

Bubble Effectiveness in Cyclohexane Non-Catalytic Oxidation Process

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ABSTRACT: *The bubble effectiveness in liquid phase cyclohexane non-catalytic oxidation process is discussed in this paper. Then the bubble effectiveness and a new proposed kinetic model are used in the mathematical model of the industrial reactor for the cyclohexane non-catalytic oxidation process. Furthermore, simulation and optimization based on this reactor model are carried out. The results of simulation show that the reactor model using the concept of bubble effectiveness agrees better with the plant data, and the results of optimization are much better than the present industrial production level, which will help to improve the operation of the reactor section and design of new installations.*

KEY WORDS: *Bubble effectiveness, Cyclohexane, Oxidation, Simulation, Optimization.*

INTRODUCTION

Gas-liquid reactors including bubbling towers, stirred tank reactors, multi-stage reactors and gas-liquid pipe reactors have found broad applications in the field of gas absorption, pharmaceutical industries, petrochemical industries and environmental engineering. In these gas-liquid reactors, take hydrocarbon air oxidation process for example, for those bubbles that stay very long in the reactor, the oxygen in these bubbles is almost used up and these bubbles seem to be useless to oxidation reaction. That means the distribution of the residence time in the equipment may cause the distribution of the concentration of the reacting component in the gas phase, thus resulting in the problem of bubble effectiveness or effective contact area between gas and liquid phase.

Liquid phase oxidation of hydrocarbons using air or oxygen as oxidants are of great industrial importance by the reason of their role in converting petroleum hydrocarbon feedstock such as alkanes, olefins and

aromatics into organic chemicals important in the polymer and petrochemical industries [1]. Liquid phase oxidation of cyclohexane is a typical example of this kind of reactions. It supplies much of the raw materials (cyclohexanol, cyclohexanone and adipic acid) needed for the production of nylon 6 and nylon 66. As a matter of fact, liquid phase oxidation of cyclohexane may be one of the least efficient of all major industrial chemical processes. On the other hand, the increasing requirement of materials for the synthetic fiber industries promoted the development of the technology for the oxidation of cyclohexane. Methods for improving the yield of the process have naturally been the focus of research effort over the decades [1]. A lot of researchers have engaged in development of new catalyst for cyclohexane catalytic oxidation to improve the yield. And some research works have been conducted on modeling and simulation of the cyclohexane non-catalytic or catalytic oxidation process.

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Schaefer investigated the autocatalytic cyclohexane oxidation in a lab-scale bubble column reactor with online measurement of bubble size [2]. These attempts have led to a better understanding of the reactor behavior as well as the relationship between reaction and mass transfer in the reactor [3-6]. In modeling such an industrial process, phenomena such as complex flow characteristics of gas and liquid, kinetics of oxidation, complicated gas liquid equilibrium relationship, and various heat and mass transfer mechanisms have to be incorporated in a suitable manner.

In this paper, the concept of bubble effectiveness was introduced into the process of cyclohexane oxidation for the first time. The bubble effectiveness in cyclohexane non-catalytic oxidation process was calculated and a mathematical model of the reactor for cyclohexane non-catalytic oxidation process was developed. Furthermore, simulation and optimization work was carried out based on this reactor model.

BUBBLE EFFECTIVENESS

Although it has been shown that the kinetics become first order in oxygen at sufficient small concentration of oxygen, the concentration of oxygen close to the interface, and hence in most of the diffusion film, will be much higher than in the bulk. Therefore, the kinetics will be considered to be zero order in oxygen in the film theory equations [7]. The diffusion plus reaction equations in the film can be written as:

$$D_O \frac{d^2 C_{O_2}}{dX^2} = (k_{01} C_p + k_{02} C_p^2) \quad (1)$$

$$D_p \frac{d^2 C_p}{dX^2} = -k_{01} C_p \quad (2)$$

$$X = 0 \quad C_{O_2} = C_{O_2}^* \quad \frac{dC_p}{dX} = 0 \quad (3)$$

$$X = \delta \quad C_{O_2} = C_{L,O_2} \quad C_p = C_{pe} \quad (4)$$

Equation (3) states that the equilibrium is achieved at the gas-liquid interface, and the products do not transfer across the interface. The profiles for the oxygen and products in the film are obtained by solving the diffusion-reaction equations:

