Design and Control of a Plant-Wide Process for the Production of Epichlorohydrin*

Chien-Chih Huang, San-Jang Wang, and David Shan-Hill Wong

Abstract—Epichlorohydin (ECH) is a primary raw material in the production of some polymers. However, traditional ECH production methods suffer from several disadvantages. Hydrogen peroxide is relatively non-toxic and widely accepted as an environmentally friendly and green oxidant. In the study, we propose the plant-wide process design and control for ECH synthesis by the epoxidation of allyl chloride with hydrogen peroxides over the catalyst of TS-1 in the presence of methanol. In the plant-wide process, the product from a plug flow reactor is separated by a distillation column. Nitrogen gas is fed into the column top for safety concerns. The column bottom product containing mostly ECH and water is decanted into two liquid phases. High purity ECH and water are obtained from the bottoms of two strippers which the liquids of organic and aqueous phases in the decanter are respectively fed into. The control strategy is constructed by steady-state analysis for the plant-wide process and its performance is evaluated by dynamic simulation. Simulation results reveal that the process can be safely operated and product purities can be maintained around the desired values by temperature control in spite of disturbances.

I. INTRODUCTION

Epichlorohydrin (ECH) is the third most abundant industrial product among the α-oxides. It is a primary raw material and can react with different classes of compounds to synthesize a number of products (such as epoxy resins, rubbers, glues, varnishes, synthetic fibers, etc.) required by industries. Now, the main method to produce ECH is the chlorohydridin process in industry. However, this process suffers from several serious drawbacks, such as significant quantities of pollutant production, a relatively high-energy expenditure, and the production of several by-products. Hydrogen peroxide is relatively non-toxic and widely accepted as an environmentally friendly and green oxidant. Recently, the epoxidation of olefins with hydrogen peroxide as the oxidant has attracted special attention [1-3]. Titanium silicate 1 (TS-1) is an efficient catalyst for the selective oxidation of hydrocarbons [4-5]. Many studies have shown that epoxidation of allyl chloride with hydrogen peroxide in the presence of TS-1 and an organic solvent to synthesize ECH has a promising industrial future [6-10]. The solvent may be alcohol, ketone, or ether. Danov et al. [11] showed that the highest epoxidation rate and a satisfactory yield of ECH are achieved with methanol. However, hydrogen peroxide may cause safety problems when catalyzed by many materials, because of its potential of large exothermic decomposition to water and oxygen. Allyl chloride and oxygen could create an explosive system in the gas phase of a reactor and a distillation column. Therefore, safety problem should be taken care in the reaction of allyl chloride and hydrogen peroxide to produce ECH.

In this study, we propose the plant-wide process design and control for ECH synthesis by the epoxidation of allyl chloride with hydrogen peroxide over the catalyst of TS-1 in the presence of methanol. Steady-state and dynamic simulations are conducted by Aspen Plus software. Firstly, the kinetic and thermodynamic models are established. A plant-wide process is then designed under safety concerns. Finally, the control strategy is constructed by steady-state analysis for the plant-wide process and its control performance is evaluated by dynamic simulation.

II. KINETIC AND THERMODYNAMIC MODELS

In the reaction system for ECH synthesis, there are components including allyl chloride (AC), hydrogen peroxide (HP), ECH, water (W), 1-chloropropane-2,3-diol (CDP), 1-chloro-3-methoxyprop-2-ol (CMP), oxygen, and methanol (M). AC epoxidation with an aqueous solution of HP over the catalyst TS-1 is conducted to synthesize ECH in the presence of M by the reaction given in Equation (1).

\[ \text{AC} + \text{HP} \rightarrow \text{ECH} + \text{W} \]  

The main reaction to produce the target product, ECH, is accompanied by a number of side reactions yielding CMP, CDP, and oxygen given in Equations (2) to (4).

\[ \text{ECH} + \text{W} \rightarrow \text{CMP} \]  
\[ \text{ECH} + \text{M} \rightarrow \text{CDP} \]  
\[ \text{HP} \rightarrow \text{W} + \text{oxygen} \]  

