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Study on the Influence of Parameter Fluctuation on Ethylene Epoxidation Reaction Process

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ABSTRACT Ethylene epoxidation reactor is a kind of critical equipment in an oxidation unit. Due to the complex coupling effect of the extreme operating environment of high temperature, high pressure and potential risk factors, the reactor tends to work abnormally under the impact of parameter fluctuation, and temperature runaway incident may occur and cause severe loss. For studying the influence of parameter fluctuation on ethylene epoxidation reaction process and preventing temperature runaway accidents, physical modeling is performed firstly in this paper to acquire the chemical reaction mechanism therein and confirm the operation parameters which should be focused. The unsteady simulation of the operation process under normal situation has been performed. On such basis, a test of single-factor effect is performed to analyze the impact of parameter fluctuation on the temperature balance and operation efficiency of the reactor. Comparison analysis has been carried out between the simulation data acquired according to the established model and real production data, and it was found that the result is consistent. The analysis result indicates: higher ethene concentration, oxygen concentration, feed flux, feed temperature, drum temperature, operating pressure or smaller porosity may improve bed temperature and accelerate reaction rate; therein, ethene concentration, oxygen concentration, drum temperature, and porosity are operation parameters that need special monitoring. Based on the risk analysis of the ethylene epoxidation reactor and the simulation of the impact of parameter fluctuation, this paper studies the cause of the reactor's temperature runaway to provide a technical basis for the forecast of reactor's temperature runaway, early warning, and high-efficient operation of equipment. Model established based on abnormal condition parameters fluctuation, can contribute to early warning reactor temperature runaway, revealing the influence mechanism of parameter fluctuation for the reaction system, monitoring reaction process, eliminating temperature runaway in the bud, and providing theoretical and technical basis for petrochemical equipment fault diagnosis, accident prevention and control and safely long-time running.

INDEX TERMS Fixed bed reactor, ethylene oxide, temperature runaway, CFD, parameter sensitivity.

I. INTRODUCTION

The fixed-bed reactor is a piece of crucial chemical equipment to perform gas-solid catalytic reaction, e.g., ethylene epoxidation reactor used to prepare epoxy ethane by ethene and oxygen [1]. In recent years, temperature runaway accidents frequently occur in fixed-bed reactors, which burn catalyst, cause carbon accumulation on reaction tube walls and damages to reaction walls and enclosures, shutdown of units, and even reactor explosion accidents [2]. For example, several accidents caused by temperature runaway of ethylene epoxidation reactors occurred in three epoxy ethane/glycol production units successively in November 2011. It was estimated that the cumulative direct loss incurred by one of the units to an enterprise was about RMB 40 million, and the indirect loss was as much as hundreds of millions of Yuan[3].

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The leading cause of temperature runaway of reactors is poor system process design. Partial heat accumulation may occur in the reactor bed and lead to temperature runaway if the heat released by an exothermic reaction in the reactor can't be removed in time. The unit has to be shut down, and it may cost a considerable quantity of workforce and material resources [4], [5]. Therefore, it's particularly essential to prevent the occurrence of temperature runaway. Many scholars and research institutes have done much work on the prevention of temperature runaway incidents of reactors. Researchers [6], [7] have carried out theoretical researches on the rules for identifying temperature runaway of the chemical reaction. It is thought that temperature runaway accidents are strictly related to the mechanism of chemical reactions, the activity of catalyst structure, and the sensitivity of operation parameters, etc. With the development of computer technology, CFD numerical simulation of reactor featuring considerable calculation precision and efficiency on the aspects of fluid flow, heat transmission, analog computation of chemical reactions, etc., may primarily reduce actual time and costs spent on unit experiments [8]–[10]. Anthony G. Dixon carried out a CFD numerical simulation of the heat transmission process of the bed under the influence of high Reynolds number [11]. Ramin Maghrebia simulated the dynamic process of oxidation reaction of methane that takes place inside a spherical catalyst bed [12]. Xiaoming Zhou established a spherical particle model by the CFD method to simulate the influence of flow-rate and size of particles on temperature distribution of particle surface in an acetone hydrogenation process [13].

This paper takes the ethylene epoxidation reactor as the object to study the effects of different factors on the reactor operation and establishes an early-warning model for preventing temperature runaway incidents. First of all, physical modeling is conducted in a fixed-bed reactor to study the chemical reaction mechanism therein, and then the operating parameters that need to be focused on are determined. Subsequently, a CFD simulation of the reaction process of the reactor under normal operating conditions has been performed, which can contribute to monitoring the changing process of material component concentration field and temperature field inside the reactor. The comparison and verification between simulation data and experimental data were carried out to establish an unsteady model. On such basis, a simulation study is conducted to acquire the influence of parameter fluctuation on the thermal equilibrium and operating state of the reactor. The sensitivity area of parameters and the appropriate operating condition scope can be determined. The simulation results and suitable operating conditions are compared with the actual production data to verify the feasibility of the model. The above study contents may provide a theoretical basis for preventing temperature runaway incidents of the fixed-bed reactor of ethylene epoxidation and ensuring long-period safe operation, and offer a new approach for dynamic monitoring and control of chemical process system.

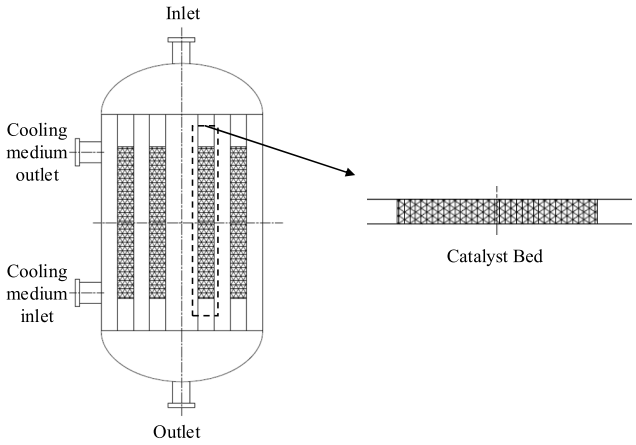

FIGURE 1. Physical model of a reactor.

II. PHYSICAL MODEL AND NUMERIC CALCULATION METHOD

A. PHYSICAL MODEL

Ethylene epoxidation reactors in epoxyethane units are mainly tubular fixed-bed reactors, as shown in Fig. 1. Catalyst particles are filled randomly in the reactor tube. The raw gas runs through the top of the reactor, the top closure head, the catalyst bed, the bottom closure head, and flows out of the bottom outlet and enters the follow-up equipment. The cooling medium flows through the reactor shell pass under the influence of pressure and removes heat generated in ethylene epoxidation reaction. When the heat generated cannot be removed sufficiently, heat accumulation will lead to a temperature runaway incident.

A tubular fixed-bed reactor composes of hundreds of reaction tubes. A single-tube reactor model may reflect the situation of the reaction process and heat transmission, and it will help further understand the overall internal characteristics of the reactor [14], [15]. Therefore, a tube inside an ethylene epoxidation reactor is taken as the object in this paper to perform unsteady simulation of the flow field, to analyze the dynamic process of component concentration distribution and temperature fluctuation inside the tube. In Table 1, the single-tube structure parameters, operating conditions, physical parameters of catalyst particles, and characteristic parameters of the tube wall, etc., have been exhibited.

