Numerical Simulation of Reaction Efficiency of Vinyl Chloride Suspension Polymerization Reactor

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Abstract. This paper establishes a mathematical method for calculating the polymerization process of industrial vinyl chloride suspension polymerization reactors. The polymerization rate, weight average molecular weight (WAMW), number average molecular weight (NAMW), monomer conversion rate and pressure are displayed throughout the reaction. Applying this model to existing experiment in the literature, the results are close. The final simulation results will be used to guide the industrial production of polyvinyl chloride (PVC).

1. Introduction

PVC is one of the oldest and most commonly used polymer products in production and life. It is reported that 80% of PVC is produced using suspension polymerization [1]. In suspension polymerization process, vinyl chloride monomers (VCM), water and initiators are mixed to form droplets. When stirred, the initiator in the droplets begins to decompose and the polymerization begins [2]. The polymerization is usually stopped at a certain time. Typical vinyl chloride polymerization process can be determined as the following steps: initiator decomposition, chain initiation, chain growth, chain transfer to monomer, coupling termination and disproportionation termination [3].

In this study, a comprehensive mathematical framework for modelling batch PVC suspension polymerization reactors was proposed. Through the method of CFD simulation, the conversion rate, MAMW and other results inside the reactor were explored.

2. Reaction kinetics and molecular weight calculation method

Typical free radical polymerization models can be simplified as follows [4].

Table 1. Typical free radical polymerization model.

| Reaction type                  | Reaction equation |
|-------------------------------|-------------------|
| Initiator decomposition       | \( \dot{I} \rightarrow 2A \) |
| Chain initiation              | \( A + M \rightarrow R \) |
| Chain growth                  | \( R + M \rightarrow R \) |
| Chain transfer to monomer     | \( R + M \xrightarrow{k_{trm}} P + R \) |
| Chain transfer to polymer     | \( R + P \xrightarrow{k_{trp}} P + R \) |
| Disproportionation termination| \( R + R \xrightarrow{k_{tc}} P \) |
In the above kinetic scheme, the symbols I, A, M, R and P denote the initiator, free radical, monomer molecules, radicals and polymers respectively. In order to obtain the kinetic equations for the polymerization of vinyl chloride, the following assumptions are usually made [5]: 1. All reaction rate constants do not change with chain length; 2. The chain length is large enough, the monomer consumption rate is consistent with the monomer rate consumed by the chain growth rate; 3. The free radicals produced by chain transfer react with monomers quickly without affecting the polymerization rate; 4. The steady state hypothesis (SSH) holds valid for free radical polymerization. SSH assumes that the rate of free radical generation and consumption is much greater than the change in free radical concentration with respect to time.

The reaction rate equation of the \([R_n]\) substance can be obtained according to the reaction of each element:

\[
\frac{d[R_1]}{dt} = k_I[A][M] - k_p[R_1][M] - k_{trt}[R_1][M] + k_{trc}[M][R_m] - k_{tc}[R_1][R_m] - k_{trp}[R_1][P_m] = 0 \tag{1}
\]

\[
\frac{d[R_n]}{dt} = k_p[M][R_{n-1}] - k_p[R_n][M] - k_{tc}[R_n][R_m] - k_{trp}[M][R_n] - k_{trp}[R_1][P_m] = 0 \tag{2}
\]

Dimensionless quantities were set: \(\tau = \left( k_{trt}[M] + k_{trp}[P] \right) (k_p[M])^{-1}\), \(\beta = k_{tc}[R](k_p[M])^{-1}\)

\([R_n] = [R](\tau + \beta)(1 + \tau + \beta)^n \tag{3}\)

\(W_n = n[R_n](\sum_{n=1}^{\infty} n P_n)^{-1} = n(\tau + \beta)(1 + \tau + \beta)^{-(n+1)} \tag{4}\)

\(W_{AMW} = \sum_{n=1}^{\infty} n W_n = (2\tau + 3\beta)(\tau + \beta)^{-2} \tag{5}\)

\(PDI = \frac{\sum_{n=1}^{\infty} n^{-1} W_n}{\overline{W}_n} = (2\tau + 3\beta)(\tau + 0.5\beta)^{-1} \tag{6}\)

\(W_{AMW} = \left( \sum_{n=1}^{\infty} n^{-1} W_n \right)^{-1} = (1 + \tau + \beta)(\tau + 0.5\beta)^{-1} \tag{7}\)

3. Experimental and simulation conditions

Suspension polymerization experiments were conducted in a laboratory scale batch reactor. The experiments used industrial-grade VCM. The experimental formulation contained the following ingredients [6]: monomer, 1.5L; water, 1.5 L, initiator(s), 1.57 g of dilauroyl peroxide/kg of VCM. The polymerization temperature was set to 63°C.