$$C_{O_2} = C^* + C_{L,O_2} - \frac{XC_{O_2}^*}{\delta} + \quad (5)$$

$$\frac{qC_{O_2}^*}{\text{Cos} \sqrt{\frac{M_1}{q}}} \left[1 - \text{Cos} \left(\frac{X}{\delta} \sqrt{\frac{M_1}{q}} \right) - \frac{X}{\delta} (1 - \text{Cos} \sqrt{\frac{M_1}{q}}) \right] +$$

$$\frac{M_2 q C_{O_2}^*}{8M_1 \text{Cos}^2 \sqrt{\frac{M_1}{q}}} \left[1 - \text{Cos} \left(\frac{2X}{\delta} \sqrt{\frac{M_1}{q}} \right) -$$

$$\frac{X}{\delta} (1 - \text{Cos}^2 \sqrt{\frac{M_1}{q}}) - \frac{M_2 C_{O_2}^*}{4 \text{Cos}^2 \sqrt{\frac{M_1}{q}}} \left[\frac{X}{\delta} (1 - \frac{X}{\delta}) \right]$$

$$C_p = \frac{C_{pe} \text{Cos} \left[\left(\frac{X}{\delta} \right) \sqrt{\frac{M_1}{q}} \right]}{\text{Cos} \sqrt{\frac{M_1}{q}}} \quad (6)$$

$$q = \frac{D_p C_{pe}}{D_O C_{O_2}^*} \quad (7)$$

$$M_1 = \frac{D_O k_{01} C_{pe}}{k_L^2 C_{O_2}^*} \quad (8)$$

$$M_2 = \frac{D_O k_{02} C_{pe}}{k_L^2 C_{O_2}^*} \quad (9)$$

Then the rate of the diffusion-reaction is:

$$r_{O_2} = -aD_O \frac{dC_{O_2}}{dX} \Big|_{X=0} \quad (10)$$

$$= ak_L C_{O_2}^* - \frac{aD_p C_{pe}}{\text{Cos}^2 \sqrt{\frac{D_O^2 k_{01}}{k_L^2 D_p}} \left[-\frac{k_L}{D_O} (1 - \text{Cos} \sqrt{\frac{D_O^2 k_{01}}{k_L^2 D_p}}) \right]}$$

$$+ \frac{ak_{02} C_{pe}^2 D_p}{8k_{01} \text{Cos}^4 \sqrt{\frac{D_O^2 k_{01}}{k_L^2 D_p}}} \left[-\frac{k_L}{D_O} (1 - \text{Cos}^2 \sqrt{\frac{D_O^2 k_{01}}{k_L^2 D_p}}) \right] +$$

$$\frac{aD_O k_{02} C_{pe}^2}{4k_L \text{Cos}^4 \sqrt{\frac{D_O^2 k_{01}}{k_L^2 D_p}}}$$

Equation (10) is simply recorded as:

$$r_{O_2} = ak_L C_{O_2}^* + B \quad (11)$$

The concept of bubble effectiveness is similar to the effective coefficient of catalyst in multi-phase catalytic reaction, and the bubble effectiveness of a certain size bubble can be defined as [8]:

$$\eta_s = \frac{r_b}{r_{O_2}(0)} = \frac{1/\tau \int_0^\tau r_{O_2}(t) dt}{r_{O_2}(0)} \quad (12)$$

