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Particle Characterization in Polymerization Kettle based on CFD-PBM Modeling

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Abstract

In order to investigate the change of particles in the polymerization kettle during the polymerization reaction, numerical simulations were carried out using a two-fluid model coupled with a population balance model (PBM) to study the effects of rotational speed and type of paddle on the particle size, particle distribution, and particle movement speed. The results show that the particle size decreases with the increase of rotational speed, the particle size is smaller in the flow area at the end of the paddle, and the particle size is larger in the low-speed area below the stirring shaft. Large polymerization kettles are usually used in industrial production, and the 5 L polymerization kettle is enlarged to 136 m3, in which the particle size and distribution are more uniform in the three-blade swept-back type polymerization kettle, and the polymerization effect is better. The results of the study can provide a reference for the actual process of polymerization reaction to produce polyester materials.

Keywords

Polymerization Kettle; Group Balance; Particle Coalescence; Particle Size Distribution; Flow Field Analysis.

1. Introduction

The suspension polymerization of vinyl chloride (VCM) faces many difficulties in modeling the process due to the complexity and variability of the polymerization reaction system as compared to the general chemical reaction process[1].

The production of polyvinyl chloride (PVC) particles to meet the specified quality indicators, quality indicators and particle size, particle size distribution is closely related. A number of flow in the kettle is more complex, the generation of PVC particle size and distribution of the description is very difficult, and the particle characteristics of the product has an important impact on the performance. At present, the liquid-solid two-phase flow field in the polymerization kettle is calculated by Euler two-fluid model, which does not take into account the kinetic behaviors of aggregation and fragmentation caused by the collision between particles, particles and the wall in the inter-phase mass transfer problem, and thus cannot accurately describe the spatial distributions of the particles in terms of particle sizes, concentrations, and so on. In order to improve the simulation accuracy, the population balance model (PBM) model is introduced on the basis of Euler's two-fluid model to establish the connection between particle behavior and macroscopic properties, and to obtain the size and distribution of phase particles[2].

Although researchers at home and abroad have studied the stirring equipment in depth, most of them mainly analyze from the flow field characteristics, while less research on the particle characteristics during polymerization reaction. Since the stirring condition is an important influence on the particle characteristics in the kettle, this paper will load the population equilibrium model on the basis of the traditional Euler two-fluid model through the finite element analysis software Fluent to study the particle size and particle distribution in a 5 L polymerization kettle under different rotational speeds and apply the principle of scaling up the kettle to 136 m3 to study the effects of the different types of paddles on the particle size and particle movement velocity in a large-scale polymerization kettle, so as to investigate the particle size and particle movement velocity in a large-scale polymerization kettle. The effect of different types of paddles on particle size and particle movement velocity of large-scale polymerization kettle is studied, so as to draw the influence law of rotational speed and paddle type on particle characteristics, and to provide reference for the design, optimization and scaling-up of polymerization kettle.

2. Polymerization Kettle Modeling Study

The general process of polymerization reaction is as follows: water and VCM monomer are added at the same time under airtight conditions, appropriate amount of additives are added at a certain temperature and pressure, and the polymerization reaction is carried out under the action of stirring to form PVC particles. Due to the complexity of the polymerization reaction process, some basic assumptions are introduced into the model: (1) the particles are spheres of uniform density; (2) only 2 components are considered, i.e., only the polymerization of the particles and deionized water.

2.1 Modeling

The structure sketch of polymerization kettle is shown in Fig. 1, and the specific size parameters in the figure are shown in Table 1.

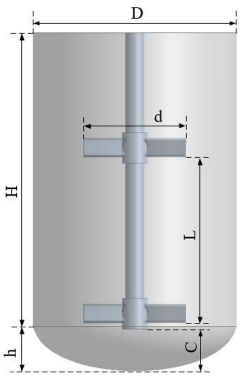

Fig.1 Polymerization kettle model

Table 1. Polymerization kettle structure size parameters[3]

name	numerical
kettle internal diameter(D)/mm	160
Kettle height(H)/mm	230
Head height(h)/mm	30
Stirrer layers	2
Paddle diameter/kettle diameter	0.5
Paddle layer spacing(L)/mm	120
Stirrer installation height(C)/mm	28

According to the actual situation of particle aggregation in the polymerization reaction process, the reaction temperature is set at 55˚C, the continuous phase medium in the calculation domain is water, with a density of 998.2 kg/m3, a viscosity of 0.89 MPa·s, a specific heat capacity of 4.18 kJ/(kg·k), and a coefficient of thermal conductivity of 0.63 W/(m·K), and the phase density of the PVC particles is 1,380 kg/m3, with a mass fraction of 30%, and its average particle size is 1.05 μm, and its particle size distribution ranges from 0.2 to 2.5 μm. The average particle size was 1.05 μm, and the distribution of particle size ranged from 0.2 to 2.5 μm.