Computational fluid dynamics (CFD) software package was applied to simulate the operation of vinyl chloride suspension polymerization reactor. During the simulation, dynamic parameters, operating conditions, reactor geometry and controller parameters were inputted. The component concentration, and energy balance were calculated. The polymerization progress and reactor process variables were obtained in tables to draw graphs. The temperature in the reactor was set at a constant number. When the initiator was added to the reactor, the reaction actually started, and the conversion rate and polymerization rate increased. As the reaction proceeded, the monomer concentration gradually decreased. When the reaction proceeded to a certain extent, the conversion rate gradually approached its final value and the reaction reached its final state. Table 2 lists the values of kinetic parameters used in the simulator.

### Table 2. Reaction Kinetic Parameters.

| Variables | Value | Units |
|-----------|-------|-------|
| \(k_d\)  | \(2.31 \times 10^{15} \exp(-29100/RT)\) | 1/s |
| \(k_p\)  | \(30 \times 10^8 \exp(-3320/T)\) | m³/kmol/min |
| \(k_{trm}\) | \(5.78 \exp(-2768/T) k_p\) | m³/kmol/min |
| \(k_{trp}\) | \(8.31 \times 10^8 \exp(-11100/T)\) | m³/kmol/min |
| \(k_c\) | \(6.08 \times 10^{-3} \exp[-5740(T^{-1} - T_0^{-1})]\) | m³/kmol/min |
| \(k_{tc}\) | \(2k_p^2k_c^{-1}\) | m³/kmol/min |
4. Results and discussion

The theoretical model predictions and experimental data were compared in the Figure 1. As shown in the figure, the pressure first increases and then maintain balanced, and the pressure in the theoretical model prediction are very close to the experimental data [7]. The calculated monomer conversion and reaction rate are also plotted in the figure. The reaction rate first increased, and then decreased. The change in conversion rate indicates that the reaction is divided into three stages, which shows a typical polymer polymerization process initiated by an initiator.

Figure 1. Comparison between theoretical and experimental reactor pressure values.
Model predictions of conversion and polymerization rate with respect to time.

Figure 2. Predicted WAMW and NAMW versus time.
Circles represent final experimental measurements.
The results of WAMW and NAMW were shown in the Figure 2. The theoretical predictions of the final WAMW and NAMW are in good agreement with the experimental data. The molecular weights of product are mainly controlled by the polymerization temperature [8]. Since the reaction rate of chain termination in the reaction is much smaller than the chain growth rate, the average length of the polymer chain is determined by the ratio of the propagation rate to the rate of chain transfer to the monomer. Therefore, it could be easily indicated that the polydispersity index (PDI) will approach 2.0. It can also be investigated from the Figure 2 that the value of PDI is very close to 2.0. The initial increase in average molecular weight observed in Figure 2 is probable due to fast reaction of polymerization.

From Figure 1, the monomer conversion rate gradually increased, and the polymerization rate also suddenly increased. In order to make full use of the cooling capacity of the reactor, the polymerization rate should be kept substantially constant at a certain level[9]. The reaction heat rate generated at this level should be equal to the maximum cooling capacity of the system. Adding initiators in stages and using two or more inhibitors are ways to keep economization and safety of the PVC production.

5. Conclusion
In this study, a comprehensive mathematical framework for modelling batch vinyl chloride suspension polymerization reactors was proposed. The detailed kinetic mechanism of polymerization process was considered and CFD methods was applied to simulate the reaction process. The pressure, monomer conversion rate, polymerization rate and the value of WAMW and NAMW were obtained. In addition, by comparing the model prediction with the reported experimental data, the pressure and molecular weights were in good agreement with the experiment data. The prediction ability of proposed model was tested. The change in monomer conversion rate indicates that the vinyl chloride suspension polymerization reaction is divided into three stages. Finally, some techniques of reactor energy saving and safety are given.

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