B. TURBULENCE EQUATION

The model of a single reaction tube includes a medium porous area where reactions occur, an inlet tube section and an outlet tube section. In non-porous medium areas, the material flow mainly meets the quality, energy, conservation-of-momentum equation, and turbulence model equation. The disappearance and generation of material components should be considered in the porous medium equation. The chemical reaction rate equation, energy source items, components transport control equation, and gas-solid energy exchange equation should also be established [16].

TABLE 1. Reactor physical model parameters.

Variate	Value	Variable	Value
Reactor parameter		Catalyst granule parameter	
Reaction tube inner diameter(mm)	31.30	Catalyst support composition	α-Al_2O_3
Reaction tube external diameter(mm)	39.00	Specific heat capacity(J·kg-1·K-1)	858.3
Reactor tube length(m)	8.00	Porosity	0.371
Catalyst bed length(m)	7.50	Particle specific surface area(m-1)	940.98
Entrance tube length(m)	0.35	Catalyst thermal conductivity(W·m-1·K-1)	1.4
Exit section tube length(m)	0.15	Gas-solid heat transfer coefficient(W·m-2·K-1)	40
Operating parameter		Pipe wall model parameter	
Operating pressure(MPa)	2.1	Pipe wall medium composition	Carbon steel
Flow(kg·h-1)	59.8	Pipe wall medium thermal conductivity(W·m-1·K-1)	53.476
Gas feed temperature(℃)	142.6	Cooling water heat transfer coefficient(W·m-2·K-1)	4980
Steam drum temperature(℃)	201.0		

① Continuity equation

Indicating the mass conservation change of infinitesimal unit element in unit time.

② Momentum equation

Indicating reciprocity between the momentum change of infinitesimal elements and sum of the external force of infinitesimal elements in unit time, equation:

$$\rho\left(\frac{\partial u_i}{\partial t}+u_i\frac{\partial u_i}{\partial x_i}+u_j\frac{\partial u_i}{\partial x_j}\right)=\rho F_i-\frac{\partial p}{\partial x}+\mu\left(\frac{\partial^2 u_i}{\partial x_i^2}+\frac{\partial^2 u_i}{\partial x_j^2}\right)$$

③ Energy equation

$$\frac{\partial(\rho T)}{\partial t}+div(\rho\vec{u}T)=div\left(\frac{K}{c_p}gradT\right)+S_T$$

④ RNG turbulence model

$$\frac{\partial(\rho K)}{\partial t}+\frac{\partial(\rho K u_i)}{\partial x_i}=\frac{\partial}{\partial x_j}\left[\alpha_k\mu_{eff}\frac{\partial k}{\partial x_j}\right]+G_k+G_b-\rho\varepsilon-Y_M+S_k$$

C. CHEMICAL REACTION DYNAMICS

The current industrial method for preparation of epoxy ethane is mainly direct oxidation of ethylene, namely, ethene and oxygen have a gas-solid catalytic reaction on the surface of silver catalyst particles and generate epoxy ethane. Accompanying the main reaction is a series of by-reactions, mainly parallel reactions between ethene and oxygen, which generate CO_2 and H_2O [17].

Many scholars have carried out a series of research works on the kinetic model, Russo selected ethylene oxidation on silver catalyst as an example reaction system, because the main product, ethylene oxide, is a key compound and an important intermediate for chemical industry. The reactor and kinetic models were able to describe all the experimental data with a very satisfactory agreement. The results proved that the models were also capable to explain the experimental data very well [18]. Salmi proposed the kinetic models which were based on the reactivities of the nonhydrolyzed sugar units and the increase of the rate constant (for heterogeneous catalysts) as the reaction progresses and the degree of polymerization decreases. General kinetic models were derived and special cases of them were considered in detail, by deriving analytical solutions for product distributions [19].

As for the mechanism of ethylene epoxidation reaction, the study focuses on the main reaction and deep oxidation by-reactions. For different types of catalysts, there are usually different dynamic equations. For the same type of catalysts, different macro kinetic mathematical models can also be established [20]. Based on the result of the macro kinetic experiment of ethylene epoxidation reaction and the reaction kinetic model of Rujun Liang [21], the reaction equations and reaction kinetic formulas used are shown in Table 2, and the parameters of reaction kinetic model are shown in Table 3. Inhibitor Dichloroethane (EDC) adsorption equilibrium constant was acquired, which is important to the reaction rate equations of kinetic model and the obtained kinetic model parameters. The negative equilibrium constants can be acquired from the experiments, and the function of the inhibitors is to inhibit the occurrence of by- reactions [22].

III. CFD MODEL OF THE FIXED-BED REACTOR

A. MESHING WORK

A single reaction tube model is established by the structural parameters of the reaction tube model, 8m in length, 31.3mm in diameter, and the length of the medium porous area filled by the catalyst is 7.5m. In consideration of the excessive length-to-diameter ratio of reaction tube and the influence of wall-surface effect, it is necessary to divide the surface mesh at the inlet and outlet and the dense axial wall surface mesh of reaction tube model respectively. The middle section of

TABLE 2. Reaction equations and reaction rate equations of kinetic model.

Main/side reaction	Reaction equation	ΔH	Reaction rate equation
Main	$CH_2{=}CH_2{+}\frac{1}{2}O_2 \xrightarrow{Ag} C_2H_4O$	-105.39kJ/mol	$R_1=\frac{k_1 p_{C_2H_4}^{\alpha_1} p_{O_2}^{\beta_1}}{1+K_1 p_{CO_2}} \bullet \frac{1}{1+e^{K(EDC)_1}[EDC]}$
Side	$CH_2{=}CH_2{+}3O_2 \xrightarrow{Ag} 2CO_2{+}2H_2O$	-1321.7kJ/mol	$R_2=\frac{k_2 p_{C_2H_4}^{\alpha_2} p_{O_2}^{\beta_2}}{1+K_2 p_{CO_2}} \bullet \frac{1}{1+e^{K(EDC)_2}[EDC]}$

TABLE 3. The obtained kinetic model parameters.

No.	Reaction rate constant	Order of reaction		Carbon dioxide adsorption equilibrium constant	Inhibitor EDC adsorption equilibrium constant
R_1	$k_1=\exp\left(6.597-\frac{8.670\times10^4}{R_gT}\right)$	α_1=0.4275	β_1=0.8522	$K_1=\exp\left(17.55-\frac{1.3055\times10^5}{R_gT}\right)$	$K(EDC)_1$ = -2.419
R_2	$k_2=\exp\left(9.539-\frac{1.106\times10^5}{R_gT}\right)$	α_2=0.5215	β_2=0.9316	$K_2=\exp\left(12.709-\frac{1.1234\times10^5}{R_gT}\right)$	$K(EDC)_2$ = -1.956

TABLE 4. The inlet component data.

Material component	Calibration
C_2H_4 (mol%)	27.007
O_2 (mol%)	7.038
CO_2 (mol%)	2.138
EO (mol%)	0.033
N_2 (mol%)	58.324
H_2O (mol%)	0.184
EDC (mol%)	2.07925

the reaction tube bed is defined as a medium porous area. The flux inlet and pressure outlet are defined, and the mesh is saved and exported.

