APPLICATION OF STIRRED TANK REACTOR EQUIPPED WITH DRAFT TUBE TO SUSPENSION POLYMERIZATION OF STYRENE

MASATO TANAKA AND TAKASHI IZUMI

Department of Chemical Engineering, Niigata University, Niigata 950-21

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The stirred-tank reactor (DSTR) equipped with draft tube (DT) was applied to suspension polymerization of styrene. In the experiments the length of DT, the impeller height and the impeller speed were changed stepwise. The following points were found.

- 1) Mean droplet diameter during the reaction and mean final particle size were not affected by impeller height.
- 2) As DT became longer, droplet circulation time increased and droplet distribution became more uniform.
- 3) As DT became longer, the size distribution and mean size of final particles became more uniform and larger, respectively.
- 4) With increasing impeller speed, the particle size and uniformity decreased at first, became minimal around 5.8 s^{-1} and then increased again.
- 5) Particle size of polymer beads produced with DSTR was more uniform than that with the conventional fully baffled stirred tank (BSTR).

Introduction

In suspension polymerization, it is strongly desired to produce polymer beads of more uniform size.^{4,5,12,13)} For this purpose, it is considered necessary to make all droplets experience the same dispersing behaviour throughout the reaction.¹³⁾

As a means of doing this, the circulation time required for a droplet to circulate in the reactor should be made as uniform as possible, because the droplet must experience coalescence and breakup of the same frequency per circulation.¹³⁾

However, a distribution of circulation times of droplets is inevitable as long as the conventional stirred-tank reactor with baffle plate (BSTR) is used.^{3,15,16)}

The draft tube (DT) installed in the reactor instead of baffles may be considered to contribute greatly to making the circulation times of droplets uniform.

In this work, suspension polymerization of styrene is performed by using a stirred-tank reactor equipped with draft tube (DSTR). In the experiments, the length of DT, the impeller height and the impeller speed were changed stepwise and the transient mean droplet diameter and the final particle size were measured. The performance of DSTR for suspension polymerization was compared with that of BSTR.

1. Experiments

1.1 Experimental apparatus and procedures

Figure 1 shows a schematic diagram of the exper-

imental apparatus. The stirred-tank reactor was a separable flask of diameter of 0.12 m and was equipped with a glass draft tube, the diameter of which was 8×10^{-2} m. Also, two glass baffles as shown in Fig. 1 were installed on the reactor wall to prevent the formation of a vortex at the free liquid surface and bubbles from being enfolded. The dispersed and continuous-phase liquids were prepared as shown in Table 1. Conversion of styrene monomer to polymer was measured by the sedimentation method.¹¹⁾ Experimental conditions are also summarized in Table 1.

Stirring was started after the reactor was filled with the continuous phase of predetermined volume. After stirring for about five minutes, the monomer phase was added to the reactor and then polymerization was started at a constant temperature of 70°C and dispersed phase volume fraction of 0.1. At constant time intervals from the beginning of polymerization, a portion of reaction mixture was drawn off with a glass pipet from the position shown in Fig. 1. The sampled droplets were transferred to a laboratory dish containing 1.0 wt% aqueous solution of polyvinyl alcohol to prevent the droplets from coalescing. Photographs of these droplets were taken, and from these the transient mean droplet diameter was measured. The mean droplet diameter is the Sauter mean diameter. Experiments described above were performed by changing impeller speed, impeller height and length of DT.

Besides polymerization experiments, in order to learn the dispersing behaviour of droplets in the

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Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Experimental conditions

$H = 0.25, 0.33, 0.50, 0.67, 0.75$
$H_d = 0.35, 0.59, 0.82$
$H_L = 18 \times 10^{-2} \text{ m}$
$h_d = 6, 10, 14 \times 10^{-2} \text{ m}$
Continuous phase = ion-exchanged water + stabilizer (PVA with polymerization degree of 500) concentration of stabilizer = 0.02 wt%
Dispersed phase = styrene + initiator (azobisisobutyronitrile) concentration of initiator = $50 \text{ mol} \cdot \text{m}^{-3}$
Impeller = six-bladed disc turbine

reactor, two preliminary experiments (Experiment A and Experiment B) were performed under the same conditions as those of the polymerization experiment by using polystyrene beads (diameter = $6 \times 10^{-4} \text{ m}$, density = $1050 \text{ kg} \cdot \text{m}^{-3}$).

