup>5</sup>. Several simulations were performed with different values of the parameters presented in Table 1. The objective

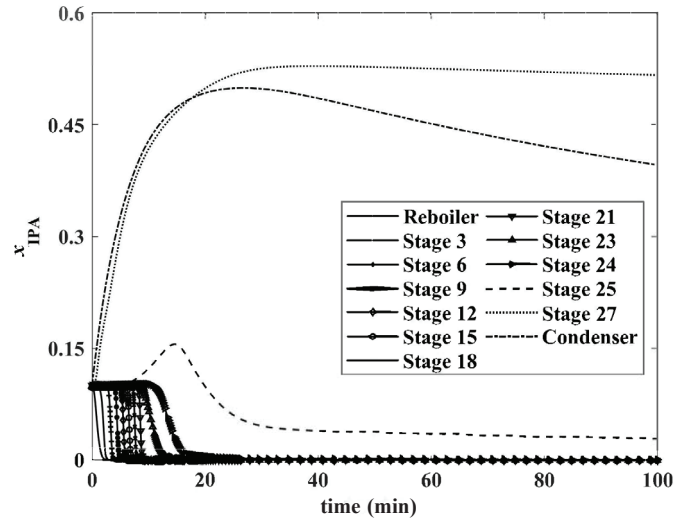


Fig. 5 – Profiles of IPA mole fraction in ideal stages of the column with respect to time

was to maximize IPA propene-free mole fraction in the distillate,  $X_{28}$ , with the constraint that distillate temperature,  $T_D$ , had to be above water freezing point. Since water is always present in the product from condenser, and due to the presence of the azeotrope point, cooling the product in condenser to very low temperatures, has no benefit because the azeotrope point prevents high purification of IPA in RD column. Other researchers, such as Niu and Rangaiah<sup>16</sup>, used cooling water as the coolant in condenser as well.

Simulation results for 8 different cases are shown in Table 3. As may be seen, by increasing reflux ratio,  $T_D$  was increased, and  $X_{28}$  firstly increased up to the reflux ratio of 24 and then decreased. Thus, the best value of reflux ratio was 24. Increasing reflux ratio to a certain value will increase IPA mole fraction, because reflux stream contains high amounts of unreacted components of water and propene, which can increase the reaction rate. However, since reflux temperature is very low compared to the stage where it enters, it decreases the stage temperature by absorbing heat. This phenomenon extends to the reaction zone causing a decrease in temperature of the zone, and hence a decrease in the reaction rate. The reflux value of 24 is an optimum value at which increasing the amounts of reactants and decreasing temperature in the reaction zone balance each other.

Propene feed flow rate,  $F_{23}$  was changed at the optimum value of reflux ratio and fixed values of other variables. In this case, increasing  $F_{23}$  continuously decreased  $T_D$  as well as  $X_{28}$ . Thus, it was concluded that 36 kmol h<sup>-1</sup> is the optimum value of this parameter. By changing water to propene feed ratio, it was observed that its best value was 1.2. A further decline of this parameter cannot be done because it is desired to have water in excess to have IPA prod-

Table 3 – Optimization results of four operating variables. Case 0 is the base case and optimum values are highlighted.

| Case number   | 0     | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Reflux ratio  | 20    | 18    | 24    | 28    | 24    | 24    | 24    | 24    | 24    |
| Propylene feed rate ( $F_{23}$ , kmol h <sup>-1</sup> ) | 36    | 36    | 36    | 36    | 43.2  | 54    | 36    | 36    | 36    |
| Water to propylene feed ratio ( $F_r$ )                 | 1.5   | 1.5   | 1.5   | 1.5   | 1.5   | 1.5   | 1.2   | 1.2   | 1.2   |
| Vapor fraction in condenser ( $\beta_{28}$ )            | 0.07  | 0.07  | 0.07  | 0.07  | 0.07  | 0.07  | 0.07  | 0.05  | 0.1   |
| Distillate temperature ( $T_D$ , K)                     | 252.0 | 237.7 | 278.4 | 317.1 | 275.9 | 273   | 278.5 | 232.8 | 390.1 |
| Temperature in stage 27 ( $T_{27}$ , K)                 | 449.1 | 427.8 | 443.1 | 448.9 | 443.2 | 443.4 | 443.1 | 423   | 452.7 |
| Temperature in reboiler ( $T_1$ , K)                    | 413.9 | 414.1 | 414.0 | 413.9 | 414.0 | 414.0 | 414.0 | 413.9 | 413.9 |
| IPA propene-free mole fraction ( $X_{28}$ )             | 0.591 | 0.502 | 0.583 | 0.577 | 0.581 | 0.578 | 0.583 | 0.598 | 0.569 |
| Water mole fraction in bottom product                   | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     |