B. BOUNDARY CONDITION SETTING

Flux inlet and pressure outlet are taken as boundary conditions. The data of flux, temperature, pressure, material component concentration and other parameters can be imported. The initial export material component data of the reactor is set as 0. The inlet component data is shown in Table 4.

Convection heat transfer is selected for wall-surface boundary conditions, and the heat exchange coefficient and cooling water temperature are imported according to Table 1. The checkboxes of the porous medium and source item are checked in the medium porous area [23]. The catalyst parameters are added following Table 1, and the viscous resistance coefficient and inertial resistance coefficient are added.

C. USER-DEFINED FUNCTION (UDF)

The reaction heat may cause pressure and temperature changes in a reaction unit. The generation, accumulation, and removal of heat will influence the chemical reaction rate and temperature distribution of the reaction tube. Ethylene epoxidation reaction process is a dynamic changing process. It will need a certain period to reach the stability of component distribution and temperature distribution if some unknown factor disturbs the reaction process. The UDF of fluent should be developed and employed to describe the dynamic process.

The UDF of ethylene epoxidation reaction model mainly includes the following modules:

① Conversion of mass concentration and molar concentration;

② C_2H_4O component source item characterizing the main reaction;

③ CO_2 component source item characterizing by-reaction;

④ C_2H_4, O_2 and H_2O component items of other materials;

⑤ Heat-generating energy source items of a chemical reaction;

⑥ Resistance coefficient source items of the medium porous area.

D. SOLUTION SETUP

The SIMPLE algorithm and second-order upwind model are selected to carry out a discrete solution, wherein the time step is set, and the residual convergence monitor is shut down. The inlet pressure, the outlet oxygen component molar concentration, and the hot-spot temperature in the reaction area are monitored. The parameter monitoring data can be verified and automatically saved. The iterative solution should be conducted. It can be deemed as calculation convergence when these three parameters remain unchanged.

E. SELECTION OF TECHNOLOGICAL PARAMETERS

The abnormal fluctuation of operation parameters is the main cause of temperature runaway of the reactor in an ethylene

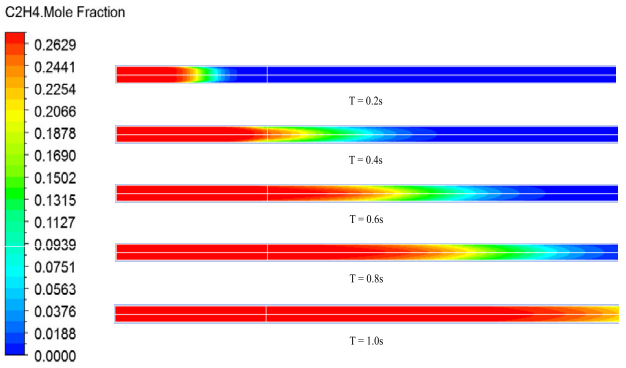

FIGURE 2. Concentration distributions of ethylene in the reaction tube at different times.

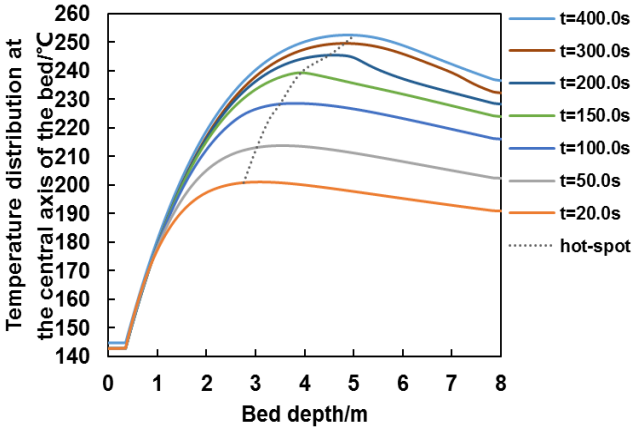

FIGURE 3. The process of temperature change in the central axial bed of reaction tube.

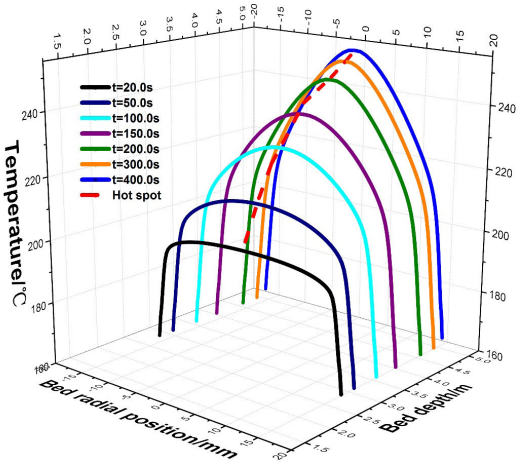

FIGURE 4. The radial distribution over time at a location 5.012m away from the hot-spot at a steady-state.

epoxidation reaction process. When the operation parameters reach a certain numerical range, the temperature will have a sharp rise, which will break the original thermal equilibrium in the reactor. The numerical ranges can be deemed as sensitive areas of parameters. In this paper, seven operation factors, i.e. ethene concentration, oxygen concentration, feed flux, feed temperature, drum temperature, operation pressure, and porosity of catalyst packing, are selected as the significant monitoring factors. Six variable fluctuation values within the upper and lower ranges are selected for each factor. The values of operation parameters of a single factor are changed under the condition that other operation parameters remain unchanged. The hot-spot temperature value and its location, reaction rate, heat release, and conversion rate are taken as inspection standards to analyze the influence effect of variable fluctuation on the operating conditions. Table 5 is a single-factor experiment table.

IV. RESULT AND DISCUSSION

A. MODEL VALIDATION

Ethylene epoxidation reaction is an unsteady process varying with the change of components and temperature in the tube. When the observed values of material components at the outlet and the max temperature of the flow field become stable, it can be thought that the catalytic reaction has reached a stable state under the operating condition. The simulation analysis of the operation process of ethylene epoxidation reactor is conducted to study the dynamic process. The steady-state of the fluid flow and heat transmission of raw materials mixture gas is taken as the initial field. Chemical reaction and material component items and energy source items are added to simulate and calculate temperature change, material component change and the change of chemical reaction rate from the initial stage to the steady stage, as shown in Fig. 2.

① Temperature distribution at the central axis of the reaction bed

Fig. 3 shows the temperature change process in the central axial bed of the reaction tube. Fig. 4 shows the radial distribution at a location 5.012m away from the hot-spot at a steady state.

The analytical simulation result indicates the catalyst bed temperature increases constantly with the reaction process, but the temperature rising rate slows down gradually and reaches a steady-state of the reaction in about 400 seconds. The location of a hot-spot inside the reaction tube moves downwards to the lower end of the bed and finally stops at a position of 5.0m. Meanwhile, the temperature at the outlet of the reaction tube rises accordingly. By monitoring the radial temperature distribution at the position of 5.0m, it is discovered that the temperature curve is similar to a para-curve, on which the temperature at the center of the bed is higher than the temperature at other positions. In the infinitesimal node element near the wall surface, the temperature change among infinitesimal elements is relatively remarkable, mainly because the node is near the wall surface, which ensures the better effect of heat transmission of the cooling water outside the tube. Heat transmission is difficult at the tube center, and the temperature is relatively high, particularly at the axial position of 4m to 5m, where the temperature tends to lose control. Therefore, special monitoring during the actual operation process is necessary.

