

Inverse Phase Suspension Polymerization of Acrylamide in a Batch Oscillatory Baffled Reactor

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ABSTRACT: We report, for the first time, our experimental investigation of inverse phase suspension polymerization of acrylamide in a batch oscillatory baffled reactor. In such a reactor, the oscillatory motion is achieved by moving a set of orifice baffles up and down the column at the top of the reactor. The effects of both operational and design parameters on the mean particle size and size distribution of polymer beads were investigated, including oscillation amplitude, oscillation frequency, baffle spacing, baffle free area, and monomer addition time. The experimental results indicated that the mean particle size and size distribution of the polymer beads depended predominantly on the product of oscillation frequency and amplitude, i.e., the oscillation velocity. The size distributions are narrow and of essentially a Gaussian distribution. The level of fines produced is consistently less than 1% for all 100 experiments performed. We demonstrated that the mean particle size and size distribution in an oscillatory baffled reactor can be controlled precisely by simply selecting the appropriate oscillation velocity. The effect of the baffle spacing on the mean particle size is much less compared with that of the baffle free area. The monomer injection time has a noticeable influence on the mean particle size, but the rate of change is relatively small. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1669–1676, 2000

Key words: oscillatory baffled reactor; oscillation frequency; oscillation amplitude; mean particle size; polyacrylamide

INTRODUCTION

The production of water-soluble polymers is part of a multibillion-pound water-treatment industry. Such polymers are extensively used in processes such as water clarification in the paper-making industry and as water-treatment coagulants. One method commonly applied to produce these polymers is a heterophase water in oil polymerization

process known as inverse phase suspension polymerization.¹ Polyacrylamide is produced by such a process. A water-based monomer phase is dispersed as droplets in a continuous oil phase and polymerized in the droplets to form polymer particles as a dispersed solid phase. During the reaction, the behavior inside each dispersed monomer droplet is that of bulk polymerization.² The polymerization process follows a free radical mechanism,³ and is initiated chemically by water-soluble free radical azo or peroxide species.^{1,3,4}

Because many polymerization reactions are highly exothermic, e.g., $\Delta H_p = 19.5$ kcal/mol for

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acrylamide,¹ temperature gradients within polymerization vessels are clearly to be avoided. Although heterophase polymerization reactions provide much greater temperature control compared with conventional suspension polymerization due to the use of the oil phase as a cooling agent, the mixing and heat transfer requirements are still vitally important. For the inverse phase bead polymerization of acrylamide in particular, the monomer droplets pass stages of viscosity changes and finally transform to solid, smooth, and clear spheres (beads). The principal problem is the formation of as uniform a suspension as possible of water-based monomer droplets in the oil phase and the prevention of coalescence of the droplets during the polymerization process. Efficient mixing within a polymerization vessel serves both purposes. Inverse phase suspension polymerization of acrylamide is traditionally carried out in batch stirred tank reactors. In this work, acrylamide beads of required size and specification are produced in a batch oscillatory baffled reactor (OBR). In an OBR, fluid mixing is achieved by eddies that are generated when a set of prespecified orifice baffles moves periodically through liquid. These vortices can be controlled by a combination of geometrical and operational parameters, such as orifice diameter, baffle spacing, oscillation frequency, and oscillation amplitude. Under certain operational conditions, an OBR can be operated as either a plug flow reactor or an enhanced mixing device.⁵⁻⁸ For a given baffle geometry, the fluid mechanical condition in an OBR is controlled by the oscillatory Reynolds number, Re_o , and the Strouhal number, St , defined as:

$$Re_o = \frac{Dx_o\omega}{\nu} = \frac{2\pi Dx_o f}{\nu} = \frac{2\pi Du_{osc}}{\nu} \quad (1)$$

$$St = \frac{D}{4\pi x_o} \quad (2)$$

where D is the tube diameter (m), x_o the center to peak oscillation amplitude (m), ω the angular frequency of oscillation ($= 2\pi f$), f the oscillation frequency (Hz), u_{osc} ($x_o f$) the oscillatory velocity (m/s), and ν the kinematic viscosity of the fluid (m^2/s). The power consumption per unit volume of an OBR can be estimated from:⁹

$$\frac{P}{V} = \frac{2\rho N_B}{3\pi C_D^2} \frac{1 - \alpha^2}{\alpha^2} x_o^3 \omega^3 \quad (3)$$