2.2 Control Equations

Since the liquid and solid phases of the polymerization process are deionized water and PVC particles, respectively, and both liquid and solid phases are regarded as continuous media, the Euler two-fluid method is used in this paper for three-dimensional numerical simulation[4-5]. The fluid flow needs to follow the conservation of mass, momentum and energy, and the required flow control equations are continuity equation, momentum equation and energy equation.

2.3 Turbulence Model

Polymerization kettle in the stirring through the rotation of the paddles to drive the fluid to produce vortex flow belongs to turbulent flow, this paper adopts the RNG k-ε turbulence model to predict the flow characteristics of the fluid in the kettle. By correcting the turbulent viscosity, the effect of swirling on turbulence is taken into account, and the accuracy of the swirling flow calculation is improved [6].

2.4 Phase Interaction Force Model

The interphase force model realizes the liquid-solid two-phase coupling in the momentum equation. Neglecting the effects of other forces, this paper focuses on the effect of trailing force on the liquid-solid dynamic properties. The trailing force coefficients are chosen from the Wen-Yu [7] model to reflect the interphase force strength.

Wen-Yu model traction coefficient:

$$\beta = \frac{3}{4} C_D \frac{\varepsilon_s \varepsilon_l \rho_l |u_l - u_s|}{d_s} \varepsilon_l^{-2.65} \quad (1)$$

$$C_{\mathrm{D}} = \begin{cases} \frac{24}{Re_{\mathrm{s}}}\left(1 + 0.15 Re_{\mathrm{s}}^{0.687}\right) & Re_{\mathrm{s}} < 1000 \\ 0.44 & Re_{\mathrm{s}} \geq 1000 \end{cases} \quad (2)$$

$$Re_s = \frac{\varepsilon_l \rho_l d_s |u_l - u_s|}{u_l} \quad (3)$$

Where: β is the momentum exchange coefficient; CD is the number of trailing forces; Res is the number of particle Reynolds; ε is the volume fraction; and u is the dynamic viscosity, Pa·s.

2.5 Population Balance Model

In order to consider the effect of interaction between particles on particle change and flow, it is necessary to use CFD-PBM coupled model. Particle aggregation plays a major role in the aggregation process, so only the effect of aggregation on particles is considered in this paper. A discrete method is used to solve the population balance equation and calculate its Sauter mean diameter. That is, the solid phase particle diameter [8]. The population equilibrium equation for the particles is as follows:

$$\frac{\partial}{\partial t}\left[n\left(V,t\right)\right]= \frac{1}{2}\int_0^v a(V-V',V')n(V-V',t)n(V',t)dV' -\int_0^{+\infty} a\left(V,V'\right)n(V,t)n(V',t)\mathrm{d}V' \quad (4)$$

Where: V is the volume of solid particles; V' is the volume of solid particles before the change in size; n(V, t) is the concentration per unit number of particles with volume V at the moment t; a(V, V') is the aggregation kernel of particles with volume V and V'; the first term on the right side of the equation is the growth rate of volume due to aggregation, with a factor of 1/2 in order to avoid the calculation of 2 calculations for each collision event, and the second term on the right side is the mortality rate of volume due to aggregation.

Sauter mean diameter (d43) is calculated as:

$$d_{43}=\frac{\Sigma(n_i\cdot d_i^{\,4})}{\Sigma(n_i\cdot d_i^{\,3})} \quad (5)$$

Where: ni is the total number of particles with particle size di.

