Numerical Simulation of Thermal Runaway and Inhibition Process on Thermal Polymerization of Styrene

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ABSTRACT
Computational fluid dynamics (CFD) technology is used to simulate the thermal polymerization reaction of styrene. The computational model is carried out with a commercial CFD code (FLUENT 6.3). The influence of viscosity and stirring speed on the fluid field and temperature field in the reactor is investigated in the simulation. Then, the locations of the temperature probe and the inhibition of hot spots are investigated by the analysis of the distribution of temperature and divergence.

KEYWORDS: Polymerization of styrene, CFD, inhibition, runaway reaction.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>speed of fluid</td>
</tr>
<tr>
<td>$S$</td>
<td>source term in respective equation (kg/(m³·s))</td>
</tr>
<tr>
<td>$K$</td>
<td>rate constant</td>
</tr>
<tr>
<td>$R$</td>
<td>reaction constant</td>
</tr>
<tr>
<td>$M$</td>
<td>monomer</td>
</tr>
<tr>
<td>$R^*$</td>
<td>radical</td>
</tr>
<tr>
<td>$w_j$</td>
<td>mass fraction of species $j$ in the mixture</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>heat of reaction (J)</td>
</tr>
<tr>
<td>$T$</td>
<td>reaction temperature (K)</td>
</tr>
<tr>
<td>$M_p$</td>
<td>average molar mass of polystyrene</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>generalized diffusion coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of the mixture (kg/m³)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Subscripts</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>dependent variable</td>
</tr>
<tr>
<td>$S$</td>
<td>number of monomer units</td>
</tr>
<tr>
<td>$Th$</td>
<td>thermal initiation</td>
</tr>
<tr>
<td>$P$</td>
<td>propagation</td>
</tr>
<tr>
<td>$T_c$</td>
<td>termination by combination</td>
</tr>
<tr>
<td>$M$</td>
<td>monomer</td>
</tr>
<tr>
<td>$P$</td>
<td>polymer</td>
</tr>
<tr>
<td>0</td>
<td>zero shear rate</td>
</tr>
<tr>
<td>$r$</td>
<td>number of monomer units</td>
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Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity (Pa⁻¹)</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>conversion rate</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate (1/s)</td>
</tr>
</tbody>
</table>

INTRODUCTION
Runaway reactions are gradually becoming a problem in the chemical industry. The study showed that 26% of major chemical industry accidents are due to runaways [1]. In chemical reactors, it can be provoked when the rate of heat generation exceeds that of heat removal. The temperature increases and leads to auto-acceleration, as well as potential fire and explosion. The runaway reaction can be prevented in three ways [2]. The first line of defense is the design of appropriate operating conditions, such as cold capacity, the coolant temperature, and the dosing rate of the reactants. However, thermal runaway is inevitable because of a great number of operating and human factors, such as control system failure, stirrer breakdown, refrigerating system inefficiency, maintenance, reactants loading errors, and dead times enlarging or shortening. The second line of defense is an...
early warning detection system to alert the operator if a runaway reaction could occur. The third line of defense is a suitable emergent system to inhibit runaway reactions. The emergency inhibition of runaway is an effective way to prevent accidents after detecting the runaway reaction.

The polymerization process is a strong exothermic reaction, of which 48% of accidents are accounted for by polymerization reaction [3]. Studies have shown that inhomogeneous mixing is one of the main reasons for runaway of polymerization reactions because it reduces the conversion efficiency significantly, easily forming hotspots [4]. The ethylene polymerization reaction in tubular reactors was simulated by Cherbanski et al. [5]; the results showed that runaway reactions may take place even after emergency inhibition. An early warning detection system to monitor the thermal runaway reaction in real time is necessary. Therefore, an appropriate location for the temperature probe becomes critical, which can achieve the runaway of online-monitoring in batch or semi-batch reactors [6, 7]. The real-time divergence can be constructed to predict the runaway reaction caused by stirred failure [8, 9].