The equilibrium relationship at the gas-liquid interface:

$$C_{O_2}^* = H_0 P \rho_m y_{O_2, \text{exit}} \quad (13)$$

According to mass balance, the reducing amount of the oxygen in the bubble is equal to the consumption at the interface:

$$-dn_{O_2} = r_{O_2} V dt \quad (14)$$

We can obtain the concentration of the oxygen in the gas phase from equation (11) and equation (14):

$$r_{O_2}(t) = a(\rho_m P H_0 k_L y_0(0) - B) e^{-k_L a R T \rho_m H_0 t} \quad (15)$$

and the bubble effectiveness in liquid phase cyclohexane non-catalytic oxidation process is:

$$\eta_s = \frac{1/\tau \int_0^\tau r_{O_2}(t) dt}{r_{O_2}(0)} = \frac{1 - e^{-k_L a R T \rho_m H_0 \tau}}{k_L a R T \rho_m H_0 \tau} \quad (16)$$

KINETIC MODEL

Cyclohexane oxidation is a complicated autocatalytic free-radical chain reaction. *Tolman* developed a reaction scheme comprising up to 154 reactions [9]. It is impractical to consider too many reactions in the scheme used for practical calculations, since it is so complicated that it requires too many kinetic constants, which can not be simultaneously determined with sufficient accuracy. Lumped kinetic models with relatively a small quantity of kinetic constants are always adopted [3,10-12]. *Bhattacharya* derived a kinetic model for liquid phase

oxidation of cyclohexane by using a reaction network based on a consistent free radical mechanism [13].

In the present work, we propose a kinetic model and apply it in the reactor model. Cyclohexane is firstly oxidized to cyclohexyl hydroperoxide. $AO\cdot$ and $AOO\cdot$ is the main free radical to form cyclohexanol and cyclohexanone. At the same time, $AO\cdot$ and $AOO\cdot$ are mainly from the decomposition of cyclohexyl hydroperoxide. Therefore, we assume reaction in eq. (18) and (20). Cyclohexanone have influences on the decomposition of cyclohexyl hydroperoxide, we consider reaction in eq. (19) and (23). Furthermore, cyclohexanone can be oxidized to organic acid (eq. (21)). Equation (24) and (25) indicate the reaction between acid and cyclohexanol. *Pohorecki* developed that cyclohexane may react with cyclohexyl hydroperoxide to form cyclohexanol [14]. The reactions are shown in table 1.

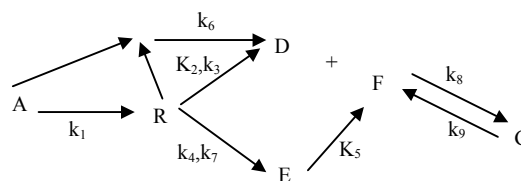


Table 1: Reactions of cyclohexane non-catalytic oxidation process.

| Reactions | Reaction rate | |
|-------------------------------------|---|------|
| $A + O_2 \rightarrow R$ | $r_1 = k_1 C_{O_2} (C_R + C_R C_E)^{1/2}$ | (17) |
| $2R \rightarrow 2D + O_2$ | $r_2 = k_2 C_R^2$ | (18) |
| $R + E \rightarrow D + E + 1/2 O_2$ | $r_3 = k_3 C_E C_R$ | (19) |
| $R \rightarrow E + H_2O$ | $r_4 = k_4 C_R$ | (20) |
| $E + 3/2 O_2 \rightarrow F$ | $r_5 = k_5 C_E C_{O_2}$ | (21) |
| $A + R \rightarrow 2D$ | $r_6 = k_6 C_A C_R$ | (22) |
| $R + E \rightarrow 2E + H_2O$ | $r_7 = k_7 C_R C_E$ | (23) |
| $2D + F \rightarrow G$ | $r_8 = k_8 C_D C_F$ | (24) |
| $G \rightarrow 2D + F$ | $r_9 = k_9 C_G$ | (25) |

The products include cyclohexanol, cyclohexyl hydroperoxide, cyclohexanone, acid and ester. The acid formed in the reaction mainly is adipic acid, and it reacts with cyclohexanol to form corresponding ester. During the oxidation process, the catalysis of the production lies in its contribution to initiate the formation of the free radicals. Reaction (17) is regarded as the sum of two radical reactions:



The cyclohexyl radicals are generated during the breakdown of the cyclohexyl hydroperoxide to the reactions (18), (19), (20) and (23), it can be derived that the rate of this non-catalytic oxidation system is proportional to the square root of the radical generating components [15]. Simplification of the radical reaction equations yields the following expression for the formation of the various components:

$$r_A = -k_1 C_{O_2} (C_R + C_R C_E)^{1/2} - k_6 C_A C_R \quad (28)$$

$$r_R = k_1 C_{O_2} (C_R + C_R C_E)^{1/2} - k_2 C_R^2 - k_3 C_E C_R - k_4 C_R - k_6 C_A C_R - k_7 C_R C_E \quad (29)$$

$$r_D = k_2 C_R^2 + k_3 C_E C_R + 2k_6 C_A C_R - 2k_8 C_D C_F + 2k_9 C_G \quad (30)$$

$$r_E = k_4 C_R + k_7 C_R C_E - k_5 C_E C_{O_2} \quad (31)$$

$$r_F = k_5 C_E C_{O_2} - k_8 C_D C_F + k_9 C_G \quad (32)$$

$$r_G = k_8 C_D C_F - k_9 C_G \quad (33)$$

$$r_{O_2} = -k_1 C_{O_2} (C_R + C_R C_E)^{1/2} + 0.5k_2 C_R^2 + 0.5k_3 C_E C_R - 1.5C_E C_{O_2} \quad (34)$$

The rate expression for the oxygen only describes the change of the oxygen concentration in the liquid phase resulting from the chemical reactions. For the full balance of oxygen in the liquid, the oxygen transfer from the gas phase to liquid phase must be considered. Reaction rate constants including $k_1 \sim k_9$ were determined by fitting the experimental data.

EXPERIMENTAL

In order to determine the reaction rate constants in equation (28)-(34), the kinetic experiments were carried

out in a pressure stainless tank with a capacity of 0.003 m³. The scheme of the experimental apparatus is shown in Fig.1.

The air from a gas cylinder was supplied through a pressure reducing valve and flow-stabilising tube. It was heated to the reactor temperature and was introduced to the bottom of the reactor through a sparger. The vaporized cyclohexane was cycled to the reactor through a condenser. Liquid samples for analysis were taken from a located hole in the reactor through a needle valve. The reaction temperature varied in the range of 155~180 °C, pressure 2 MPa, stirrer speed 2000 rpm, and gas flow 0.001-0.005 Nm³/min. The cyclohexane, cyclohexanol and cyclohexanone were analyzed by the chromatographic method, and the cyclohexyl hydroperoxide, acid and esters were analyzed by chemical method [11].

RESULTS AND DISCUSSION

Mathematical Model and Simulation

In the industrial cyclohexane non-catalytic oxidation process, the cyclohexane is oxidized by air in a cascade of five continuous-stirred tank reactors. A simplified diagram of the setup is shown in Fig. 2. The air is introduced through spargers at the bottom of each reactor. The oxidation products including cyclohexyl hydroperoxide, cyclohexanol, cyclohexanone, acid, ester and large amount of unreacted cyclohexane flow continuously out from the fifth reactor. Since the oxidation takes place without added catalyst, the main oxidation product is cyclohexyl hydroperoxide. Therefore, the oxidation products undergo a further decompose process to change the cyclohexyl hydroperoxide into cyclohexanol and cyclohexanone, and then separate the cyclohexane to recycle. The operating temperature is about 158~175 °C, and the pressure is about 1.2 MPa.