3. Numerical Simulation

3.1 Boundary Conditions and Simulation Schemes

In order to solve the problem of data transfer in steady state analysis in the flow region, the multiple coordinate system method (MFR) is used to divide the computational domain into a paddle region containing the paddle motion and a stationary region in addition to the paddle region, and the 2 regions exchange data through the Interface surface. The inner and lower surfaces of the polymerization kettle are set as no-slip wall surfaces, and the upper surface is set as a symmetric boundary. The flow field simulation adopts the steady state calculation method, and the SIM-PLE algorithm is used as the pressure-velocity coupling method, and the convergence accuracy is set to 10-4.

3.2 Simulated Working Conditions

Table 2. Initial particle size distribution

serial number	particle size /μm	volume fraction /%
Bin-0	2.54	0
Bin-1	2.02	0
Bin-2	1.60	0
Bin-3	1.27	0
Bin-4	1.01	0
Bin-5	0.80	0
Bin-6	0.63	0
Bin-7	0.51	0
Bin-8	0.40	0
Bin-9	0.32	0
Bin-10	0.25	0
Bin-11	0.20	100

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To conduct the small test, the rotational speeds simulated in this paper were 100 r·min-1, 200 r·min-1, and 300 r·min-1. Since the distribution of particle size needs to be obtained, the particle size distribution of the particles was obtained by using the discrete method. The particle population was categorized into 12 subintervals (Bin-0~Bin-11) according to the size of the particles, as shown in Table 2.

3.3 Mesh Independence Verification

A tetrahedral unstructured mesh is used for meshing with local encryption in the paddle region. In this paper, four grid quantities, 295034, 563407, 839309, and 1101168, are used for grid-independence verification. The numerical simulation results of the average diameter of particles are obtained as shown in Fig. 2. From the figure, it can be seen that when the number of grids is increased to 839309, the number of grids has less influence on the numerical simulation results of particle size. Therefore, 839309 grid sizes are selected as the calculation baseline.

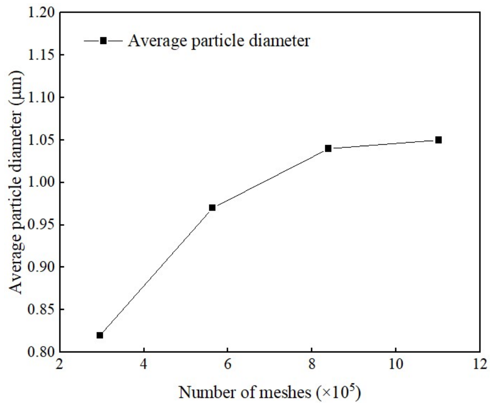

Fig.2 Effect of the number of meshes on the average diameter of particles

4. Model Validation and Data Analysis

4.1 Model Validation

Figure 3 compares the calculation results of this paper with the experimental results of literature [3], in which the CFD-PBM model is selected for simulation and the same rotational speed as that of the experiment is set to be 200 r·min-1. As can be seen in Fig. 3, the distribution of particle sizes obtained from the numerical simulation has the same pattern as that obtained from the experiment, which is normally distributed, and the standard deviation is applied to analyze the error, and the result of the error is obtained to be 9.6%. Among them, the particle size is mainly distributed between 0.7 μm-1.3 μm. Therefore, this numerical model is feasible for subsequent simulation analysis.

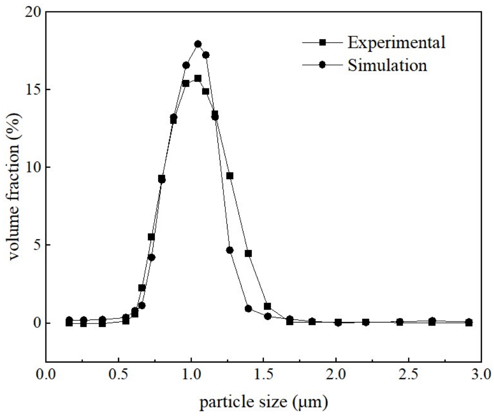

Fig.3 Comparison of experimental and simulation results of particle size distribution

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4.2 Particle Size Distribution