uct in distillate. At steady-state conditions for a conventional distillation column, changing feed flow rate does not affect product compositions. However, in a RD column with a reaction zone, increasing flow rates of reactants causes increased reaction rate, and thus more products are produced, in this case more IPA. In addition, since the reaction is exothermic in this case, increasing feed rate also increases temperature of the reaction zone due to higher reaction rate, and thus affects compositions of all components in RD column because of changing phase equilibrium conditions.

As previously mentioned, a partial condenser was considered to maintain  $T_D$  at a desired level. This goal was achieved by considering a certain vapor fraction,  $\beta_{28}$ , in the condenser. Decreasing its value from the base value of 0.07 resulted in a sharp decrease in  $T_D$ , while its increase caused  $T_D$  to in-

crease and  $X_{28}$  to decrease. Thus, the base value of  $\beta_{28}$ , i.e., 0.07, was found to be optimal.

Additionally, temperature of vapor outlet from stage 27, which entered into condenser, is shown in 7th row of Table 3, which was about 443 K for the optimum case. This value was high enough to be cooled down to 278.5 K by chilled water at 275.5 K assuming the temperature difference of 3 K between hot and cold stream outlets from the condenser. However, a larger condenser may be needed to perform the cooling task.

Another tip is that the temperature of stage 27, which was near the reaction zone, was the highest one in the column, even higher than the temperature in reboiler, as reported in 8th row of the Table 3. This was because the reaction was highly exothermic and increased the temperature near the reaction zone.

Fig. 6 shows the comparison of profiles of IPA propene-free contents at steady-state conditions for the base case and optimum case depicted with respect to the stages of the column. Stage 1 is the reboiler, and stage 28 is the condenser. As may be seen, profiles are very similar for both cases; IPA propene-free mole fraction in condenser for the base case was even slightly higher than in the optimum case. The reason for selecting the optimum case rather than the base case was the higher condenser temperature for the optimum case, which allows using chilled water as a coolant. IPA mole fraction increased sharply from stage 25 due to the reaction taking place in the reaction zone, stages 23 to 25, and also because of decreasing temperature in stages near the condenser.

### Process control

As mentioned previously, distillate temperature and reflux ratio were selected as controlled and manipulated variables, respectively. Firstly, reflux ratio was changed from 24 to 26 at time 20 min at opti-

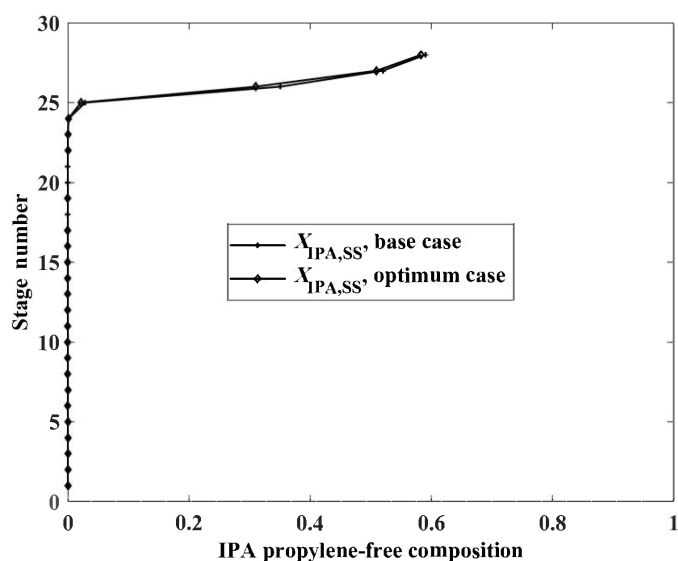


Fig. 6 – Comparison of profiles of water and IPA propene-free compositions through RD column at steady-state conditions for base case and optimum case. SS means steady-state.