where N_B is the number of baffles per unit length (/m) referring to the baffle spacing, α the baffle free area ratio [$= (D_o/D)^2$] accounting for the baffle diameter, where D_o is the orifice diameter (m), ρ the density of liquid (kg/m^3), C_D the orifice discharge coefficient (taken as 0.7). For a given baffle geometry, both the fluid mechanical conditions and the power input in an OBR are proportional to the oscillatory velocity. In the past 10 years, a substantial body of scientific papers has been published and a number of engineering applications are being pioneered.⁵⁻¹⁵ This project was the first of its kind linking the scientific research in an OBR with a real industrial application in polymerization, and we report, for the first time, our experimental investigation of particle size and size distribution of polyacrylamide in a batch OBR.

EXPERIMENTAL FACILITIES

The batch OBR system is shown schematically in Figure 1. Unlike the predecessors of OBRs in the previous investigations, the oscillatory motion of fluid in this case is achieved by moving a set of periodically spaced baffles up and down the liquid medium at the top of the column, rather than pulsing fluid through a set of stationary baffles at the base of the reactor. Such an oscillating mechanism also has the advantages in scale-up. Essentially the reactor consisted of a vertical glass tube of 50 mm in diameter, 1000 mm in height, and 5 mm in thickness. Two ports along the reactor were used for monomer charging and nitrogen purging, respectively (Fig. 1). A stainless steel plate was flanged onto the bottom of the glass column and was fitted with a 25-mm diameter valve, which allows the reactor content to be discharged when required. A set of orifice baffles, between 6 and 9 depending on the baffle spacing tested, was used in the investigation. The baffles were made of 3-mm thick stainless steel plates and connected by two 3-mm-diameter stainless steel rods, which were then attached to a coupling plate at the top. The baffles were designed to fit closely to the wall of the column.

An oscillating unit, consisting of an electric motor with a flywheel, an inverter, and a linkage cam, provides the periodical motion of the baffles. The speed of the motor can be controlled to generate oscillation frequencies from $f = 1$ to 5 Hz with a 0.01-Hz increment. The oscillation amplitudes of $x_o = 10$ to 50 mm peak-to-peak with an

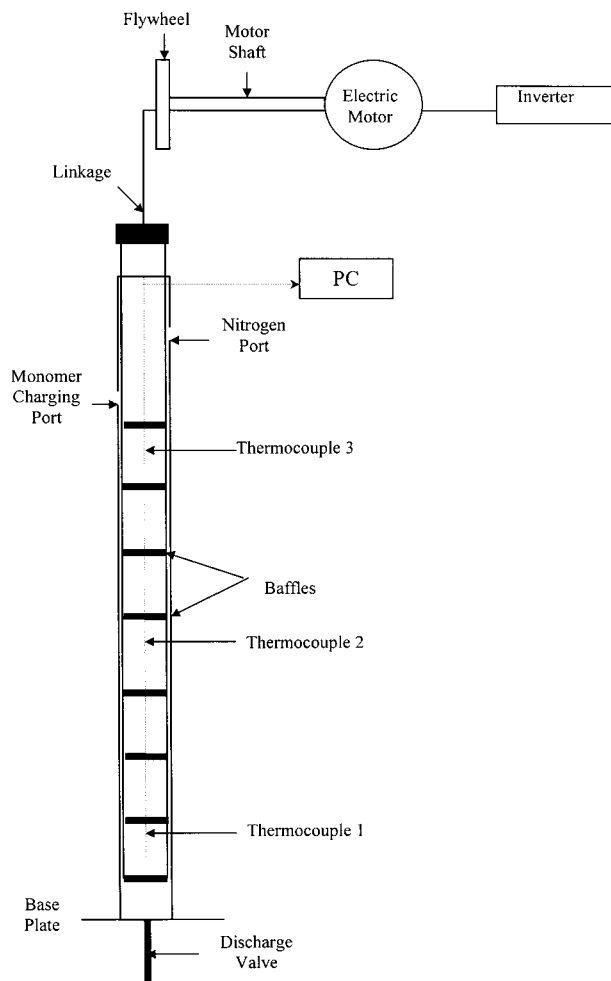


Figure 1 The batch oscillatory baffled reactor.

increment of 10 mm can be obtained by adjusting the eccentric positions of the linkage cam on the flywheel. Three free baffle area ratios (α), defined as the ratio of the orifice area to the tube area, of 19, 22, and 27% were investigated. In addition, four baffle spacing of 62.5 mm, 75 mm, 87.5 mm, and 100 mm were examined also, which correspond to 1.25, 1.5, 1.75, and 2 times the tube diameter.