Inhibition is one of the common methods for preventing thermal runaway, which is usually carried out at the initial stage of reaction runaway. The inhibition effect of an inhibitor in stirred reactors and turbine jet stirred reactor were studied [10-13]. Snee and Cusco [14] concluded that the increase of reaction temperature and the change of the temperature distribution reduce the inhibition rate. Dusija [15] used a two-dimensional CFD model of propylene oxide hydrolysis reactor to study the effect of inhibitor on the temperature distribution. Due to the danger and complexity of experiments, CFD simulation so is a good method to study thermal runaway.

In this paper, the CFD technology is used to simulate thermal runaway and inhibition process on the thermal polymerization of styrene. User Defined Functions (UDF) is created and applied to add the source terms of species transport equation and the energy equation. The influence of viscosity and stirred speed on the temperature field in the reactor is investigated. The system divergence distribution is then studied to investigate the location of temperature probe. Finally, the inhibition process of hotspots is studied by a comparison of the different addition locations of the cold diluents.

**CFD MODEL**

**Physical model**

The diameter of the reactor and the liquid height both equal to 0.3 m. Four straight stirring blades (0.1 m in diameter and 0.05 m wide) are located at an axial distance of 0.1 m from the bottom of the reactor. The diameter of the impeller shaft is 0.016 m (Fig. 1).

![Figure 1. Computational domain and grid.](image)
cells (Inner region: 326345 Cells, Outer region: 552762 Cells). Besides, the mesh of inner region is refined for calculation.

**Mathematical modeling**

*Governing equations*

A set of mathematical equations are usually used to describe the simulation process. Continuity equation, momentum equation, energy equation and species transport equation in the styrene polymerization reactor can be replaced by the following general equation:

\[
\frac{\partial (\rho \phi)}{\partial t} + \frac{\partial (\rho U \phi)}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \Gamma_{\phi} \frac{\partial \phi}{\partial x_i} \right) + S_{\phi}
\]

(1)

where \( \phi \) is the dependent variable, \( \rho \) is the fluid density, \( U_j \) is the speed of fluid in \( x, y, z \) directions, \( \Gamma_{\phi} \) is the generalized diffusion coefficient, \( S_{\phi} \) is the source term.

*Source term*

Styrene polymerization reaction is a typical radical polymerization process including chain initiation, chain transfer and chain termination. A number of authors have studied the reaction mechanism of thermal polymerization of styrene, and it is given as follows.

Chain initiation: \( 3M \xrightarrow{k_{th}} 2R^* \),

(2)

Chain transfer: \( R^* + M \xrightarrow{k_{tr}} R^*_1 \), \( r \geq 1 \),

(3)

Chain termination: \( R^* + R^*_s \xrightarrow{k_{tc}} P \), \( r, s \geq 1 \),

(4)

where, \( M, R^* \), \( P \) represent styrene, free radical and polystyrene respectively. Their subscripts represent the length of the polymer chain. \( k_{th}, k_{tr}, k_{tc} \) represent rate constants.

Rate of styrene polymerization \( R \):

\[
R = -K \left[ M \right] \left[ R^* \right] = -K_p \left[ M \right] \sqrt{\frac{2K_{th} \left[ M \right]^3}{K_{tc}}},
\]

(5)

Since the concentration of styrene and the density of styrene are associated, \( [M] = \rho w_m / M_m \), where, \( w_m \) is styrene content and \( M_m \) is Styrene molecular weight, the polymerization rate is calculated as follows:

\[
R = K_p \sqrt{\frac{2K_{th}}{K_{tc}} \left( \frac{\rho w_m}{M_m} \right)^{2.5}},
\]

(6)

Kinetic parameters are shown in Table 1 [16].

<table>
<thead>
<tr>
<th>Table 1. Values of kinetic parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>( A_{th} )</td>
</tr>
<tr>
<td>( A_p )</td>
</tr>
<tr>
<td>( A_{tc} )</td>
</tr>
</tbody>
</table>
Source term in species transport and energy equations can be calculated as follows, respectively:

\[ S_f = M_m \times R, \quad (7) \]
\[ S_f = \Delta H \times R, \quad (8) \]

where \( \Delta H \) is reaction enthalpy \[17\].

**Viscosity calculation**

Since the polymerization reactions occurs in the system of high viscosity, viscosity has a great impact on the fluid field.