Table 4 – Parameters of system identification model obtained by the reaction curve and curve fitting methods

| Method                       | $\tau_d$ (min) | $K_p$ (K) | $\tau_p$ (min) |
|------------------------------|----------------|-----------|----------------|
| Reaction curve <sup>21</sup> | 0.27           | 3.89      | 38.42          |
| Curve fitting                | 0.27           | 9.57      | 130.12         |

Table 5 – Settings of different controllers calculated using Ziegler-Nichols method

| Controller type | $K_c$ (Controller gain) (min) | $\tau_i$ (Integral time) (min) | $\tau_d$ (Derivative time) (min) |
|-----------------|-------------------------------|--------------------------------|----------------------------------|
| P               | 39.64                         | –                              | –                                |
| PI              | 35.68                         | 0.90                           | –                                |
| PID             | 47.57                         | 0.54                           | 0.14                             |

imum conditions in order to obtain step response of distillate temperature, shown in Fig. 7. In the next step, parameters of the assumed first order model with time delay, eq. (10), were estimated by the reaction curve<sup>21</sup> and curve fitting methods as described previously. The results are shown in Table 4, and estimated responses with two methods are shown in Fig. 7. As it is evident, the curve fitting method gave a better fitting of the response.

The results of system identification were used for the controller design. After calculating ultimate controller gain,  $K_u$ , and ultimate period,  $p_u$ , using frequency response method<sup>22</sup>, the appropriate values of controller settings were calculated using Ziegler-Nichols method<sup>22</sup>, as presented in Table 5.

The designed controllers were applied on RD system to control the distillate temperature and, as a result, the IPA content in the distillate. Two experiments, including set-point tracking and disturbance rejection were performed to reveal the performance of controllers. In the first experiment, set-point of distillate temperature was changed suddenly by +20 K from its optimum value after 10 minutes from the start of simulation, and the value of distillate temperature was recorded and depicted for different controllers. Fig. 8 shows the results. As shown, all controllers tracked set-point change rapidly and reached the final value in less than 5 minutes. Both PI and PID controllers had no offset, and PID controller generated smaller overshoot than PI. Even P controller exhibited good performance but with some oscillations and resulted in a very small offset of about 0.05 K. Thus, PID controller had the best performance, although, considering economic issues, P controller may be the best choice.

In the second experiment, the performance of controllers for disturbance rejection was examined. For this purpose, propene feed flow rate was changed stepwise by +10 % from its optimum value at time 10 min. As shown in Fig. 9, PI and PID