The axial longitudinal section of the polymerization kettle was selected for analysis. Figure 4 gives the cloud diagrams of particle size distribution at 100 r·min-1, 200 r·min-1 and 300r·min-1 respectively. From the figure, it can be seen that at different rotational speeds, the particle size distribution on the cross-section of the polymerization kettle is characterized by a smaller particle size at the paddle and a relatively larger particle size at the bottom of the polymerization kettle. In the area near the stirring paddles, due to the strong flow shear, the particle movement speed is fast, the particle aggregation is weak, resulting in smaller particle size, while at the bottom of the polymerization kettle, there may be a stirring dead zone, so that the large-size particles are deposited at the bottom. When the rotational speed is 100 r·min-1, the particles can not be evenly dispersed in the kettle, and the aggregation of particles is stronger, resulting in the formation of particles with a larger size; when the rotational speed is 200 r·min-1, the number of large-size particles decreases significantly, and the size of the particles in the area around the stirring paddle is more uniform; when the rotational speed is 300 r·min-1, the particles are shifted to the direction of the small particle size. Under different rotational speeds, the particle size changes significantly, with the increase of rotational speed, the particle size gradually decreases.

Figure 5 shows the distribution of particle size in the Y-Z section, where (a) is Z=85 mm, (b) is Z=105 mm, and (c) is the distribution of particle size along the Y-axis direction at Z=215 mm. From the analysis of the figure, it can be seen that the particle size distribution range fluctuates greatly at Z=85 mm and Z=215 mm. Under different rotational speeds, the particle size distribution changes are more obvious. In the kettle, the paddle area has the smallest particle size, which is due to the stronger flow shear in the blade area, the high-speed shear generated by the paddles leads to particles that are not easy to aggregate, thus resulting in a smaller particle size near the slurry; while near the mixing shaft and near the wall, the particle size gradually increases, which is due to the weaker fluid flow shear near the mixing shaft and the near-wall distribution of particles is more uniform, so that it is easier for the particles to get together and form a large particle. Large particles.

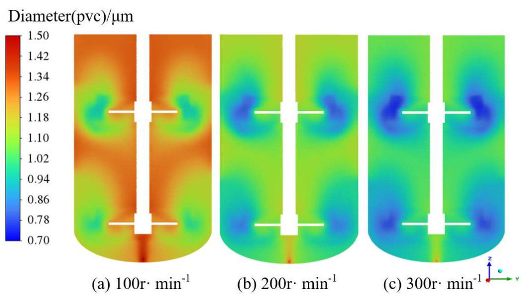
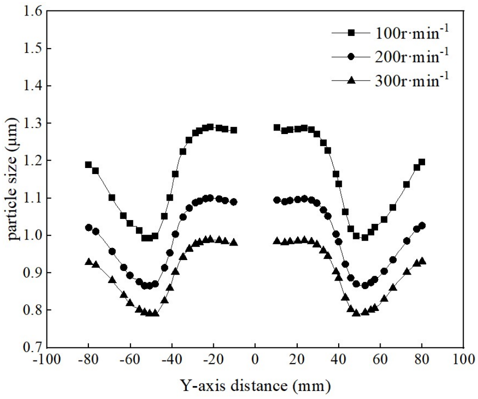


Fig.4 Effect of rotational speed on particle size distribution



(a) Z=85 mm particle size distribution along Y direction

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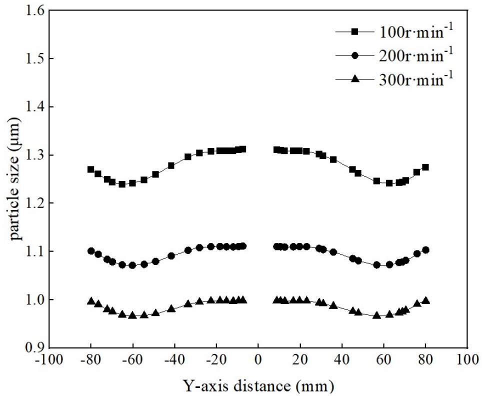
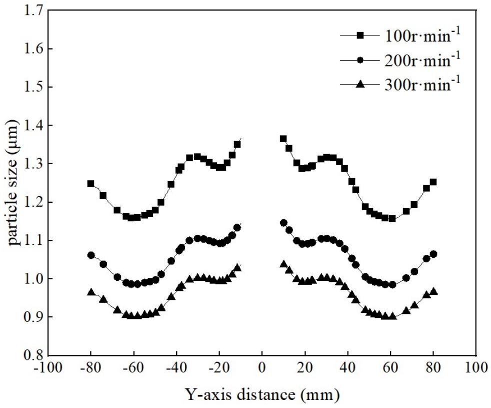