The reaction kinetic model described above, together with the concept of bubble effectiveness and the suitable hydrodynamic model of the industrial reactor have been used to establish a mathematical model of the industrial reactor for the cyclohexane non-catalytic oxidation process. In this reactor model, firstly, the reaction rate at the gas-liquid phase is considered to be the same as the single bubble, all of the bubbles are almost the same size and shape, and there are no coalescence and breakage during the reaction. *Suresh* studied mass transfer with chemical reaction from bubble swarms in a stirred tank,

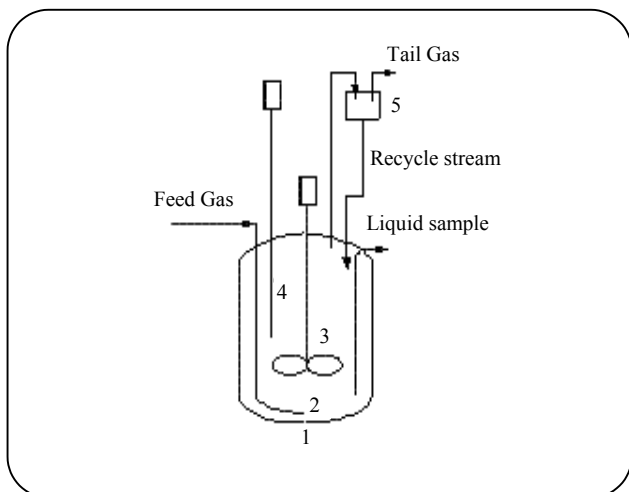


Fig. 1: Scheme of the setup (1: Reactor, 2: Sparger, 3: Stirrer, 4: Temperature Controller, 5 Condenser).

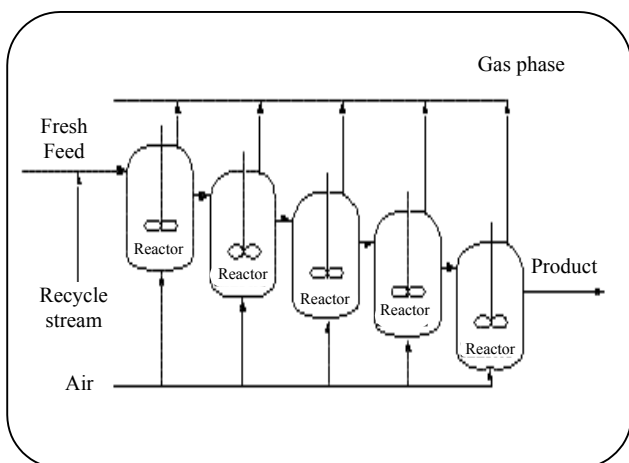


Fig. 2: Scheme of the industrial cyclohexane non-catalytic oxidation process.

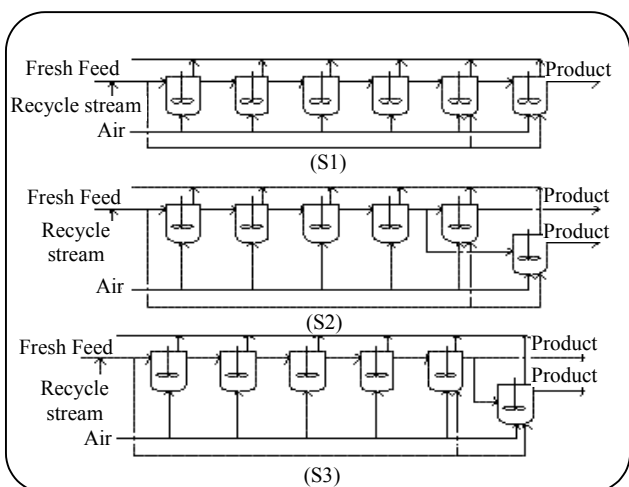


Fig. 3: Scheme of the structure optimization.

the gas bubble are assumed to be spherical and all of the same size [16]. Gal-Or and Hoelscher have investigated the effect of imposing a bubble size distribution on mass transfer and show that little error results by replacing the variable bubble radius by the Sauter mean bubble radius [17]. Secondly, the physical properties of the reactants and the products do not change with the time. Furthermore, the liquid phase is supposed to be mixing flow, and the gas phase is supposed to be plug flow since the stirrer speed is very slow and the superficial velocity of gas phase is large.