Experiment A: The circulation time of a single polystyrene bead was measured. This is the time required for a bead to circulate along the circulation path where a bead is discharged from the impeller region, circulate outside DT and come back to the impeller region.¹³⁾ A particular case was observed in which the flowing direction of fluid reversed, depending on the combination of impeller height and length of DT. However, the path described above was found to be the main circulation path. In this preliminary experiment, the density of continuous phase was adjusted so as to equal that of polystyrene bead by dissolving sodium chloride.

Experiment B: The impeller speeds required for the complete dispersion⁸⁾ and for the uniform dispersion⁹⁾ of polystyrene beads were measured by visual observation⁸⁾ and the electric conductivity method,^{2,10)} respectively.

2. Experimental Results

2.1 Initial mean droplet diameter

Figure 2 shows the dependence of initial mean

Fig. 2. Dependence of initial mean droplet diameter on impeller speed.

Fig. 3. Transient feature of mean droplet diameter.

droplet diameter on impeller speed. For comparison, the results¹⁴⁾ obtained with BSTR are also shown in the figure. The droplet diameters obtained with DSTR are proportional to the -1.4 power of impeller speed and have minor dependence on impeller height.

On the other hand, the droplet diameters obtained with BSTR are affected by impeller height and are proportional to the -0.4 to -0.6 power of impeller speed.

2.2 Transient mean droplet diameter

Figure 3 shows the transient mean droplet diameters together with those obtained with BSTR. In DSTR and BSTR, at the early stage of the reaction, the droplet diameters decrease with increasing impeller speed. This dependence is kept throughout the reaction in BSTR, but disappears with reaction time in DSTR.

In DSTR, at the lower impeller speed, droplets remain at constant average diameter throughout the reaction, while at the higher impeller speed, they grow steadily due to coalescence. A difference between the transient droplet diameter in BSTR and that in DSTR was also observed at all conditions. Accordingly, the dependence of droplet diameter on impeller speed after the middle stage of the reaction is considered to

Fig. 4. Dependence of mean final particle size on impeller speed.

Fig. 5. Dependence of mean final particle size on length of draft tube.

be characteristic of DSTR.

2.3 Mean final particle size

Figure 4 shows the dependence of final particle size on impeller speed together with the results¹⁴⁾ obtained with BSTR. In the case of BSTR, final particle size is proportional to the -1.3 power of impeller speed.

In the case of DSTR, it is found that with increasing impeller speed the final particle sizes decrease at first, become minimal around 5.8 s^{-1} and then increase again. This dependence on impeller speed is also considered to be characteristic for the case of DSTR, as discussed in the previous section.

Furthermore, no consistent dependence of final particle size on impeller height is observed.

Figure 5 shows the dependence of final particle size

Fig. 6. Dependence of uniformity of final particle size on impeller speed.

on the length of DT. The final particle sizes increase slightly with the length of DT and are proportional to the 0.2 power.

2.4 Final particle size distribution

As a measure to demonstrate the uniformity of final particle size, the volume fraction of particles included within $\pm 20\%$ of mean particle size, $(1 \pm 0.2)d_p$, was adopted.

Figure 6 shows how this uniformity was changed by the operational conditions. The uniformity shows the same dependence as that of final particle size on impeller speed.

With respect to the effect of impeller height, no consistent results were observed. However, the uniformity was improved with increasing length of DT. As an example, at an impeller speed of 5.8 s^{-1} the uniformities for DT lengths of 0.35 , 0.59 and 0.82 are 20 , 33 and 42% , respectively.

By comparing the best uniformity (about 70%) obtained in DSTR with that (about 50%) in BSTR,¹⁴⁾ DSTR is favoured for the production of polymer beads of more uniform size.

3. Discussion

Generally, in BSTR, the effect of impeller height on both droplet diameter during the reaction and final particle size is considered to be attributable to the change of ratio of coalescence to circulation frequency.¹³⁾ However, in DSTR, as shown in Figs. 2 and 4, no effect of impeller height was observed.

To find out the reason for this result, the relation between circulation time and impeller height was investigated with the result of Experiment A, shown in Fig. 7. The circulation time or circulation frequency¹³⁾ is found to be independent of impeller height. This may be considered to be attributable to

Fig. 7. Dependence of mean circulation time of a bead on impeller height.