Three K-type thermocouples with a diameter of 7 mm were used to monitor the temperature profiles along the column during polymerization. Such thermocouples are very thin, minimizing any disturbance to the flow pattern within an OBR. They are also flexible and easily located. In our experiments, the thermocouples were freely suspended in the reactor, the first one placed between the bottom two baffles, the second between the middle two baffles, and the third between the top two baffles, as shown in Figure 1. The tem-

perature data were then recorded via a PC computer.

EXPERIMENTAL PROCEDURE

The reaction method investigated in this work was the redox method and a pair of redox initiators and one thermal initiator were used. The two phases in the reaction consist of an organic phase of iso-paraffinic hydrocarbon (Isopar) with a steric stabilizer, and a monomer phase, which is comprised primarily of water and acrylamide.

Based on a confidential and scaled-down formulation of a proprietary polyacrylamide resin supplied by Ciba Water Treatment Division (Bradford, UK), the recipe was specifically formulated to give off much less heat than the traditional ones, e.g., the maximum reaction temperature is approximately 50°C. At such a low temperature, the conversion of monomer is still very high, in excess of 95%. This recipe also allows the performance of the inverse phase suspension polymerization tests without considering heat transfer element, as in our case, in a glass OBR with no jacket. The use of the glass vessel provides good visual observation of what is really happening in the reactor, and a good feel of the temperature change during the reaction by touching. In addition, the temperature variations during each polymerization test were monitored precisely by the thin wire-type thermocouples to produce accurate temperature profiles, a typical example of which is shown in Figure 2. Two features are clearly seen in the graph. First, the

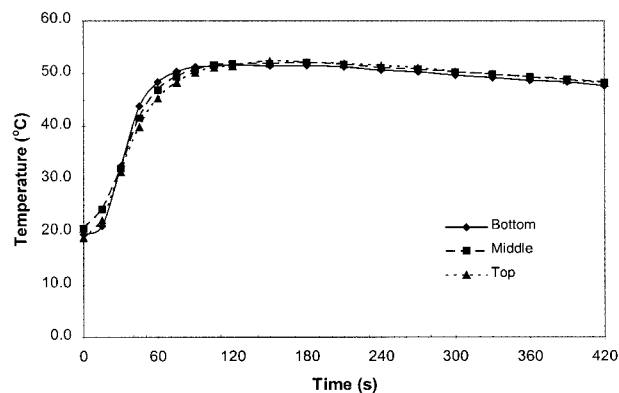


Figure 2 Temperature profile of a polymerization test (oscillation amplitude = 40 mm, oscillation frequency = 2.25 Hz, baffle free area = 23%, baffle spacing = 75 mm, and monomer addition time = 20 s).

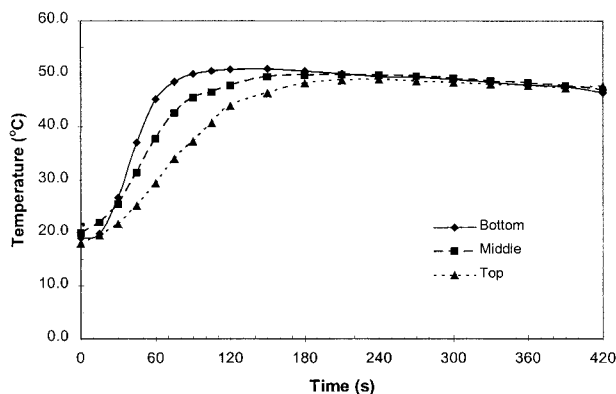


Figure 3 Temperature profile of a polymerization test (oscillation amplitude = 40 mm, oscillation frequency = 1.50 Hz, baffle free area = 23%, baffle spacing = 75 mm, and monomer addition time = 20 s).

temperature change is within 30°C from the room temperature due to the specially formulated recipe. Second, the temperature readings from all three thermocouples within the reactor were more or less the same, indicating that uniform mixing had been achieved throughout the column.