TABLE 5. Single factor variable test of reactor operation parameters.

Factor	Feed composition ratio		Feed flowrate	Feed	Steam drum	Operating	Porosity
	yC_2H_4-in/%	yO_2-in/%	(kg·h-1)	temperature(℃)	temperature(℃)	pressure(MPa)	
0	27.007	7.03	59.8	142.6	200.98	2.1	0.371
1	15.00	3.50	20.0	120	185	1.4	0.2
2	20.00	4.50	40.0	145	200	1.6	0.3
3	25.00	5.50	60.0	170	215	1.8	0.4
4	30.00	6.50	80.0	195	230	2.0	0.5
5	35.00	7.50	100.0	220	245	2.2	0.6
6	40.00	8.50	120.0	245	260	2.4	0.7

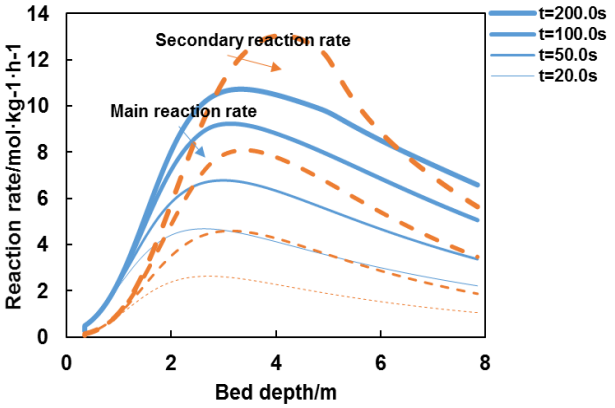

FIGURE 5. The trend of the main reaction and secondary reaction rates of ethylene epoxidation reaction along with the bed depth over time.

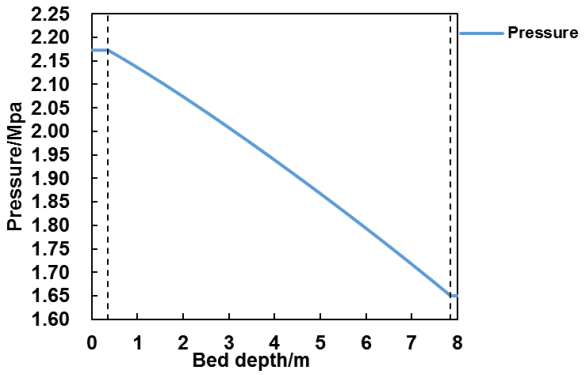

FIGURE 6. The pressure distribution along with the central axis of the bed when the reaction reaches a steady-state.

② Chemical reaction rate

Fig. 5 shows the changing trend of the main reaction rates and by-reaction rates along with the bed depth over time. As shown in the figure, the rates of main reactions and by-reactions rise firstly and then decline along with the bed depth. With the increase of reaction time, the reaction speed grows gradually. The main reaction rate decreases gradually, and the by-reaction rate increases rapidly after the reaction turns steady.

The result indicates that the reaction rate is relevant to the material component concentration, reaction temperature, and activation energy of the reaction. At the inlet of the reaction tube, the energy cannot meet the activity energy requirement of reaction due to the relatively low reaction temperature. The reaction rate is relatively slow, and the heat release of reaction begins to accumulate. The temperature in the reaction tube begins to increase gradually along with axial and radial directions, and the reaction speed rises. When the reaction heat and heat transmission outside the tube reach a balance, the temperature inside the tube will not increase anymore, and the chemical reaction rate begins to decline. Moreover, in the late half of the reaction tube, the chemical reaction rate begins to decline due to the gradual decrease of ethene and oxygen components.

③ Pressure distribution at the central axis of the bed

Fig. 6 indicates the pressure distribution along with the central axis of the bed when the reaction reaches a steady state. As shown in the figure, the fluid pressure decreases gradually under the resistance of the catalyst particles in the reaction tube, and the pressure difference is formed at the front and rear ends of the medium porous area. The pressure drop in a single reaction tube is 0.52 MPa.

④ Component distribution along with the central axis of the bed

When the reaction reaches a steady state, the molar concentration distribution of material components along with the central axis of the bed is shown in Fig. 7. The simulation result indicates that the molar concentrations of C_2H_4 and O_2 decrease gradually along with the bed depth with the progress of the chemical reaction, but the molar concentrations of CO_2 and EO increase gradually. The molar concentration values of material components in different positions of the reaction tube can be acquired from the simulation result. The conversion rate of ethene materials can be obtained, which reflects the ethene production capacity and operation efficiency of industrial equipment.

B. COMPARISON OF SIMULATED DATA VALIDATION

Based on the experimental data, a physical model of the reaction tube is established. Through the comparison between

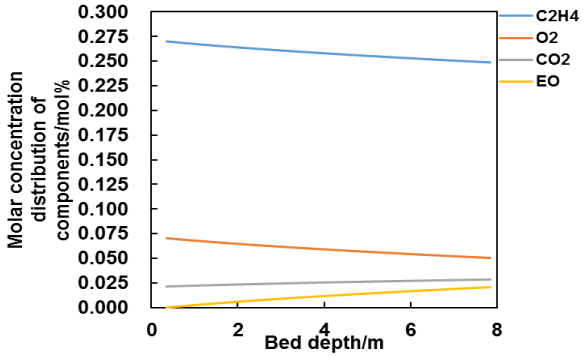

FIGURE 7. The molar concentration distribution of material components of the reaction tube along with the central axis of the bed.

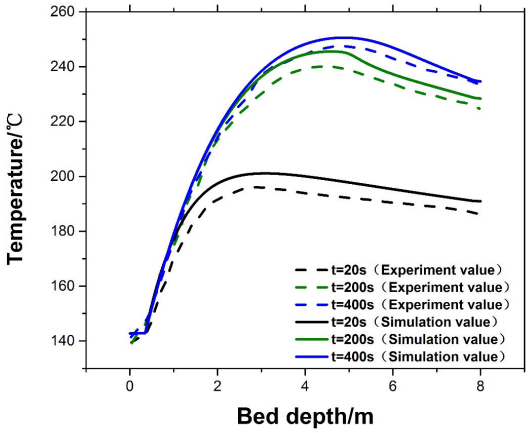

FIGURE 8. The comparison between the experimental data and the simulation data of the central axis temperature changing with the depth of the bed.

each material component concentration and conversion rate at the outlet of the reaction tube and the experimental data, it could be found that the error is basically within a 10% error range. Therefore, the simulation result data can be thought to be consistent with the experimental data. The experimental data and calculation result data of the reaction tube components are shown in Table 6.

Three groups of experimental data are selected to be compared with the simulation data, as shown in Fig. 8. The correlation between numerical simulation results and experimental data can be obtained. Table 7 shows that the central axis temperature changes with the bed depth at t = 20s, t = 200s, and t = 400s. It can be found that the simulation results and experimental results maintain consistency. The location and temperature of the hot spot (i.e., the highest temperature) are almost identical. The overall error is kept within 10%, as shown in Table 7. It fully reflects the accuracy of the numerical simulation results.