(b) Z=105 mm particle size distribution along Y direction



(c) Z=215 mm particle size distribution along Y direction

Fig.5 Distribution of particle size in the Y-Z cross section

4.3 Particle Volume Fraction Distribution

In order to deeply study the degree of uniform mixing of liquid-solid materials by rotational speed, the volume fraction of particles on the Y-Z cross-section of the polymerization kettle was selected for observation and analysis. From the analysis of Figure 6, it can be seen that with the increase of rotational speed, the particle distribution is more uniform, the reason is that the particles in the polymerization kettle will be subjected to their own gravity and the liquid phase of the high-speed jet discharged by the stirring paddles, due to the smaller mass of the particles, the gravity effect is also smaller, the particles with the fluid movement tendency is stronger, and the greater the rotational speed, the stronger the liquid flow, the particles of the suspension height increases, and thus the dispersion effect is better. When the rotational speed is 100 r·min-1, the particle distribution appears obvious stratification phenomenon, the particles are mainly distributed in the lower part of the kettle area, which may be due to the rotational speed of the paddles is small, the flow shear produced by the paddles is weak, the particle movement speed is also small, which leads to the particles failed to suspend in the upper part of the kettle area, the volume fraction of particles in the upper part of the area is also small. When the rotational speed was increased, the particle stratification phenomenon was gradually weakened, and the particle dispersion effect was better when it was increased to 300 r·min-1.

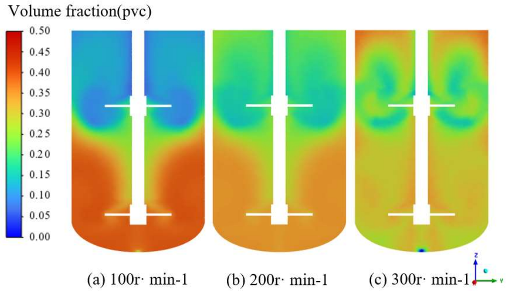


Fig.6 Effect of rotational speed on particle volume fraction

5. Scale-up Studies of Polymerization Kettles

Due to the complexity and diversity of actual production processes, reliable design of production equipment mostly requires small pilot experiments to obtain the required design parameters[9]. Laboratory results obtained using small reactors often differ significantly from engineering results obtained from large production units under the same operating conditions, and these differences are called amplification effects[10]. In the industrial production process, in order to reduce industrial costs and improve production efficiency, factories usually use large reactors for material production, in which the stirring paddle type is crucial for reactor effectiveness, the appropriate stirring paddle type can make the material distribution in the reactor more uniform, the stirring dead zone volume fraction is smaller, thus shortening the time of generation and improving the production efficiency[11].

In this paper, non-geometrically similar enlargement principle is used for the enlargement study of polymerization kettle[12]. The enlarged polymerization kettle is 136 m3, with three-layer paddle type and two baffles inside the kettle, in which the inner diameter of the cylinder is 4200 mm, the height is 8500 mm, the height of the head is 1000 mm, and the length of the baffle plate is 8000 mm and the width is 200 mm. According to the operation of the 136 m3 kettle in the industry, the rotational speed of the present study is set to be 70 r·min-1. In this paper, we mainly choose three kinds of paddle The paddle structure is shown in Fig. 7, of which (a) is two-bladed inclined paddle; (b) is two-bladed straight paddle; and (c) is three-bladed swept back type. According to the three paddle structures, the particle size and distribution in the kettle are compared, so as to select the appropriate paddle type and provide data reference for the production of industrial polymerization kettle.

Fig.7 Polymerization kettle paddle model

5.1 Power Consumption Characteristics

Stirring power can reflect the energy consumption of the polymerization kettle, and it is important for the optimization design of the polymerization kettle to achieve better polymerization effect under lower energy consumption. The stirring power can be calculated by the following formula:

$$P = \frac{2\pi Mn}{60} \tag{6}$$

Where: P is the stirring power, W; M is the torque, N·m; n is the rotational speed, r·min-1.
After calculation, the power consumption results of the three paddles are shown in Table 3.

Table 3. Effect of paddle structure on power

Paddle type	Power /kW
two-blade diagonal paddle 2-blade straight paddle type three-lobe swept-back	108.11 112.68 120.38

According to Table 3, it can be seen that the power difference between the two-blade inclined paddle type and two-blade straight paddle type is small, and the three-blade swept back type has the largest power. Under the consideration of energy consumption, the two-bladed swash-paddle type and two-bladed straight paddle type can be prioritized.