It should be noted that for the majority of the polymerization tests, the thermocouple profiles are almost identical to that shown in Figure 2, except those in which the mixing intensity has fallen below a “critical” level. In this case, a temperature gradient is generated along the tube during the start of the reaction, as shown in Figure 3. This will have a measurable impact on the mean particle size and size distribution of the polymer in question, which will be discussed below.

The experimental procedure for each run was as follows: the oil phase, consisting of 750 g of Isopar and 3.75 g of stabilizer was prepared and charged into the column. The baffles were then oscillated at a frequency of 1 Hz. Nitrogen sparge was switched on for 30 min at 0.1 Bar to degas the oil phase.

The monomer phase was prepared using 122.5 g of acrylamide, 122.5 g of distilled water, 5 g of a pH buffer, and 0.5 g of Sequestrant solution. It was then placed in warm water and stirred occasionally to allow acrylamide to fully dissolve. In addition, a solution of 20% acetic acid was made.

Fifty milliliters of distilled water was used to prepare a Redox Initiator A solution. Another 50 mL of distilled water was used for a Redox Initiator B solution.

The 20% acetic acid was added dropwise to the monomer phase until a pH of 6 was achieved and maintained. Redox Initiator A, 2.5 mL, was then added to the monomer phase, which was stirred and added immediately to the OBR. Once all the monomer had been charged, the reactants were left for 3 min in order for oxygen in the monomer phase to disperse into the oil phase. After the 3 min, 2.5 mL of the Redox Initiator B was added to the OBR under oscillation, to initiate the reaction. After 30 min of oscillation, the contents of the reactor were discharged into a container with the presence of 500 mL of acetone and were then filtered using a Buchner funnel. The polymer beads were then dehydrated and left to dry for 48 h.

Samples of dried polymer particles were sent to the Ciba Water Treatment Division for analyses, and the particle size distributions were measured using a Sympatec machine (which utilizes a light scattering technique), and the molecular weight distributions were measured by the intrinsic viscosity.

RESULTS AND DISCUSSION

Figure 4 is one of the typical size distributions obtained in the OBR, where $d_{v,0.5}$ is the commonly used terminology for describing the mean particle size, i.e., particle size at 50% cumulative volume. It can be seen that the size distribution is fairly narrow and essentially of a Gaussian function. There are very few fines (beads with a particle

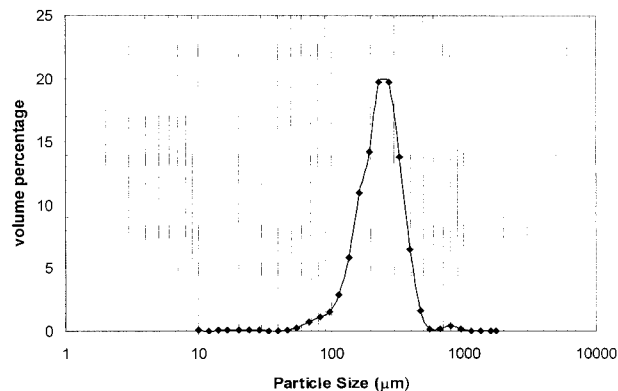


Figure 4 Particle size distribution with $d_{v,0.1} = 138.3 \mu\text{m}$, $d_{v,0.5} = 234.6 \mu\text{m}$, and $d_{v,0.9} = 355.3 \mu\text{m}$ (oscillation amplitude = 40 mm, oscillation frequency = 2.25 Hz, baffle free area = 23%, baffle spacing = 75 mm, and monomer addition time = 20 s).

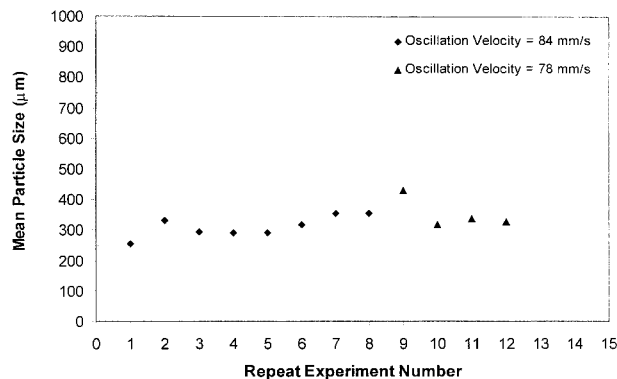


Figure 5 Repeatability tests at two oscillation velocities.

size less than 150 (m), the level being consistently less than 1% for all the experimental runs. The results shown in Figure 4 represent merely one of 100 experiments performed at a wide range of oscillation conditions; it is impossible to show them all. In the following sections only mean particle size, $d_{v,0.5}$, are presented. It should be noted that among the 100 experiments, 15% of runs were repeated for the purpose of repeatability. One of the typical repeatability tests is shown in Figure 5. Those were performed under identical operating conditions but within 14 different days. A reasonable closeness for the entire mean particle sizes can be seen, indicating a confidentable degree of repeatability of the experiments.