Fig. 8. Dependence of mean circulation time on length of draft tube.

the fact that the length of the main circulation path does not change owing to DT, even if impeller height is changed. Accordingly, droplet diameter and final particle size may not be affected by impeller height.

To find out the reason for the effect of DT length as shown in Figs. 5 and 6, how the variance and mean value of circulation time distribution were affected by the DT length was investigated by the results of Experiment A, shown in Figs. 8 and 9. With increasing DT length, the variance of circulation time distribution decreases and its mean value increases. These results mean that with increasing DT length, coalescence per circulation increases and the circulation time becomes more uniform. Accordingly, the final particle size becomes larger and more uniform with DT length. The variance of circulation time distribution tends to decrease with increasing impeller speed.

The dispersing behaviour of polymer beads observed in Experiment B are as follows.

As the impeller speed is gradually increased, polymer beads start to float off the reactor bottom,

Fig. 9. Dependence of variance of circulation time distribution on length of draft tube.

Fig. 10. Relation between impeller speed required for uniform dispersion and impeller height.

Fig. 11. Relation between impeller speed required for uniform dispersion and length of draft tube.

revolve concentrically and then circulate along the circulation path. When the impeller speed is increased further, the concentric revolution of polymer beads disappears and soon polymer beads disperse uniformly. Furthermore, as shown in Figs. 10 and 11, the impeller speeds required for uniform dispersion of polymer beads are almost independent of both impeller height and DT length and change between 5.8 and 6.3 s⁻¹. These critical impeller speeds for uniform dispersion nearly agree with the impeller speeds at which the final particle size and its uniformity become minimal, as shown in Figs. 4 and 6.

From the results with Experiment A and Experiment B as described above, the unique dependencies of the final particle size and its uniformity

on impeller speed can be qualitatively interpreted as follows.

At an impeller speed larger than that for uniform dispersion, polymer beads of more uniform and larger size must be produced because of the increase in coalescence and the more uniform circulation time.

On the other hand, at an impeller speed fairly smaller than that for uniform dispersion, the final particle size must become larger and more uniform, because coalescence is considered to decrease owing to both the systematic concentric revolution of droplets and the lower impeller speed, and the droplet during the reaction becomes larger owing to the lower shear stress.

As the impeller speed increases to approach that for uniform dispersion, concentric revolution gradually disappears and coalescence increases. Accordingly, the final particle size and its uniformity must decrease due to the larger shear stress as compared with the case described just above and the increase in coalescence, respectively.

To interpret quantitatively the results obtained in this work, a more detailed investigation is considered necessary.

By complementary experiments, in which deposition of polystyrene beads on the doubled-faced cohesive tape stuck to the walls of reactor and DT was measured, the deposited amount measured in DSTR was found to be about 1.7 times that in BSTR. Effective countermeasures should be worked out to prevent polymer deposition.

Conclusion

The following results were obtained by performing suspension polymerization of styrene with a stirred-tank reactor equipped with draft tube.

- 1) Mean droplet diameter and final particle size were not affected by impeller height.
- 2) As the draft tube became longer, particle circulation time increased and particle distribution became more uniform.
- 3) As the draft tube became longer, size distribution and mean size of final particles became more uniform and larger, respectively.
- 4) As impeller speed was increased, final particle size and its uniformity decreased at first, became minimal around 5.8 s^{-1} and increased again.

- 5) Final particle size produced in the stirred tank with draft tube was more uniform than that in the conventional fully baffled stirred tank.

Nomenclature

d_p	= mean droplet diameter or final particle size	[m]
F	= volume fraction of final particle included within $\pm 20\%$ of mean final particle size	[%]
H	= dimensionless distance of impeller from liquid surface, $(H_L - H_i)/H_L$	[—]
H_d	= dimensionless draft tube length, (h_d/H_L)	[—]
H_i	= impeller height from bottom of reactor	[m]
H_L	= liquid depth	[m]
h_d	= draft tube length	[m]
N_r	= impeller speed	$[\text{s}^{-1}]$
N_{rc}	= impeller speed required for uniform dispersion	$[\text{s}^{-1}]$
θ	= circulation time	[s]
σ_t^2	= variance of circulation time distribution	[—]

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