The comparison of the plant data and the calculated conversion of cyclohexane and the mole fraction of the products in the liquid phase outlet are shown in table 2, here conversion is defined as the proportion of the amount of the total products to the amount of the unreacting cyclohexane and the products in the liquid phase outlet. Table 3 shows the comparison of the plant data and the calculated oxygen flow in the gas phase outlet. In table 2 and 3, Cal.2-1 and Cal.3-1 are the results of the reactor model that the gas phase is supposed to be mixing flow, Cal.2-2 and Cal.3-2 are the results of the reactor model that the gas phase is supposed to be plug flow, Cal.2-3 and Cal.3-3 are also the results of the reactor model that the gas phase is supposed to be plug flow but revised by using the concept of bubble effectiveness. Comparing the results between Cal.2-1 and Cal.2-2, Cal.3-1 and Cal.3-2, we can find that it is closer to the real process when the gas phase is supposed to be plug flow.

The results of Cal.2-3 show that the calculated conversion and the mole fraction of desired products including cyclohexanol, cyclohexyl hydroperoxide and cyclohexanone are very close to the plant data. For the bubbles in the reactor, the oxygen in it is gradually consumed, the longer the bubbles stay in the reactor, the smaller the concentration of the oxygen is, and the smaller the bubble effectiveness is. By this token, there undoubtedly exist the problem of the bubble effectiveness. The calculated results also testify this. From table 2 and 3, we can find that the simulation result calculated from the reactor model revised by bubble effectiveness is better.

OPTIMIZATION

Based on the mathematical model of the industrial

Table 2: Comparison of the results of liquid phase outlet.

| | Conversion % | R+D +E % | F % | G % |
|------------|--------------|----------|-------|-------|
| Plant data | 3.68 | 3.48 | 0.089 | 0.037 |
| Cal.2-1 | 4.09 | 3.93 | 0.081 | 0.025 |
| Cal.2-2 | 3.83 | 3.68 | 0.073 | 0.025 |
| Cal.2-3 | 3.71 | 3.58 | 0.071 | 0.024 |

reactor, the influences of operation parameters such as air flow rate, temperature and liquid phase flow rate were investigated. The results showed that the conversion increased as the gas flow rate increased, however, the selectivity decreased and at the same time excessive large air flow rate may cause safety trouble. The results of the influences of temperature and liquid phase flow rate also showed that the selectivity varies in opposite way with the conversion. The problem lies in how to effectively increase the yield of the process. This might be the work of process optimization, including parameter optimization (temperature, pressure, flow rate of the materials etc.) and structure optimization.

The results of optimization are shown in table 4. In table 4, P1 and P2 are the results of parameter optimization. Here, P1 is the result of using sequential quadratic programming algorithm, and P2 is the result using adaptive genetic algorithm. The sequential quadratic programming algorithm is a generalization of *Newton's* method for unconstrained optimization in that it finds a step away from the current point by minimizing a quadratic model of the problem. In sequential quadratic programming algorithm, it uses nonlinear equation obtained from the Kuhn Tucker condition to carry out iterative calculation, and the iterative process just can be replaced by the corresponding quadratic programming problem, then the problem solving process is changed to solve a quadratic programming sequence. The adaptive genetic algorithm begins with a group of randomly generated viable solution, with the aid of genetic operation of duplication, recombination and mutation, automatically obtain and accumulate the information to the solution space, and gradually approach the optimum solution. In the adaptive genetic algorithm, a special adaptive crossover and mutation operator was constructed. The crossover and mutation probability was adjusted

Table 3: Comparison of the results of gas phase outlet.

| Oxygen flow (mol/s) | Reactor | | | | |
|---------------------|---------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 |
| Plant data | 0.111 | 0.180 | 0.280 | 0.467 | 0.722 |
| Cal.3-1 | 0.008 | 0.019 | 0.036 | 0.069 | 0.127 |
| Cal.3-2 | 0.058 | 0.126 | 0.262 | 0.508 | 0.910 |
| Cal.3-3 | 0.076 | 0.157 | 0.290 | 0.523 | 0.933 |

adaptively according to the corresponding fitness value. The result from the adaptive genetic algorithm is better than that from the sequential quadratic programming algorithm.