5.2 Particle Size Distribution

The axial longitudinal section of the polymerization kettle is selected for analysis. Figure 8 shows the cloud diagram of particle motion velocity for different paddle structures, and it can be analyzed from the figure that the maximum particle motion velocity is in the tail region of the paddle, and the minimum is at the bottom region and the kettle wall surface, which is due to the strong fluid flow at the paddle, which leads to the particle motion, and at the bottom due to the small turbulent kinetic energy, there is a dead zone of stirring, and the particle motion velocity is small, and the particle motion velocity is also small at the kettle wall surface, which may be affected by the baffle plate. The speed is also smaller. In the two-blade inclined paddle type, the overall speed of the particles is small; the axial flow caused by the two-blade straight paddle type is increased, and the overall speed of the particles is also increased; the speed of the particles in the kettle of the three-blade swept back type is significantly increased, which is due to the radial and axial flow effect brought about by the three-blade swept back type is more ideal, and it can make the particles in the polymerization kettle to enhance the suspension effect, which in turn produces the particles with better quality.

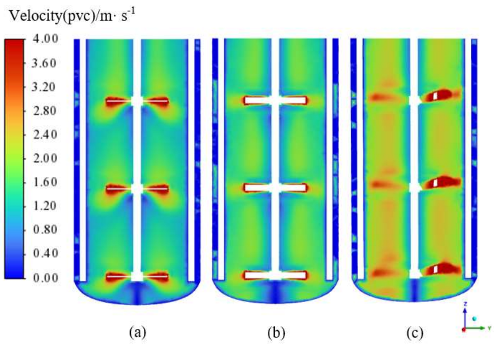


Fig.8 Effect of paddle structure on particle motion velocity

5.3 Velocity of Particle Movement

Figure 9 shows the distribution cloud of the effect of different blade structures on particle size. From the analysis of the figure, it can be seen that relative to the two-bladed straight paddle type and three-bladed swept back type, the particle size distribution range in the kettle corresponding to the two-

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bladed slanting paddle type has been enlarged, and the large particles and small particles have increased significantly. The reason is that the radial flow generated by the two-blade pitched paddle type is weaker, and the stirring dead zone exists in the stirring shaft area and the bottom area, which leads to the aggregation of particles more easily, and thus the existence of large-size particles.The overall particle size distribution in the kettle corresponding to the two-bladed straight paddle type and three-bladed swept back type is relatively uniform, in which the three-bladed swept back type has less large-size particles in the bottom area, which is better for the polymerization of particles.

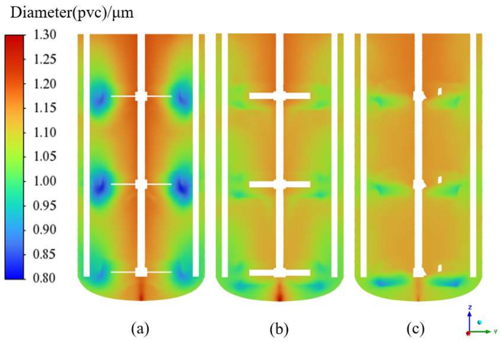

Fig.9 Effect of paddle structure on particle size distribution

6. Conclusion

A kinetic model of particle aggregation was established by applying the group equilibrium theory to study the particle characteristics in the polymerization kettle. Taking 5 L polymerization kettle as the research object, the effect of different rotational speeds on particle size and particle distribution was studied; the principle of non-geometric similarity enlargement was applied to enlarge the polymerization kettle to 136 m3, and the effect of different paddle structures on the particle size and particle velocity distribution was investigated, and the conclusions were obtained as follows.

(1) Under different rotational speeds, the particle size changes significantly. With the increase of rotational speed, the particle size gradually decreases, the particle stratification phenomenon is gradually weakened, and the particle dispersion is more uniform.

(2) After the polymerization kettle amplification, the paddle structure for the three-bladed swept back polymerization kettle power consumption is larger, but the axial and radial flow effect is better, the particle size and distribution of particles is more uniform, and the resulting polymerization effect is better.

Acknowledgments

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