The Effect of Oscillatory Velocity on Mean Particle Size

Since the oscillatory velocity affects both the fluid mechanic conditions and the power input in an

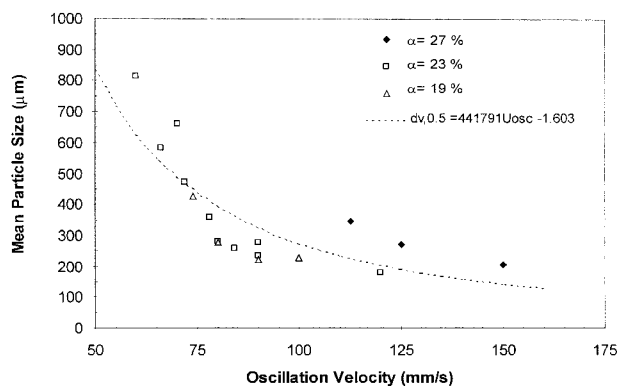


Figure 6 Effect of oscillation velocity on the mean particle size (baffle spacing = 75 mm).

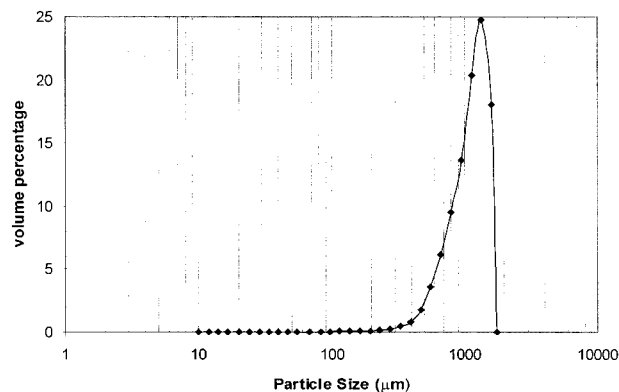


Figure 7 Particle size distribution with $d_{v,0.1} = 559.0 \mu\text{m}$, $d_{v,0.5} = 1160.0 \mu\text{m}$, and $d_{v,0.9} = 1595.2 \mu\text{m}$ (oscillation amplitude = 40 mm, oscillation frequency = 1.50 Hz, baffle free area = 23%, baffle spacing = 75 mm, and monomer addition time = 20 s).

OBR, our investigation concentrated on the effect of the oscillatory velocity on the mean particle size ($d_{v,0.5}$), the results of which are shown in Figure 6. An increase in the oscillation velocity caused a decrease in the mean particle size; the trend was more pronounced at lower oscillatory velocities. For instance, an increase in the oscillation velocity from 60 to 80 mm/s (33.3% increase) decreased $d_{v,0.5}$ from 1200 μm to 250 μm (75.8% decrease). Further increases in the oscillation velocity resulted in much less changes in the mean particle size. The trend described here is applicable to all three baffle areas investigated. The decrease of the mean particle size with the increase of the oscillatory velocity is expected as the increase of the oscillatory velocity enhances the power input to the OBR, which consequently results in more even distribution of smaller droplets. At extremely low oscillatory conditions, e.g., oscillation frequencies less than 2 Hz at 40-mm amplitude, the mixing intensity applied to the column was no longer sufficient to suspend all the monomer, which is of higher density than the bulk liquid in the column. Consequently, a temperature gradient within the column occurred, as shown in Figure 3, where the temperature at the bottom of the reactor was higher than that at the top. This indicates that the denser monomer, charged into the reactor in a one slot manner, sank to the bottom of the column, causing more reaction there than the middle and top parts of the reactor. Note that this effect is diminished when the oscillatory intensity is increased over the “minimum” state. The corresponding particle size distribution under such a condition is shown