A kinetic model derived from Sulimov et al. [12] is given in the following for the main and side reactions of Equations (5) to (8).

\[ r_1 = \frac{k_{\text{H}} C_{\text{AC}} C_{\text{W}}}{1 + b_{\text{H}} C_{\text{WH}} + b_{\text{ECH}} C_{\text{ECH}}} \]  
\[ r_2 = \frac{k_{\text{ECH}} C_{\text{ECH}} C_{\text{W}}}{1 + b_{\text{ECH}} C_{\text{ECH}} + b_{\text{ECH}} C_{\text{ECH}}} \]
where \( r_1 \) is the rate of the main reaction (1) \((\text{mol} \cdot \text{s}^{-1} \cdot \text{g}^{-1})\); \( r_2 \) to \( r_4 \) are the rates of side reactions (2) to (4), respectively \((\text{mol} \cdot \text{s}^{-1} \cdot \text{g}^{-1})\); \( k_1 \) is the rate constant of the target reaction \((L \cdot \text{s}^{-1} \cdot \text{g}^{-1})\); \( k_2 \) to \( k_4 \) are the rate constants of the side reactions \((L \cdot \text{s}^{-1} \cdot \text{g}^{-1})\); \( b_{\text{HP}} \) and \( b_{\text{ECH}} \) are the adsorption coefficients for HP and ECH, respectively \((\text{mol} / \text{L})\). The temperature dependences of rate constants \( k_i \) and adsorption coefficients \( b_{\text{HP}} \) and \( b_{\text{ECH}} \) were described by the Arrhenius and van’t Hoff equations, respectively.

\[
k_i = k_{0i} \cdot \exp\left(\frac{E_i}{RT}\right), \quad (i = 1, 2, 3, 4)
\]

\[
b_{\text{HP}} = b_{0,\text{HP}} \cdot \exp\left(\frac{Q_{\text{HP}}}{RT}\right)
\]

\[
b_{\text{ECH}} = b_{0,\text{ECH}} \cdot \exp\left(\frac{Q_{\text{ECH}}}{RT}\right)
\]

\( k_0 \) and \( b_0 \) are pre-exponential factors. \( E_i \) is the apparent activation energy of reaction \( i \) while \( Q_{\text{HP}} \) and \( Q_{\text{ECH}} \) are heat of adsorption for HP and ECH, respectively. These kinetic parameters are given in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{01} ) (L s^{-1} g^{-1})</td>
<td>11.06×10^7</td>
</tr>
<tr>
<td>( k_{02} ) (L s^{-1} g^{-1})</td>
<td>1.12×10^3</td>
</tr>
<tr>
<td>( k_{03} ) (L s^{-1} g^{-1})</td>
<td>6.71×10^3</td>
</tr>
<tr>
<td>( k_{04} ) (L s^{-1} g^{-1})</td>
<td>12.93</td>
</tr>
<tr>
<td>( E_1 ) (J/mol)</td>
<td>55.0×10^4</td>
</tr>
<tr>
<td>( E_2 ) (J/mol)</td>
<td>66.0×10^4</td>
</tr>
<tr>
<td>( E_3 ) (J/mol)</td>
<td>70.6×10^4</td>
</tr>
<tr>
<td>( E_4 ) (J/mol)</td>
<td>50.0×10^4</td>
</tr>
<tr>
<td>( b_{0,\text{HP}} ) (L/mol)</td>
<td>3.06×10^4</td>
</tr>
<tr>
<td>( b_{0,\text{ECH}} ) (L/mol)</td>
<td>4.59×10^4</td>
</tr>
<tr>
<td>( Q_{\text{HP}} ) (J/mol)</td>
<td>19.4×10^3</td>
</tr>
<tr>
<td>( Q_{\text{ECH}} ) (J/mol)</td>
<td>18.0×10^3</td>
</tr>
</tbody>
</table>