C. EFFECTS OF OPERATING CONDITIONS

Based on the technological parameters of ethylene epoxidation reactor and deviation selection, a single-factor effect experiment is conducted to analyze and study the impact

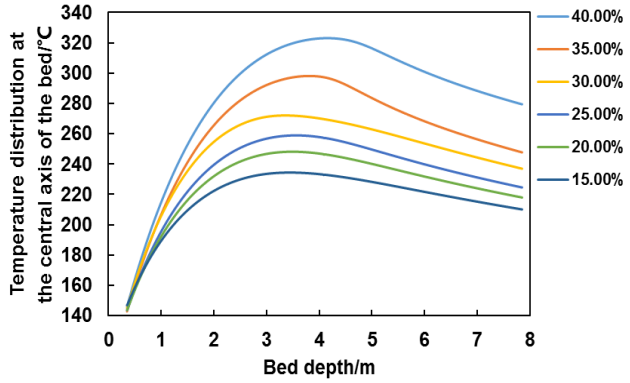

FIGURE 9. Effect of feeding ethylene on reaction and heat release in the bed layer.

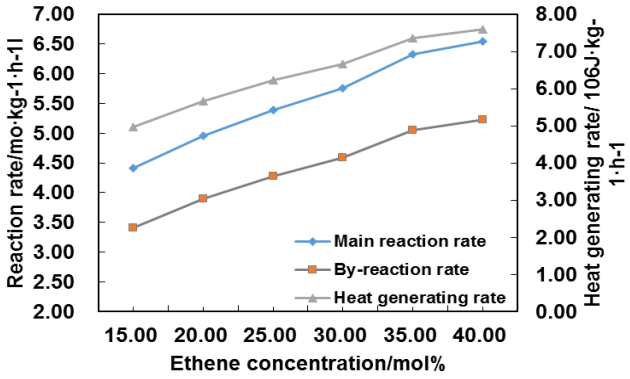

FIGURE 10. Effect of feeding ethylene on reaction and heat release in the bed.

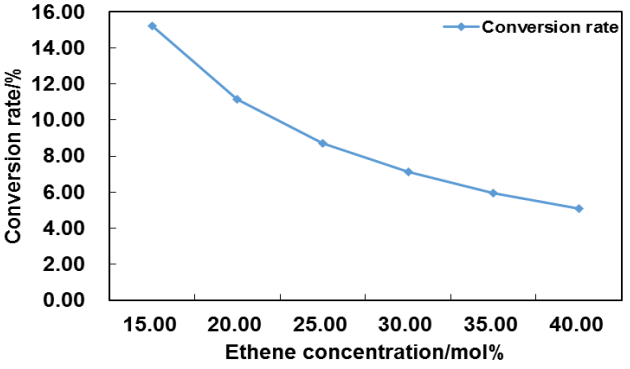

FIGURE 11. Effect of feeding ethylene on C_2H_4 conversion rate.

of parameter fluctuation on the thermal equilibrium and operation efficiency of the reactor bed. The parameters mainly include material component concentration, feed flux, feed temperature, drum temperature, operating pressure, and porosity catalyst packing rate.

1) EFFECTS OF ETHENE CONCENTRATION (CONCENTRATION OF MATERIALS)

Fig. 9, Fig. 10, and Fig. 11 indicate: with the increase of ethene concentration in the raw materials mixture gas, the overall bed temperature of reaction tube rises remarkably

TABLE 6. Numerical simulation results are compared with experimental data.

Parameter	C_2H_4 /mol%	O_2 /mol%	CO_2 /mol%	EO /mol%	H_2O /mol%	EDC /ppm	Conversion rate /%
Experimental value	24.920	4.444	2.894	2.233	0.874	1.991	7.76
Computation value	24.850	4.813	2.860	2.096	0.885	2.101	7.91
Error(%)	0.30	8.30	1.17	6.14	1.26	5.52	1.93

TABLE 7. The error of the temperature simulation data and experimental data at the center axis of bed.

Bed depth/m	**0-1**			**1-2**			**2-3**			**3-4**			**4-5**		
t/s	20.0	200.0	400.0	20.0	200.0	400.0	20.0	200.0	400.0	20.0	200.0	400.0	20.0	200.0	400.0
Experimental mean	152.73	154.52	155.98	181.92	195.77	194.56	194.53	222.70	226.36	195.07	235.11	240.77	193.02	239.71	246.72
Simulated mean	155.95	155.57	155.57	189.51	199.22	199.48	199.90	227.48	228.76	200.74	241.12	244.00	198.94	245.21	249.87
Error /%	2.11	0.68	0.26	4.17	1.76	2.53	2.76	2.15	1.06	2.91	2.56	1.34	2.76	2.29	1.28
Bed depth/m	**5-6**			**6-7**			**7-8**			**Total**					
t/s	20.0	200.0	400.0	20.0	200.0	400.0	20.0	200.0	400.0	20.0	200.0	400.0			
Experimental mean	191.17	236.48	245.62	189.66	231.27	240.45	187.54	226.59	235.48	185.70	217.77	223.24			
Simulated mean	196.56	240.68	249.18	194.14	234.76	243.70	191.83	230.23	237.20	190.95	221.78	225.97			
Error /%	2.82	1.78	1.45	2.36	1.51	1.35	2.29	1.61	0.73	2.83	1.84	1.22			

and the hot-spot temperature of bed also rises accordingly. The temperature rising rate increases with the growth of ethene concentration. The hot-spot in the bed moves toward the lower end of the bed. When the concentration ratio of ethylene to oxygen is less than 2:1, the oxygen is excessive, and the conversion rate of ethylene will increase gradually with the increase of the concentration of ethylene in the inlet. In the reaction process, the oxygen concentration should not exceed 7.1%, because the reaction process should keep off the explosion limit of the reaction gas. The ethylene oxide products should be obtained as far as possible in production. Therefore, the concentration ratio of ethylene to oxygen is usually higher than 2:1. The simulation results show that the reaction rate and heat production rate increase with the increase of ethylene concentration, but the conversion rate of ethylene decreases gradually.

When the ethene concentration reaches 30.0%, the hot-spot temperature of the reaction tube bed reaches an alarm limit 270°. When the ethene concentration is lower than 30.0%, the bed temperature grows gradually with the increase of ethene concentration. When the ethene concentration exceeds 30.0%, the bed temperature rises remarkably. Therefore, ethene concentration has a relatively big impact on temperature runaway incidents, which is an operation parameter that needs special monitoring. With the increase of ethene concentration, ethene conversion rate decreases eminently, which is a waste of technological energy consumption during the production process. According to the above analysis, it's advised to set the operation range of ethene concentration as 25.0∼30.0%.

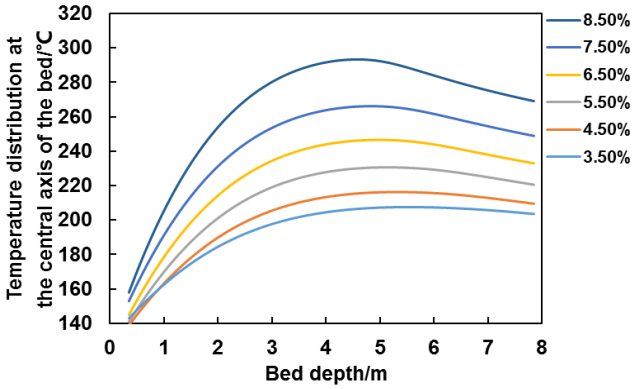

FIGURE 12. Effect of feeding oxygen on the hot spots in the bed.