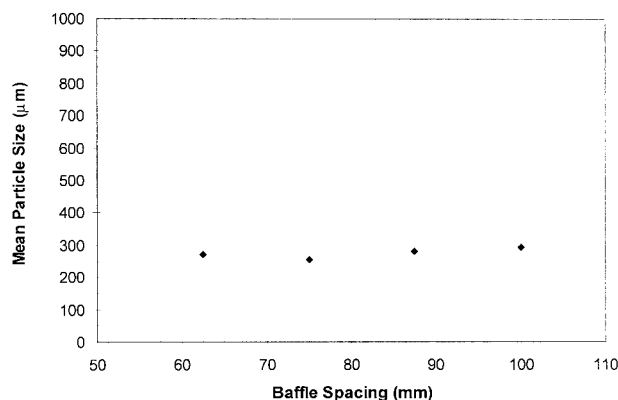


Figure 8 Effect of baffle spacing on the mean particle size at a fixed oscillation velocity (oscillation amplitude = 30 mm, oscillation frequency = 2.8 Hz, and baffle free area = 23%).

in Figure 7 in which much larger mean particle sizes clearly resulted with a skewed size distribution.

It should be pointed out, however, the particle size curves for all the oscillatory velocities are essentially of a Gaussian distribution. This is very important because it indicates that the mean particle size and size distribution in the OBR can be controlled simply by selecting the appropriate oscillatory velocity. The range of the mean particle size achieved while maintaining the Gaussian size distribution in the OBR is a key for product engineering.

The Effect of Baffle Spacing on Mean Particle Size

The effect of the baffle spacing on the mean particle size is shown in Figure 8 at a fixed oscillatory velocity of 84 mm/s. It can be seen that the mean particle sizes, $d_{v,0.5}$, were similar and all within a range of 40 μm for the four baffle spacings applied. This limited effect of the baffle spacing on the mean particle size is in good agreement with our recent study of the effect of the baffle spacing on mixing time for this type of device.¹⁶ The fact is that for an OBR with moving baffles as the oscillatory mechanism, the oscillation amplitude used is often larger than that for an OBR with pulsing fluid as the oscillatory mechanism. This leads to an enhanced effect of the oscillation amplitude on process characteristics compared with that of the baffle spacing. Thus, the limited effect of the baffle spacing on the mean particle size is rather expected.

The Effect of Baffle Free Area on Mean Particle Size

The effect of the baffle free area on the mean particle can be seen in Figure 9 for three oscillation velocities at a fixed baffle spacing. Although the general trend is similar to that of the baffle spacing, there is a slight indication of an optimum baffle free area of approximately 23%, at which a minimum mean particle size was obtained. This value is again very close to the 20–22%, which was reported in the studies of mixing time in oscillatory baffled columns.¹⁵

The Effect of Monomer Addition Time on Mean Particle Size

When the monomer addition time is increased, this effectively means that for the same amount of monomer used, the ratio of monomer to bulk liquid is decreased, i.e., a lower density of monomer is charged into the column at any given time. What effect would such an increased injection time have on the mean particle size? Figure 10 illustrates the results of our investigation. It is evident that the longer monomer addition time produced larger mean polymer particles at very similar temperature profiles from each of the three thermocouples. The percentage increase in the mean particle size is also within the expected range of 10–15 % in relation to the increase in the monomer addition time. This suggests a linearity that exists between the increase of the mean particle size and that of the monomer addition time. This is an interesting finding and could lead to an optimal monomer density to be identified in the inverse phase suspension polymerization, since we are aware that excess monomer dosage is al-

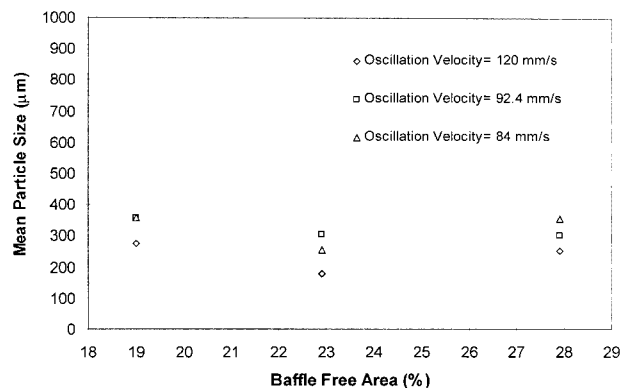


Figure 9 Effect of baffle free area on the mean particle size (baffle spacing = 75 mm).