In the study, a rigorous model provided by Aspen Plus software is used to simulate the ECH synthesis process. The vapor-liquid and vapor-liquid-liquid equilibrium relationships are described by the NRTL activity coefficient model. The phase-equilibrium relationships for the pairs not built in the Aspen Plus data bank are determined by UNIFAC model or ideal model. Table 2 provides the boiling points of pure components, boiling points and compositions of azeotropes in the reaction system. In these pure components, AC has the lowest boiling points while two side products, CMP and CDP, have higher boiling points than other components. Three minimum boiling azeotropes, including one homogeneous azeotrope and two heterogeneous ones, can be found in the system. Fig. 1 shows the binodal plot for ECH/W/MEOH. Table 2 and Fig. 1 indicate that, in the reaction system, the mixture containing AC, MeOH, and oxygen may be distilled at the top of a distillation column while ECH, water, and two side products (CMP and CDP) can be withdrawn from column bottom under the excess reactant AC. The bottom product can then be cooled and sent into a decanter with two liquid phases, aqueous and organic ones. Aqueous phase contains mostly water while ECH can be obtained from organic phase. The kinetic and thermodynamic models established here are utilized to design and control the following plant-wide processes for ECH synthesis.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (wt%)</th>
<th>Boiling point (°C)</th>
<th>Azeotrope type</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td></td>
<td>45.2</td>
<td></td>
</tr>
<tr>
<td>HP</td>
<td></td>
<td>150.2</td>
<td></td>
</tr>
<tr>
<td>ECH</td>
<td></td>
<td>118.8</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td></td>
<td>64.7</td>
<td></td>
</tr>
<tr>
<td>CMP</td>
<td></td>
<td>171.0</td>
<td></td>
</tr>
<tr>
<td>CDP</td>
<td></td>
<td>213.0</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>-182.9</td>
<td></td>
</tr>
<tr>
<td>AC/MeOH</td>
<td>(88.1, 11.9)</td>
<td>40.2</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>AC/W</td>
<td>(97.8, 2.2)</td>
<td>43.4</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>ECH/W</td>
<td>(78.4, 21.6)</td>
<td>91.0</td>
<td>Heterogeneous</td>
</tr>
</tbody>
</table>

III. DESIGN OF A PLANT-WIDE PROCESS

In the study, the reaction conversion of HP to ECH is designed to be 98.5% and the product purity of ECH achieved is limited to be 99.5 wt%. AC and aqueous HP solution with a concentration of 34 wt% are fed into a plug flow reactor (PFR) to synthesize ECH. The M composition in the feed is designed to be 55 wt%, as suggested by Danov et al. [11], in order to activate the catalyst. In the kinetic experiment study of...
Sulimov et al. [12], ECH synthesis reaction was implemented between 40°C and 60°C. However, gas-phase explosive system can be observed in the reactor under the pressure of 1 atm. Therefore, in our study, the PFR is chosen to be operated at 60°C and 3.5 atm and then the fluid in the reactor is liquid one. The same feed flow rates (10 kmol/h) of AC and HP are initially used to produce ECH. However, the desired reaction conversion (98.5%) of HP to ECH cannot be obtained in the PFR under the condition of stoichiometric balance. Excess AC is then designed in order to increase the HP reaction conversion and decrease the reaction extent of the HP decomposition to oxygen given in reaction (4). Fig. 2 gives the relationship between the catalyst weight and ECH production rate under the feed mole ratio of AC and HP equal to 2.77. The desired reaction conversion can be achieved when the amounts of catalyst is 340 kg. Fig. 3 shows the configuration of the plant-wide process to synthesize ECH. The product from the PFR is then fed into a distillation column with a partial condenser and a total reboiler. According to the study of Zhang et al. [13] about gas phase safety-control conditions for epoxidation of AC with HP catalyzed by TS-1, the oxygen content should be kept under a value half of that represented by its limiting oxygen concentration, i.e. oxygen content should be set to 4.9 vol%. Therefore in the study, nitrogen is also fed into the column to dilute oxygen concentration for safety consideration. Some amounts of tail gas are purged from the condenser. The distillate liquid product containing mostly AC and M is recycled back to the PFR for further reaction. ECH, water, and slight amounts of CMP and CDP are withdrawn from the column bottom and then fed into a decanter with 40°C AC and M compositions at the column bottom is limited not to be greater than 500 ppm. There are aqueous and organic phases formed in the decanter. The aqueous liquid containing mostly water is introduced into the first stripper column (CD2). Water about 99 wt% is withdrawn from the stripper bottom and the top product containing mostly ECH and W is recycled back to the decanter. The organic liquid involving mostly ECH is fed into the second stripper column (CD3). High purity ECH with 99.5 wt% is obtained from the stripper bottom and top product close to ECH/W azeotrope is also recycled back to the decanter.