Viscosity of the mixture can be calculated as follows:

\[ \mu = \frac{\mu_0}{(1 + \mu_0 \dot{\gamma}^{1.2} / 35000)^{0.6}}, \quad (9) \]

where \( \dot{\gamma} \) is shear rate. Zero-shear viscosity can be calculated from empirical formula \[18\]:

\[ \ln(\mu_0) = -11.091 + \frac{1109}{T} + M_p^{0.1413} \left[ 12.032 w_p - 19.501 w_p^2 + 2.92 w_p^3 + \frac{(-1327 w_p + 1359 w_p^2 + 3597 w_p^3)}{T} \right], \quad (10) \]

where, \( M_p \) is average molar mass of polystyrene, \( T \) is the reaction temperature, \( w_p \) is the mass fraction of polystyrene in the mixture. It is seen from the above equation that the viscosity of the mixture increases with the increasing temperature, so we should consider the effect that viscosity changes on the reaction.

**Critical criterions for thermal runaway**

A large number of scholars are dedicated to the research of critical criterion for thermal runaway and proposed different thermal runaway critical criterions, such as the Chaos criterion, the Singularity criterion, the MV criterion and the VR criterion et al. The critical criterion for thermal runaway based on Chaos theory is widely applied, because it can monitor the thermal runaway online \[19\]. The system divergence is defined as the trace of Jacobian matrix by Zaldivar et al. \[20\].

\[ \text{div} = j_{11} + j_{22}, \quad (11) \]

namely, \( \text{div} = j_{11} + j_{22} \) where \( T \) is the temperature of reactor, \( \zeta \) is the conversion rate of reactants. Further, the divergence can be used as a generalisation of former criteria for on-line detection, and the thermal runaway critical criterion is defined as \( \text{div} > 0 \). The studies \[19\] show that for the online-monitoring of the thermal runaway reaction in batch or semi-batch reactor, system divergence can be calculated in real time with only one temperature probe.

**RESULTS AND DISCUSSION**

**Model validation**

Hungenberg et al. \[21\] made a comparative study with Hui-Hamielec, Weickert and Marten-Hamielec models, and they found the three models show good agreement for the experimental results of styrene polymerization reaction. In this paper, the three models are used for the comparison with the CFD model. As a measure for comparison, the average temperature curves of different models with 80 and
150 °C as initial temperatures are given in Fig. 2. Table 2 shows the time of the four models elapsed for a temperature increase of 30 °C. It is clear that the average temperature curves of the CFD model coincides with those predicted by the three different models. The time elapsed for a temperature increase of 30 °C of the four models differ by less than 15%.

![Figure 2. Temperature rise curves.](image)

**Table 2.** Time elapsed for a ΔT=30 °C temperature increase.

<table>
<thead>
<tr>
<th>Model</th>
<th>Time for 80-110 °C increase (s)</th>
<th>Time for 150-180 °C increase (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hui-Hamielec Model</td>
<td>16377</td>
<td>254</td>
</tr>
<tr>
<td>Weickert Model</td>
<td>16740</td>
<td>263</td>
</tr>
<tr>
<td>Marten-Hamielec Model</td>
<td>14608</td>
<td>297</td>
</tr>
<tr>
<td>CFD Model</td>
<td>17145</td>
<td>253</td>
</tr>
</tbody>
</table>

**Effect of operating parameters to polymerization reaction**

*Effect of the temperature-dependent viscosity*

Viscosity is an important parameter of the thermal polymerization reaction. To accurately describe the effects of increased viscosity on the thermal polymerization reaction, the difference between the maximum and minimum temperature (ΔT), in the constant viscosity system (S1) and the temperature-dependent viscosity system (S2), with same RPM and same initial temperature, are given in Fig. 3, and the value of the viscosity in the S1 is 0.00027 pa · s (150 °C, Styrene).

![Figure 3. Temperature difference of different systems.](image)

Due to the high local temperature caused by uneven mixing, the ΔT in the S2 continues to increase.
and reaches 70 °C at 2000 s. In the S1, the low and constant viscosity results in a good mixing, and the $\Delta T$ is nearly zero. Therefore, it is obvious that the viscosity has a significantly influence on the temperature distribution in the reactor.