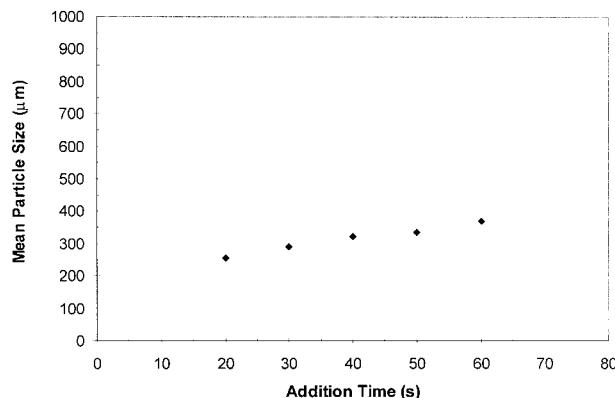


Figure 10 Effect of monomer addition time on the mean particle size at a fixed oscillation velocity (oscillation amplitude = 30 mm, oscillation frequency = 2.8 Hz, baffle free area = 23%, and baffle spacing = 75 mm).

ways applied in the industrial scale polymerization to ensure adequate reaction and productivity. However, further increases in the monomer addition time were not advised because this may slow the reaction significantly, causing difficulty in controlling the reaction; consequently, no experiments were performed beyond a 60-s addition time. In summary, the effect of the monomer addition time on the mean particle size is linear, but of a small magnitude.

$d_{v,0.5}$ CORRELATION

In this work, we are particularly interested in establishing a correlation linking the mean particle size with the oscillatory velocity and also the power dissipation per unit mass ε ($= P/V\rho$) in the OBR. Based on a large number of experiments performed, the following correlation was obtained, as shown in Figure 6:

$$d_{v,0.5} = 4.4 \times 10^5 (x_o f)^{-1.603} \quad (\mu\text{m}) \quad (4)$$

for $50 < (x_o f) < 150$ mm/s and

$$d_{v,0.5} = 2212 \varepsilon^{-0.6511} \quad (5)$$

for $5 < \varepsilon < 100$ W/kg.

CONCLUSIONS

We have reported our experimental investigation of particle size and size distribution of inverse

phase suspension polymerization of acrylamide in a batch OBR in which the oscillation mechanism is relied upon to move the set of orifice baffles up and down the column. The results have shown that uniform temperature profiles are achieved along the height of the reactor. Under those conditions, the particle size distributions are of an essentially Gaussian function with a narrow spread. The level of fines is constantly below 1% for all the experimental tests.

The experimental results have also shown that the oscillatory velocity has a significant effect on the mean particle size; the trend is that with the increase of the oscillatory velocity, the mean particle size decreases sharply initially and then levels off. The correlation linking the mean particle size with the oscillation velocity is established as $d_{v,0.5} = 4.4 \times 10^5 (x_o f)^{-1.603}$.

The effect of the baffle spacing on the mean particle size is much less evident as compared with the effect of the baffle free area. Although the increase of the monomer injection time caused a linear increase in the mean particle size, the rate of the increase is very small.

The significant feature from this work is that the OBR is not only suitable for the inverse phase suspension polymerization process, but also offers a great controllability on both the mean particle size and size distribution. We have demonstrated that we are able to maintain the Gaussian size distribution while shifting the mean particle size from 200 to 800 μm with ease by simply selecting the appropriate oscillation velocity. This is a key factor to achieving product engineering utilizing the OBR.

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NOMENCLATURE

Notations

C_D	orifice discharge coefficient
D	internal tube diameter (m)
D_o	orifice diameter (m)
f	oscillation frequency (s^{-1})
ΔH_p	heat of polymerization (kcal mol^{-1})
N_B	number of baffles per unit length (m^{-1})
P/V	power density (W m^{-3})
Re_o	oscillatory Reynold's number
St	Strouhal number

- u_{osc} oscillation velocity (m s^{-1})
 x_o oscillation amplitude (m)
 X_{10} point at which lowest decile ends (μm)
 X_{50} mode size (μm)
 X_{90} point at which highest decile begins (μm)

Greek

- α ratio of the effective baffle orifice area to the tube area
 ε power dissipation per unit mass (W kg^{-1})
 ρ density of fluid (kg m^{-3})
 ω angular oscillation frequency (radians s^{-1})
 ν kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)

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