In the plant-wide process to synthesize EPC, conventional single distillation column is designed on the basis of 1.1 times the minimum reflux ratio under the requirement of bottom product specification. The location of feed tray is determined by minimizing the reboiler duty. Fig. 3 also shows the stream information and operating conditions in the plant-wide process configuration. The total numbers of trays for the CD1, CD2, and CD3 are 68, 6, and 3, respectively. The feeds of CD1, CD2, and CD3 are located at trays 36, 1, and 1, respectively. The bottom purities of three columns all satisfy their respective specifications. Fig. 4 shows the explosion triangular plots given by Zhang et al. [13] for AC-O2-N2 and M-O2-N2 systems. Explosion zone is denoted by red color. However, in their experiment study, oxygen composition is limited not to be greater than that in air. A wider explosion area is used in our study to guarantee more safe operation conditions in the reactor and distillation column. The dotted line denotes the margin of the extended explosion area. The oxygen and explosive material (AC or M) concentrations of A, the interaction point of two dotted lines, denote that below which explosion is impossible. The cyan line connects point A and air composition (79% nitrogen and 21% oxygen). The green region corresponds to the safe one when the gas in the pipeline of the partial condenser is discharged into air. Composition profile (denoted by blue line) of CD1 is also given in Fig. 4. Nitrogen gas with the flow rate of 15 kg/h is fed into the first tray of CD1. Points B and C represent the first tray composition of CD1 before and after introducing nitrogen gas into the first tray of CD1. Point B located in explosion region is placed to point C located in the safe region by feeding nitrogen gas into the first tray of CD1. In addition, more nitrogen gas is added into the gas outlet pipeline of the partial condenser. This can shift the gas composition in the partial condenser into the green safe region before discharging the gas to air. The more robust operation condition denoted by circle symbol in the green safe region of Fig. 4 is the desired one to be designed. In the study, CD1 can be operated under safe condition by feeding nitrogen gas with the flow rate of 210 kg/h into the gas outlet pipeline of the partial condenser.

Figure 2. Relationship between catalyst amounts and reaction conversion of HP to ECH.

Figure 3. Plant-wide process configuration for ECH synthesis.
In the study, tray temperature control is used to indirectly hold the product purity in order to facilitate wider industrial application. In every column, reboiler duty is manipulated to maintain bottom product purity by controlling some stage temperature. The controlled stage temperature is selected by an open-loop sensitivity analysis. The temperatures at stages 62, 2, and 2 are selected as the controlled variables for CD1, CD2, and CD3, respectively due to their highest sensitivity to the corresponding reboiler duty. Constant reflux ratio at CD1 top is used to maintain overhead product purity. Bottom product flow rate is manipulated to control the bottom liquid level for every column. The organic and aqueous levels in the decanter are controlled by changing organic and aqueous outlet flow rates, respectively. The pressures of CD1, CD2 and CD3 are maintained by changing corresponding overhead vapor flowrates, respectively. In addition, the temperatures of overhead products through two condensers in CD1 and two strippers are controlled by manipulating corresponding flow rates of cooling waters, respectively.

Fig. 5 gives the temperature profiles of three columns when feed flow rates of reactants are increased and decreased, respectively, by 20% under the requirements of product purities at three column bottoms. Different temperature profiles appear because the same amounts of catalyst are used. Especially, large discrepancy can be observed between the temperature profile of +20% change of feed flow rate and the other two temperature profiles. This reveals that the set points of three temperature control loops need to be altered when feed flow rates change. Therefore, feedforward control is used to reset the set points of three temperature loops in face of the disturbances of feed flow rates.