Through parameter optimization, the yield could only be improved in a finite number of possibilities. Furthermore, the structure optimization was carried out. The plot (S1) in Fig. 3 showed that the new added reactor was connected with the origin five reactors in series, and the outlet from the fifth reactor is entirely fed into the sixth reactor. Part of the fresh raw material feed was introduced into the last two reactors because the concentration of the free radical increased along with the reaction proceeding. The plot (S2) in Fig. 3 showed that the new added reactor was connected in parallel with the origin reactors. The outlet from the fourth reactor was simultaneously fed into the fifth and the new added reactor. And both of the outlets from the fifth and the sixth reactor are the final oxidation products. Similar with the first case, part of the fresh feed was introduced into the last two reactors. And the plot (S3) in Fig. 3 showed that the new added reactor is in parallel-series connection with the origin five reactors. Part of the outlet from the fifth reactor is as the result of final oxidation product and part of the outlet from the fifth reactor was fed into the new added reactor. The optimization results were shown in table 4, as it could be seen from the table that the added reactor in parallel-series connection was the best case.

CONCLUSIONS

The bubble effectiveness in cyclohexane liquid phase non-catalytic oxidation process is discussed in this paper. A new reaction kinetic model together with the concept of the bubble effectiveness is used in the reactor model for cyclohexane non-catalytic oxidation process.

Table 4: Results of optimization.

| | Before optimization | Parameter optimization | | Structure optimization | | |
|-------|---------------------|------------------------|--------|------------------------|--------|--------|
| | | P1 | P2 | S1 | S2 | S3 |
| Yield | 3.48 % | 4.60 % | 5.18 % | 8.15 | 7.14 % | 8.38 % |

Furthermore, simulation and optimization based on this reactor model are carried out. The reactor model using the concept of bubble effectiveness obtains better simulation results. And the results of optimization are much better than present industrial production level, which will contribute towards improvement of operation of the existing reactor section as well as more accurate design of new installations.

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Nomenclatures

| | |
|----------------|---|
| a | Interfacial area per unit volume of liquid, (m^2/m^3) |
| A | Cyclohexane |
| C | Concentration, (kmol/m^3) |
| C* | Concentration at interface (equilibrium value), (kmol/m^3) |
| D _O | Molecular diffusivity of oxygen in cyclohexane, (m^2/s) |
| D | Cyclohexanol |
| D _p | Diffusivity of reaction products in medium of oxidizing cyclohexane, (m^2/s) |
| E | Cyclohexanone |
| F | Acid |
| G | Ester |
| H _o | Henry's law coefficient, (mol frac/atm) |
| k | Reaction rate constants, ($\text{m}^3/\text{kmol s}$, $1/\text{s}$, $\text{kmol}^{1/2}/\text{m}^{3/2} \text{ s}$) |
| k _L | Physical mass transfer coefficient in liquid, (m/s) |
| P | Reactor pressure, (atm) |
| r | Rate of reaction, ($\text{kmol}/\text{m}^3 \text{ s}$) |
| r _b | The actual rate of reaction, ($\text{kmol}/\text{m}^3 \text{ s}$) |
| r(t) | Rate of reaction at time t, ($\text{kmol}/\text{m}^3 \text{ s}$) |
| R | Cyclohexyl hydroperoxide |
| t | Time, (s) |

| | |
|---|---|
| T | Temperature, (K) |
| V | Volume, (m^3) |
| X | Distance in liquid from the gas-liquid interface, (m) |
| y | Mole fraction in the liquid phase |

Greek Letters

| | |
|----------|---|
| η_s | Bubble effectiveness of a single bubble |
| τ | Residence time, (s) |
| ρ_m | Molar density of liquid, (kmol/m^3) |

Subscripts

| | |
|---|-----------|
| i | Component |
| p | Product |

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