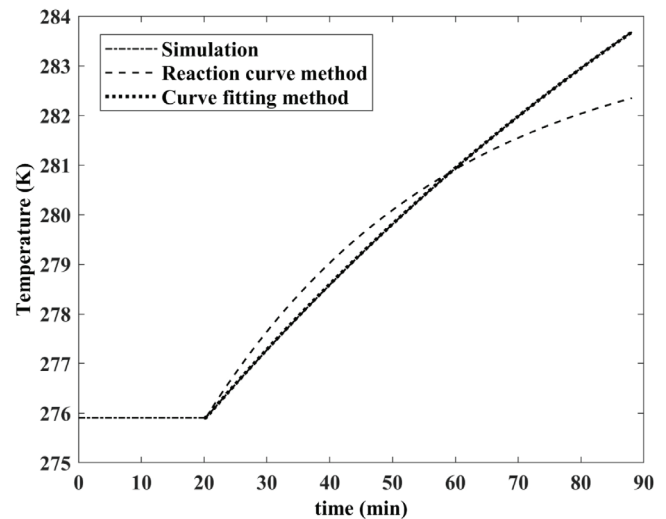


Fig. 7 – Results of system identification for distillate temperature

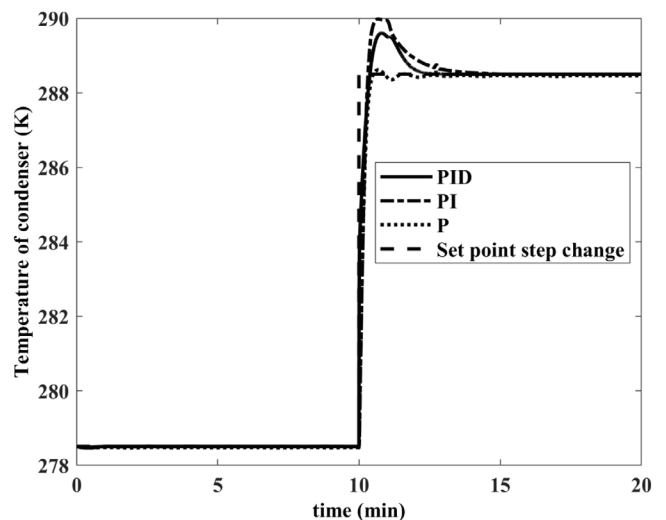


Fig. 8 – Performance of different controllers for tracking set-point step change in distillate temperature

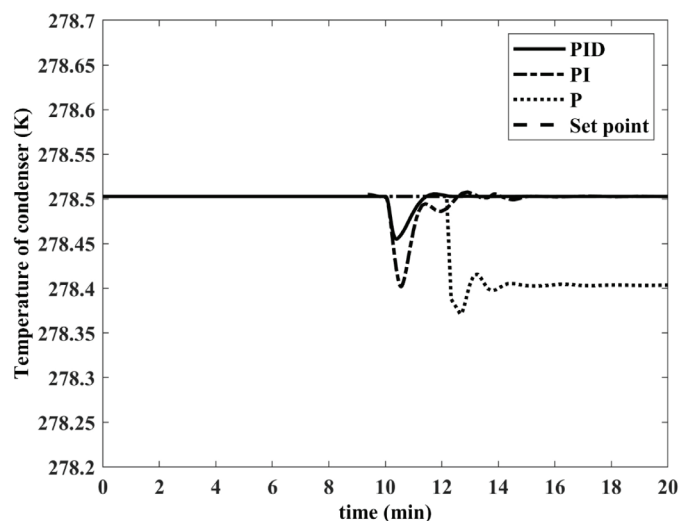


Fig. 9 – Performance of different controllers for rejection of disturbance in propylene feed flow rate



controllers had good performance with no offset, and PID reached the final value after 2 min with a very small undershoot. P controller could not reach the final value and left an offset of about 0.07 K. Thus, in this case, PID controller was the best choice, however, P controller could also be chosen if economic considerations should be taken into account.

## Conclusions

In this study, dynamic modeling and simulation of isopropanol production in a reactive distillation column were performed. Direct hydration of propylene on HZSM5 catalyst was considered, and a reaction kinetics from the literature was used for calculation of the reaction rate. Results of simulation of a base case showed that the model was able to simulate RD column with good accuracy, and IPA product was obtained from distillate with a near-to-azeotrope composition. Since distillate temperature in the base case was below the freezing point of water, an optimization study was conducted to force the process to obey this constraint while maximizing IPA content in the distillate. Four operating variables, including reflux ratio, propene feed flow rate, water to propene feed ratio, and vapor fraction in condenser were selected, and their values were optimized by performing several simulations. The results of optimization showed that the reflux ratio of 24, propene feed flow rate of 36 kmol h<sup>-1</sup>, water to propene feed ratio of 1.2, and condenser vapor fraction of 0.07 were the best values of these variables. IPA propene-free content in the distillate reached the value of 0.583 and distillate temperature was 278.5 K. Control of distillate temperature was then performed at optimum conditions by designing and applying different classic controllers. The controllers designed with Ziegler-Nichols method displayed good performance in terms of rapid response, minimum overshoot, and minimum or no offset. All previous works lack the kinetics for IPA production, but only consider chemical equilibrium. In this work, process simulation was performed by considering reaction kinetics for propene hydration.