2) EFFECTS OF OXYGEN CONCENTRATION

Fig. 12, Fig. 13, and Fig. 14 indicate: with the increase of oxygen concentration in the gas mixture of raw materials, the overall bed temperature of reaction tube rises remarkably and the hot-spot temperature of the bed also rises. The temperature increases with the growth of oxygen concentration. The hot-spot in the bed moves toward the lower end of the bed. The rates of main reactions, by-reactions, and heat-generating increase with the rise of oxygen concentration. Meanwhile, the ethene conversion rate rises sharply.

When the oxygen concentration reaches 7.5%, the hot-spot temperature in the reaction tube bed hits the high alarm value 270°, and the by-reaction rate and the heat generation of reaction increase rapidly. If safety measures are not taken in time, thermal equilibrium may be broken easily, and the

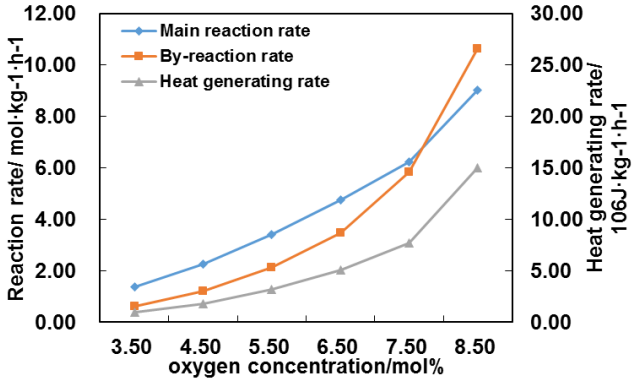

FIGURE 13. Effect of feeding oxygen on the material reaction and heat release in the bed.

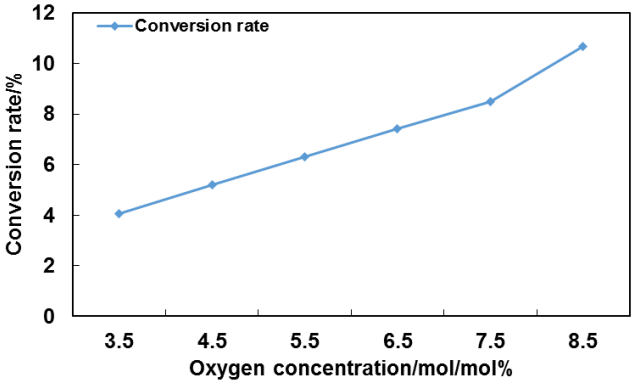

FIGURE 14. Effect of feeding oxygen on C_2H_4 conversion rate.

bed temperature may rise rapidly. Therefore, the oxygen concentration in the raw gas composition is also an operation parameter that needs special monitoring.

With the rise of oxygen concentration, ethene conversion rate rises subsequently. It is favorable for the increase of the unit production capacity. However, the oxygen concentration shall not exceed 7.1% when nitrogen is used as stabilizing gas, as the flammable gas composed of oxygen and ethene has a certain explosion limit. Based on the above analysis of factors, the suitable operation range of oxygen concentration should be 6.0%∼7.0%.

3) FEED FLUX

As shown in Fig. 15, Fig. 16, and Fig. 17, with the increase of feed flux, the bed hot-spot temperature rises slightly, the position of hot-spot moves backward, and the chemical reaction and heat release speeds increase accordingly, while the ethene conversion rate declines.

The analysis result indicates that feed flux has a limited impact on the temperature rise of the entire bed, but has a relatively strong impact on the bed temperature distribution. With the increase of flux, the flow velocity of the gas in the bed increases, which causes the hot-spot position to move downward. The outlet temperature rises, and thus there will be the risk of ''tail burning'' of the reactor.

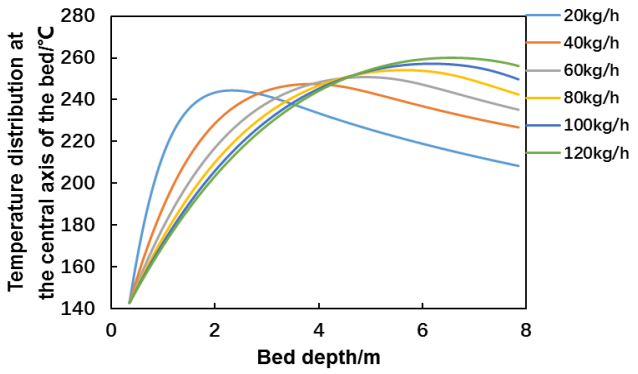

FIGURE 15. Effect of feed flow rate on the hot spots in the bed layer.

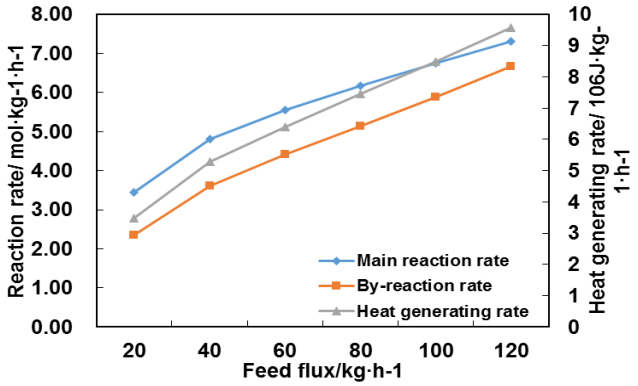

FIGURE 16. Effect of feed flow rate on reaction and heat release in the bed layer.

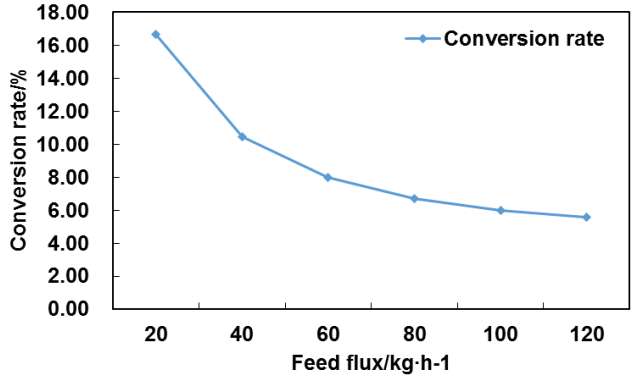

FIGURE 17. Effect of feed flow rate on C_2H_4 conversion rate.

The analysis of the feed flux change impact on ethene conversion rate reveals that ethene conversion rate turns slowly after a sharp decline with the increase of raw gas feed flux. In consideration of the feed flux impact on the bed temperature distribution, the feed flux should be 40∼60 kg· h−1.

4) DRUM TEMPERATURE

Analysis of Fig. 18 and Fig. 19 reveals that the bed hot-spot temperature rises remarkably with the rise of the cooling water drum temperature outside the tube. The chemical reaction rate and heat-generating rate also rise remarkably.