The three-dimensional model makes the divergence distribution more intuitive and accurate. The divergence in the constant viscosity system and the temperature-dependent viscosity system are calculated, the divergence distribution profile of axial section at 1800 s is shown in Fig. 4. According to the divergence criterion, the thermal runaway take place in the two systems at 1800s. In the constant viscosity system, the distribution of temperature and divergence are relatively uniform, and the difference between the maximum and minimum divergence in the section differ by less than 0.0001. It is seen from Fig. 4(b) that the divergence distribution is quiet uneven in the temperature-dependent viscosity system, the maximum value of divergence at the top of the reactor is 0.009, while the minimum value of divergence attached to the impellers is only 0.0055.

Figure 4. Local divergences of the reacting system.

Effect of stirring speed

To study the effect of the stirring the temperature-dependent viscosity system speed on the thermal runaway. Temperature distribution at 240s and 540s with a speed of 25 r/min are shown in Fig. 5(a) and Fig. 5(b) respectively. Temperature distribution at 540 s with a speed of 50 r/min is shown in Fig. 5(c). The comparative results of Fig. 5(a) and Fig. 5(b) show that the convective heat transfer rate increases and the temperature is getting lower in the region attached to the impeller. The high temperature region moves upwards constantly gradually, and the low temperature region moves downward gradually, the region of local high temperature forms at the top of the reactor, this phenomenon of uneven temperature distribution in local region is known as hot spots.

Figure 5. Predicted temperature distribution.
It indicates that the overall temperature distribution are similar in different speeds by comparing Fig. 5(b) with Fig. 5(c), because the characteristic of temperature distribution mainly depends on the flow pattern produced by impeller. But there are less high temperature regions in Fig. 5(c) compared to Fig. 5(b), one possible reason is that high speed can achieve a better mixing and speed up the convective heat transfer between reaction materials.

Fig. 6 shows the hot spots percentage at different stirring speeds. It is known from Fig. 6 that the stirring speed has a great influence on the hot spots percentage, hot spots percentage fluctuate within a certain range under the given operating parameters. The rate of convective heat transfer is low at the speed of 5 r/min, and more hot spots forms at the same time, which is different from that at the speed of 25 r/min and 50 r/min.

The system temperature at 550 s is given in Table 3. It is seen that $\Delta T$ decreases with the increase of stirring speed. $\Delta T$ is 0.02 °C at the speed of 100 r/min. While $\Delta T$ reaches 12 °C at the speed of 5 r/min. This indicates that increasing the stirring speed can acquire a more uniform temperature distribution, to a certain extent. However, the average temperature does not decrease correspondingly; it reaches a minimum at the speed of 25 r/min and a maximum at 100 r/min. The stirring speed results in more effective collisions between particles, which accelerates polymerization and increases the system temperature rapidly. However, more hot spots accelerate the exothermic reaction at a speed of 5 r/min, which increases the average temperature of the reactor. To prevent thermal runaway, polymerization should be under an appropriate stirring speed.

![Figure 6. Hot spots percentage profiles.](image)

<table>
<thead>
<tr>
<th>String speed (rad/min)</th>
<th>$\Delta T$ (°C)</th>
<th>Average temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>12.11</td>
<td>234</td>
</tr>
<tr>
<td>25</td>
<td>3.41</td>
<td>232</td>
</tr>
<tr>
<td>50</td>
<td>0.83</td>
<td>235</td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
<td>238</td>
</tr>
</tbody>
</table>

**Table 3. Temperature condition at 550 s.**

**Temperature probe location**

In order to monitor the runaway in the reactor accurately, the temperature probe should be set at an appropriate location. The temperature distribution in the reactor axial section at 1800s is shown in
Fig. 7. The comparative study with Fig. 7 and Fig. 4(b) shows the contact between temperature distribution and divergence distribution, which turns out that the hot spots increase the reaction rate in the region away from the impeller and results in high local divergence value.

