CALCULATION OF THE OPTIMUM SYSTEM OF A FLOW-THROUGH CHEMICAL REACTOR

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A liquid-phase unidimensional flow-through chemical reactor with diffusion is discussed. The role of diffusion in such a reactor was studied in [1, 2] for a simple chemical reaction (A \to C). An analysis of the principles of the occurrence of complex reactions in the front of the flame [3-6] indicated that, depending on the type of the reaction, the degree of conversion of the reagent, and the conditions of mixing, the optimum systems of operation of the flow-through reactor with respect to the yield of the final product should exist.

A degenerate branched-chain reaction of oxidation of cyclohexane—one of the complex oxidative chain reactions studied in sufficient detail in [7]—was selected for the investigation. The oxidation of cyclohexane lies at the basis of the industrial process of production of cyclohexanone—an intermediate product in the synthesis of caprolactam [8]. The initial period of oxidation of cyclohexane (to an extent of 6-8%) can be represented by the following scheme:

\[
\begin{align*}
\text{RH} + \frac{1}{2} \text{O}_2 & \to \text{R} + \text{HO}_2 \quad \text{with rate} \quad w_1 = k_1 [\text{RH}] \\
\text{R} + \text{O}_2 & \to \text{RO}_2 \quad \text{with rate} \quad w_2 = k_2 [\text{R}][\text{O}_2] \\
\text{RO}_2 + \text{RH} & \to \text{ROOH} + \text{R} \quad \text{with rate} \quad w_3 = k_3 [\text{RO}_2][\text{RH}] \\
\text{RO}_2 + \text{ROOH} & \to \text{ROOH} + \text{R} + \text{O}_2 \quad \text{with rate} \quad w_4 = k_4 [\text{ROOH}] \\
\text{ROOH} + \frac{1}{2} \text{O}_2 & \to \text{HO}_2 \quad \text{with rate} \quad w_5 = k_5 [\text{ROOH}] \\
\text{ROOH} + \frac{1}{2} \text{O}_2 & \to \text{H}_2\text{O} \quad \text{with rate} \quad w_6 = k_6 [\text{ROOH}] \\
\text{ROOH} + \text{RH} & \to \text{ROOH} + \text{R} \quad \text{with rate} \quad w_7 = k_7 [\text{ROOH}][\text{RH}] \\
\text{ROOH} + \frac{1}{2} \text{O}_2 & \to \text{H}_2\text{O} \quad \text{with rate} \quad w_8 = k_8 [\text{ROOH}] \\
\text{ROOH} + \frac{1}{2} \text{O}_2 & \to \text{H}_2\text{O} \quad \text{with rate} \quad w_9 = k_9 [\text{ROOH}] \\
\end{align*}
\]

and the system of kinetic equations

\[
\begin{align*}
W_1 &= d [\text{RH}] / dt = -w_1 - w_2 - w_3 - w_4 - w_5 - w_6 - w_7 - w_8 - w_9 - w_{10} - w_{11} \\
W_2 &= d [\text{R}] / dt = w_1 + w_2 + w_3 + w_4 + w_5 + w_6 + 2w_7 + 2w_8 + 2w_9 + 2w_{10} + 2w_{11} \\
W_3 &= d [\text{ROOH}] / dt = w_7 + w_8 + w_9 - w_4 + 2w_5 + 2w_6 - 2w_2 - 2w_3 - 2w_7 - 2w_8 - 2w_9 \\
W_4 &= d [\text{ROH}] / dt = w_3 + w_4 - w_7 - w_8 - w_9 - w_{11} - w_{12} - w_{13} - w_{14} \\
\end{align*}
\]
To compare the solution of the system (15)-(23) with the experiment, we selected the results on the oxidation of cyclohexane in a glass reactor without a catalyst [9] at 135°, pressure 0 atm, concentration of dissolved oxygen \([O_2] = 5.06 \cdot 10^{-3} \text{ M (oxidizing agent air)}\) and initial concentration \([RH]_0 = 9.28 \text{ M (all the remaining concentrations at } t = 0 \text{ were assumed to be equal to } 0)\).

The system (15)-(23) was solved on an electronic computer at the following values of the constants:

\[
\begin{align*}
k_1 & = 1.61 \cdot 10^{-11}, \\
k_2 & = 3.53 \cdot 10^8, \\
k_3 & = 15.2, \\
k_4 & = 3.81 \cdot 10^2, \\
k_5 & = 5 \cdot 10^7, \\
k_6 & = 1.05 \cdot 10^3, \\
k_7 & = 6.8 \cdot 10^{-2}, \\
k_8 & = 3.9 \cdot 10^{-4}, \\
k_9 & = 5 \cdot 10^{-4}, \\
k_{10} & = 3.3 \cdot 10^{-3}, \\
k_{11} & = 2.81 \cdot 10^{-4}, \\
k_{12} & = 3.67 \cdot 10^{-4}.
\end{align*}
\]

All the values of the rate constants are cited in sec\(^{-1}\) and liters/mole/sec for the mono- and bimolecular reactions, respectively.

The constant \(k_2' = 7 \cdot 10^7\) was assumed to be the same as in the case of the oxidation of tetralin [10]. The constant \(k_4\) was calculated according to the ratio \(k_4/k_7 = 2.8 \cdot 10^{-3}\) at 140° [11] and the activation energy \(E_3 = 12 \text{ kcal/mole [7]}\). The constant \(k_4\) was calculated from the ratio \(k_4/k_3 = [RH]/[ROH]_{\text{max}} = 25\).