TABLE 8. Comprehensive analysis of the parameter fluctuations influence on the reactor temperature runaway accident.

Operating parameter	Deviation	Effect on the temperature	Can lead to thermal runaway	Alarm value	Appropriate working range	Actual working range	Error range
C2H4 concentration	Concentration increase	Hot-spot temperature rise greatly	Can	30.0mol%	25.0~30.0mol%	26.0~28.0mol%	3.8~7.1%
O2 concentration	Concentration increase	Hot-spot temperature rise greatly	Can	7.5mol%	6.0~7.0mol%	6.5~7.5	6.6~7.6%
Feed flowrate	Flowrate increase	Hot-spot temperature rise slightly	Limited effectiveness	120kg/h	40~60kg/h	40~65kg/h	0~7.7%
Feed temperature	Temperature rise	Hot-spot temperature rise slightly	Limited effectiveness	220℃	180~200℃	180~190℃	0~5.3%
Steam drum temperature	Temperature rise	Hot-spot temperature rise greatly	Can	215℃	185~200℃	190~210℃	2.6~4.8%
Operating pressure	Pressure rise	Hot-spot temperature rise proportionally	Limited effectiveness	2.4MPa	2.0~2.2MPa	2.0~2.3MPa	0~4.3%
Porosity	Porosity lower	Hot-spot temperature rise greatly	Can	0.3	0.4~0.6	0.4~0.6	0

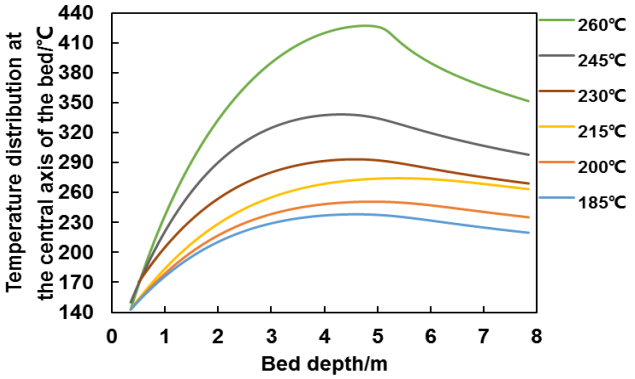

FIGURE 18. Effect of steam drum temperature on the hot spots in the bed.

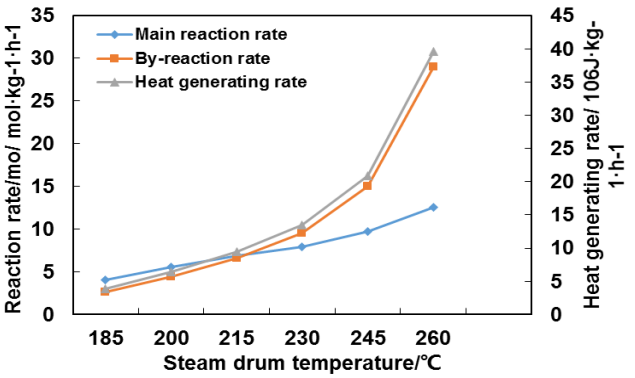

FIGURE 19. Effect of drum temperature on reaction and heat release in the bed.

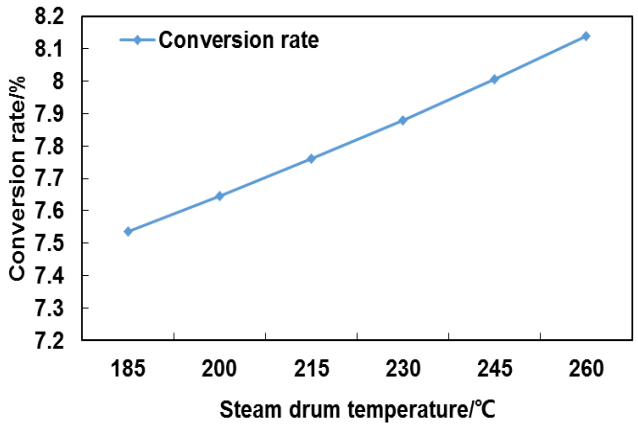

FIGURE 20. Effect of drum temperature on C_2H_4 conversion rate.

When the drum temperature is 215°, the bed hot-spot temperature reaches the high alarm temperature 270°. Meanwhile, the by-reaction rate is larger than the main reaction rate with the continuous rise of temperature. When the drum temperature exceeds 230°, the bed hot-spot temperature and main/by-reaction rate and the heat-generating speed rise rapidly. The by-reaction rate exceeds the main reaction rate. At this moment, the temperature runaway incident may occur without the intervention of external safety measures. When the drum temperature reaches 260°, the high bed temperature (427°) may burn the catalyst. The reaction tube may burst due to excessive pressure, and leakage, explosion, and other serious accidents may also occur. Drum temperature is a parameter that needs special monitoring for avoiding temperature runaway incidents.

From the perspective of the chemical reaction rate, the abrupt rise of bed temperature is mainly due to the by-reaction action. As the heat release rate of the by-reaction is more than ten times of that of the main reaction, it will cause loss of control of reaction temperature. Therefore, weakening by-reaction rate by improving the selectivity of catalyst is an efficient measure to prevent temperature runaway incidents.

Analysis of Fig. 20 reveals that ethene conversion rate rises slightly with the rise of drum temperature. In consideration of the equipment safety and operation efficiency, it is advised to choose lower drum temperature to avoid temperature runaway incidents or ensure higher selectivity of catalyst to inhibit by-reactions. 200° drum temperature is recommended after careful consideration.

5) EFFECTS OF OTHER OPERATION PARAMETERS

According to similar simulations, the effects of feed temperature, operating pressure, and porosity on reactor operation are also studied. With the increase of feed temperature,

the bed hot-spot temperature rises slightly, and the position of hot-spot moves forward substantially. The chemical reaction and heat release rate increase accordingly. There is little impact on ethene conversion rate. With the rise of operating pressure, the bed hot-spot temperature rises slightly pro-rata, and the position of hot-spot moves downward. The chemical reaction rate, heat release rate, and ethene conversion rate rise. With the increase of catalyst packing porosity, bed hot-spot temperature declines substantially, and the position of hot-spot moves forward. The chemical reaction rate, heat release rate, and ethene conversion rate decline accordingly. The comparison among document data reveals that the simulation result is basically in compliance with the experimental data of ethylene epoxidation reactor.

Based on the simulation analysis, the operation alarm value of each parameter and its proper operating range may be confirmed. The bed temperature 270° is considered as the high-temperature alarm value, as shown in Table 8. By comparing the simulation results with the actual operating conditions, the maximum and minimum error of the operating range is within 10%. The simulation results are consistent with the actual operating conditions. Therefore, the research model of this paper can be used in the study of the operation mechanism of ethylene epoxidation reactor and the influence of parameter fluctuation on the temperature runaway accident.

V. CONCLUSIONS

Based on the study of the kinetic mechanism of the chemical reaction and the assumption of medium porous area, a two-dimension model of gas-solid reaction tube based on a porous medium is established.