In all the closed-loop tests, relay feedback [14] which gets ultimate gain and ultimate period, and Tyreus–Luyben [15] PI tuning rule are selected to determine the controller parameters of these three temperature control loops. The sequential iterative tuning procedure is used to find the final controller parameters. The final PI tuning parameters are the following: for CD1, $K_{C1} = 79.49, \tau_{11} = 1.98$ (min); for CD2, $K_{C2} = 14.94, \tau_{12} = 1.98$ (min); for CD3, $K_{C3} = 43.19, \tau_{13} = 1.32$ (min). Figs. 6 and 7 show the dynamic responses of controlled stage temperatures and bottom product purities, respectively, when feed flow rates are changed by ±20%. Three stage temperatures are quickly settled at new set points and three product purities can be operated around their corresponding desired values. In the case of +20% feed flow change, more amounts of HP are unreacted and withdrawn from the CD2 bottom. In the case of -20% feed flow change, more amounts of impurities CDP and CMP are produced and also withdrawn from the CD2 bottom. Therefore, the water purity at CD2 bottom is lower than its initial value under feed rate disturbances.

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**Figure 4. Explosion area and safe region for (a) AC-O$_2$-N$_2$ and (b) M-O$_2$-N$_2$ systems.**

**IV. CONTROL OF A PLANT-WIDE PROCESS**

In the study, tray temperature control is used to indirectly hold the product purity in order to facilitate wider industrial application. In every column, reboiler duty is manipulated to maintain bottom product purity by controlling some stage temperature. The controlled stage temperature is selected by an open-loop sensitivity analysis. The temperatures at stages 62, 2, and 2 are selected as the controlled variables for CD1, CD2, and CD3, respectively due to their highest sensitivity to the corresponding reboiler duty. Constant reflux ratio at CD1 top is used to maintain overhead product purity. Bottom product flow rate is manipulated to control the bottom liquid level for every column. The organic and aqueous levels in the decanter are controlled by changing organic and aqueous outlet flow rates, respectively. The pressures of CD1, CD2 and CD3 are maintained by changing corresponding overhead vapor flowrates, respectively. In addition, the temperatures of overhead products through two condensers in CD1 and two strippers are controlled by manipulating corresponding flow rates of cooling waters, respectively.

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Figure 5. Temperature profiles of (a) CD1, (b) CD2, and (3) CD3 when feed flow rates of reactants are increased and decreased, respectively, by 20%.

Figure 6. Responses of controlled stage temperature and product purities under temperature control and feed flow disturbances.

Figure 7. Responses of product purities under temperature control and feed flow disturbances.
Figure 8 Dynamic responses of gas compositions in the first tray of CD1 and in the outlet pipeline of partial condenser for (a) AC-O₂-N₂ and (b) M-O₂-N₂ systems, respectively, under ±20% changes of feed flow rate.

Fig. 8 gives the dynamic responses of gas compositions in the first tray of CD1 and in the outlet pipeline of partial condenser for AC-O₂-N₂ and M-O₂-N₂ systems, respectively, under ±20% changes of feed flow rate. These two gas compositions in different locations change only slightly under temperature control. These simulation results indicate that the ECH synthesis process can be operated under safe condition.

V. CONCLUSION

In the study, kinetic and thermodynamic models are established for ECH synthesis by the epoxidation of allyl chloride with hydrogen peroxide in the presence of catalyst TS-1 and solvent methanol. A plant-wide process including one plug flow reactor, one distillation column, two strippers, and one decanter is then designed to satisfy the requirements of product purities and gas-phase safety. Furthermore, the temperature control strategy is designed by steady-state analysis and set points of temperature loops are reset to maintain product purities. Dynamic simulation results demonstrate that the proposed control strategy can not only maintain product purities around designed values but also assure the control conditions of gas-phase safety in face of reactant feed flow disturbances.

ACKNOWLEDGMENT

This work was financially supported by the Ministry of Science and Technology of Taiwan under grant no. MOST 103-2622-E-007-025.

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