## Symbols

|       |   |
|-------|---|
| $c$   | – Number of components, –                                       |
| $C_i$ | – Concentration of component $i$ , mol m <sup>-3</sup>          |
| $D_n$ | – Product molar flow rate from stage $n$ , kmol h <sup>-1</sup> |
| $D$   | – Distillate molar flow rate, kmol h <sup>-1</sup>              |

|                           |   |
|---------------------------|---|
| $F_n$                     | – Feed flow rate into stage $n$ , kmol h <sup>-1</sup>                |
| $H_n$                     | – Liquid molar enthalpy in stage $n$ , J mol <sup>-1</sup>            |
| $H_{F,n}$                 | – Molar enthalpy of feed into stage $n$ , J mol <sup>-1</sup>         |
| $h_n$                     | – Vapor molar enthalpy in stage $n$ , J mol <sup>-1</sup>             |
| $I_n$                     | – Identifier for the stages of reaction zone, –                       |
| $k_{LH}$                  | – Modified reaction rate constant, s <sup>-1</sup>                    |
| $K_C$                     | – Controller gain, –  |
| $K_i$                     | – $K$ – value of component $i$ , –                                    |
| $K_p$                     | – Process gain, K   |
| $K_u$                     | – Ultimate controller gain, –   |
| $L_n$                     | – Liquid mole flow rate from stage $n$ , mol min <sup>-1</sup>        |
| $N$                       | – Number of plates of the column, –                                   |
| $P$                       | – Column total pressure, Pa   |
| $P_i^*$                   | – Vapor pressure of component $i$ , Pa                                |
| $p_u$                     | – Ultimate period, min  |
| $Q_C$                     | – Condenser duty, MW  |
| $Q_R$                     | – Reboiler duty, MW   |
| $R$                       | – Reflux ratio, –   |
| $r$                       | – Reaction rate, mol m <sup>-3</sup> s <sup>-1</sup>                  |
| $r_n$                     | – Reaction rate in stage $n$ , mol m <sup>-3</sup> min <sup>-1</sup>  |
| $T_n$                     | – Temperature in stage $n$ , K  |
| $t$                       | – Time, min   |
| $V_n$                     | – Vapor mole flow rate from stage $n$ , mol min <sup>-1</sup>         |
| $v_{L,n}$                 | – Liquid holdup on stage $n$ , m <sup>3</sup>                         |
| $x_i$                     | – Mole fraction of component $i$ in liquid phase, –                   |
| $x_{i,n}$                 | – Mole fraction of component $i$ in liquid phase and in stage $n$ , – |
| $x_{F,i,n}$               | – Mole fraction of component $i$ in feed entering into stage $n$ , –  |
| $X_n$                     | – IPA propylene-free mole fraction in stage $n$ , –                   |
| $y(t)$                    | – System response in time domain, –                                   |
| $y(t \rightarrow \infty)$ | – Ultimate value of the system response, –                            |
| $y_i$                     | – Mole fraction of component $i$ in vapor phase, –                    |
| $y_{i,n}$                 | – Mole fraction of component $i$ in vapor phase and in stage $n$ , –  |

## Greek symbols

|                |  |
|----------------|--|
| $\Delta H_r^0$ | – Heat of reaction in standard pressure, kJ mol <sup>-1</sup>          |
| $\gamma_i$     | – Activity coefficient of component $i$ , –                            |
| $\nu_i$        | – Stoichiometric coefficient of component $i$ in hydration reaction, – |
| $\tau_d$       | – Time delay, min  |
| $\tau_p$       | – Time constant of the process, min                                    |
| $\tau_D$       | – Derivative time constant, min  |
| $\tau_I$       | – Integral time constant, min  |

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