P1, P2, P3 shown in Fig. 8 are chosen as three monitoring points. To choose the most appropriate monitoring point, a comparison of different temperature profiles is conducted. Fig. 9 shows the average temperature profiles in the reactor and the temperature profiles at the three monitoring points. The differences of the temperature profiles are obvious. The average temperature in the reactor is much lower than the temperature at P1, which proves that the average reaction temperature and the reactor temperature are not the same definitely.

![Figure 7. Predicted temperature distribution.](image)

![Figure 8. The location of the points and line.](image)

It is known in Fig. 7 that the temperature at the top of the reactor is higher. To study the variation of the temperature at the top of the reactor intuitively, the temperature rise rate of the analysis line L (Fig. 10). The temperature rise rate is high at the radial distance of 0.12 and 0.15 m away from the stirring shaft, since the reactor wall is at the radial distance of 0.15 m away from the stirring shaft and the temperature probe cannot fit the wall, the monitoring point should be set at the radial distance of 0.12 m away from the stirring shaft. In order to monitor the behavior of the hot spots more effectively and trigger the system of temperature alarm timely, the temperature probe should be set at the top of the reactor, namely at 4/5 of the axial distance.

![Figure 9. Temperature curves at different detecting positions.](image)

![Figure 10. Curves of temperature rise rate.](image)

**Cooling diluent addition location**

In order to investigate the inhibition effect of cold diluents addition locations on the runaway, 230 g ethylbenzene as the cold diluent is patched into the reactor at 1510 s. The addition locations are respectively set at A1 (Top of the reactor), A2 (Stirring region) and A3 (Bottom of reactor). Fig. 11 shows the concentrations of cold diluents at different monitoring points. Fig. 12 shows the average temperature in the reactor with and without cold diluents respectively.
It is seen from Figs. 11 and 12 that the cold diluents can reduce the temperature of reaction mass significantly, and the average temperature of the reaction mass and the mixing time reach the minimum when the cold diluent is patched into in the stirring region, which is consistent with the conclusion proposed by Zhang et al. [22]. Injecting cold diluent at A2 shorten the mixing time and reduce the reactor temperature, and the transfer and diffusion rate of the cold diluent are higher than the rate when the cold diluents are patched at A1 and A3.

Fig. 13 shows the variation of the hot spots percentage. It is known in Fig. 13 that the hot spots percentage drops to 6% after the injection of cold diluents 200 s, which indicates that the inhibition is the most effective when the cold diluent is patched at A1. The reaction in the top of the reactor is accelerated because of the high viscosity and high temperature, which leads the formation of hot spots easily. When the cold diluent is patched at the top of the reactor, the reaction temperature and the styrene concentration decrease, the rate of polymerization in the top region slows down. Besides, cold diluent reduces the system viscosity and the gel effect. Therefore, the formation of hot spots will be inhibited effectively.

The divergence distribution profiles at 1800 s are shown in Fig. 14. The comparison of Fig. 4(b) and Fig. 14 shows that cold diluents injection can significantly slow down the runaway rate, but it can not eliminate the thermal runaway fundamentally. Secondly, the value of the system divergence is small when the cold diluents addition location is A1, which makes the runaway under better control.
CONCLUSIONS

A three-dimensional model is used to simulate styrene polymerization, which makes the temperature distribution and divergence more intuitive compared to two-dimensional model. The effect of viscosity and stirring speed on the fluid field and temperature field are studied for understanding the temperature distribution under different operation conditions. The results show that the viscosity has a significant effect on flow field and temperature field, which will obstruct the convective heat transfer between the fluids and generate hot spots more easily. The increase of stirring speed can accelerate the convective heat transfer appropriately, and make the temperature distribution more uniform. However, the high stirring speed will exacerbate thermal polymerization and increase average reaction temperature, which can result in thermal runaway.

For online monitoring of thermal runaway, the temperature probe location should be optimized. For the reactor in this paper, it is appropriate to set the sensor at 4/5 from the top of the shaft. For the inhibition of runaway, the injection of cold diluents in the impeller region can reduce the mixing temperature and inhibit the formation of hot spots. Injecting cold diluents in the hot spots gathering region can inhibit the formation of hot spots more effectively.

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