The calculation results of the numerical simulation of the CFD software are visualized. The changes of temperature, chemical reaction rate, material component concentration, and pressure field during the operation process of ethylene epoxidation reactor are analyzed. The theories of the chemical reaction and heat transmission are analyzed and explained. The distribution of ethene conversion rate when the reaction reaches the steady-state is acquired. Compared with the data of experimental devices, the result is in line with the actual production condition.

The result of the simulation analysis indicates that higher ethene concentration, oxygen concentration, feed flux, feed temperature, drum temperature, operating pressure, and lower porosity play a role in improving the bed temperature and accelerating reaction rate. Drum temperature, ethene concentration, oxygen concentration, and porosity have a significant impact on the occurrence of temperature runaway accidents. These parameters need special monitoring. However, feed flux, feed temperature, and operating pressure have little impact on the occurrence of temperature runaway accidents. With bed temperature 270° as the high-alarm value, the operation sensitivity area is confirmed for each parameter. Based on the analysis of parameter fluctuation that impacts the ethene conversion rate and other factors that impact the production capacity of the reactor, the appropriate operation scope is confirmed for each parameter. The research result will contribute to providing a theoretical basis for the safe and high-efficient operation of the reactor.

REFERENCES

[1] X. M. Cui, "Production technologies advance and market analysis of ethylene oxide," *Fine Specialty Chem.*, vol. 22, no. 5, pp. 12–18, May 2014.
[2] C.-S. Kao and K.-H. Hu, "Acrylic reactor runaway and explosion accident analysis," *J. Loss Prevention Process Ind.*, vol. 15, no. 3, pp. 213–222, May 2002.
[3] B. Shi, "Mechanism study on the temperature runaway of ethylene epoxidation reaction," M.S. thesis, Beijing Univ. Chem. Technol., Beijing, China, 2013.
[4] T. Varga, F. Szeifert, J. Réti, and J. Abonyi, "Analysis of the runaway in an industrial heterocatalytic reactor," *Comput. Aided Chem. Eng.*, vol. 24, no. 7, pp. 751–756, Jun. 2007.
[5] P. Ling and Z.-H. Chen, "The safety of ethylene oxide production: Temperature control in thermo-mechanical effect," *China Saf. Sci. J.*, vol. 18, no. 5, pp. 87–90, May 2008.
[6] J. M. Zaldívar, J. Cano, M. A. Alós, J. Sempere, R. Nomen, D. Lister, G. Maschio, T. Obertopp, E. D. Gilles, J. Bosch, and F. Strozzi, "A general criterion to define runaway limits in chemical reactors," *J. Loss Prevention Process Ind.*, vol. 16, no. 3, pp. 187–200, Mar. 2003.
[7] T. Obertopp, M. A. Alós, and E. D. Gilles, "Runaway prevention in chemical reactors using model-based estimation of parametric sensitivities," *Comput. Chem. Eng.*, vol. 23, pp. S211–S214, Jun. 1999.
[8] W. Strasser, "CFD study of an evaporative trickle bed reactor: Mal-distribution and thermal runaway induced by feed disturbances," *Chem. Eng. J.*, vol. 161, nos. 1–2, pp. 257–268, Jul. 2010.
[9] A. Guardo, M. Coussirat, F. Recasens, M. A. Larrayoz, and X. Escaler, "CFD study on particle-to-fluid heat transfer in fixed bed reactors: Convective heat transfer at low and high pressure," *Chem. Eng. Sci.*, vol. 61, no. 13, pp. 4341–4353, Jul. 2006.
[10] X. Chen, J. Dai, and Z. Luo, "CFD modeling using heterogeneous reaction kinetics for catalytic dehydrogenation syngas reactions in a fixed-bed reactor," *Particuology*, vol. 11, no. 6, pp. 703–714, Dec. 2013.
[11] A. G. Dixon, G. Walls, H. Stanness, M. Nijemeisland, and E. H. Stitt, "Experimental validation of high Reynolds number CFD simulations of heat transfer in a pilot-scale fixed bed tube," *Chem. Eng. J.*, vols. 200–202, pp. 344–356, Aug. 2012.
[12] R. Maghrebi, N. Yaghobi, S. Seyednejadian, and M. H. Tabatabaei, "CFD modeling of catalyst pellet for oxidative coupling of methane: Heat transfer and reaction," *Particuology*, vol. 11, no. 5, pp. 506–513, Oct. 2013.
[13] X. Zhou, Y. Duan, X. Huai, and X. Li, "3D CFD modeling of acetone hydrogenation in fixed bed reactor with spherical particles," *Particuology*, vol. 11, no. 6, pp. 715–722, Dec. 2013.
[14] G. D. Wehinger, T. Eppinger, and M. Kraume, "Detailed numerical simulations of catalytic fixed-bed reactors: Heterogeneous dry reforming of methane," *Chem. Eng. Sci.*, vol. 122, pp. 197–209, Jan. 2015.
[15] Y.-Q. Zhuang, X. Gao, Y.-P. Zhu, and Z.-H. Luo, "CFD modeling of methanol to olefins process in a fixed-bed reactor," *Powder Technol.*, vol. 221, no. 5, pp. 419–430, May 2012.
[16] S. F. Sun, X. Y. Lan, S. J. Ma, and J. S. Gao, "Numerical simulation of the transfer and reaction processes in catalytic reforming fixed bed reactors," *Acta Petrolei Sinica*, vol. 24, no. 1, pp. 38–45, Feb. 2008.
[17] J. T. Gleaves, A. G. Sault, R. J. Madix, and J. R. Ebner, "Ethylene oxidation on silver powder: A tap reactor study," *J. Catal.*, vol. 121, no. 1, pp. 202–218, Jan. 1990.
[18] V. Russo, T. Kilpiö, J. H. Carucci, M. Di Serio, and T. O. Salmi, "Modeling of microreactors for ethylene epoxidation and total oxidation," *Chem. Eng. Sci.*, vol. 134, pp. 563–571, Sep. 2015.
[19] T. Salmi, D. Y. Murzin, P. Mäki-Arvela, B. Kusema, B. Holmbom, S. Willför, and J. Wärnå, "Kinetic modeling of hemicellulose hydrolysis in the presence of homogeneous and heterogeneous catalysts," *AIChE J.*, vol. 60, no. 3, pp. 1066–1077, Mar. 2014.
[20] R. J. Liang, J. W. Li, B. H. Chen, and Y. Z. Na, "Macrokinetics of epoxidation of ethylene over YS-7 Ag-based catalyst," *J. Henan Univ.*, vol. 37, no. 2, pp. 141–146, Mar. 2007.
[21] R. J. Liang, J. W. Li, J. B. Li, and J. S. Chen, "Macrokinetics of epoxidation of ethylene over Y-type silver catalyst," *Chem. Eng.*, vol. 43, no. 1, pp. 51–54, Jan. 2015.

[22] R. J. Liang and J. W. Li, "Macrokinetics of ethylene epoxidation over B-type silver catalyst," *Petrochem. Technol.*, vol. 44, no. 1, pp. 51–54, Jan. 2015.
[23] Z. Zhang, Z. Guo, and S. Ji, "Numerical simulation of fixed bed reactor for oxidative coupling of methane over monolithic catalyst," *Chin. J. Chem. Eng.*, vol. 23, no. 10, pp. 1627–1633, Oct. 2015.

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