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Styrene Suspension Polymerization Using a Stirred Vertical Tubular Reactor

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Summary: Suspension polymerization reactions are commonly carried out in tank reactors designed with low values for the H/D ratio (Height/Diameter). As polymerization reactions are frequently high exothermic, the superficial area of these equipments are not enough high to adequately release the heat generated by the reaction. In this case, additional systems are necessary to provide cooling fluids with sufficiently low temperatures in order to maintain constant the polymerization temperature in the tank reactor. On the other hand, tubular reactors can be considered economically attractive because their high superficial area for heat exchange (high H/D) can improve temperature control and reduce operational costs. The present work uses a vertical tubular reactor to carry out the batch styrene suspension polymerization and evaluate the effects of the reactor and stirring system configuration on the polystyrene PSD (Particle Size Distribution). According to the results, besides a very good temperature control due to the reactor geometry, polystyrene particles with relatively narrow particle size distributions can be successfully produced in a stirred vertical tubular reactor.

Keywords: batch; particle size distribution; polystyrene (PS); suspension polymerization; tubular reactor

Introduction

Depending on the monomer used, extremely high heat generation should occur in the system due to the reaction exothermicity. In this case, equipments with low H/D ratio (Height/Diameter), as the typical stirred tank reactors used by industries, may not have enough superficial area to adequately release the heat generated and, consequently, maintain the reaction conditions under control. Frequently it is necessary to use low temperature cooling fluids to efficiently remove this heat, as cooled water, ammonium, etc. However, to obtain fluids with these characteristics, it is required additional industrial installations (e.g. gas compression and liquefaction, liquid refrigeration), which increases process costs.

To overcome or, at least, minimize this problem, tubular reactors could be used as an alternative equipment. Tubular reactors are economically attractive because their simple shape reduces fixed and operating costs. Moreover, the large surface area (high H/D ratio) for heat exchange is particularly advantageous for polymerization reactions because of its high exothermicity. The high H/D ratio of these reactors is capable to improve the heat transfer efficiency, reducing operational costs and allowing a better temperature control.

In spite of these advantages, tubular reactors are not used in the commercial production of suspension polymers. Industrial suspension polymerization reactions are commonly carried out in tank reactors designed with low values for the H/D ratio.

Some applications of stirred tubular reactors to carry out suspension polymerization

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reactions, installed in the vertical position, similar to towers, can be found in many patents.[1–4] However, rarely found in scientific studies.[5] Although these works had been developed to study a way to continuously carry out suspension polymerizations, they affirm that the proposed reactors can be successfully used to carry out batch suspension polymerizations.

The present work intends to show that stirred vertical tubular reactors (tower reactors) can be successfully used to carry out the batch styrene suspension polymerization reaction and produce polystyrene beads with narrow particle size distributions (PSD). Different stirring systems and holdup values were tested to evaluate the reactor feasibility.

Experimental Procedures

The reactor used in the present study is simply a boro-silicate tube (no cooling jacket) positioned in the vertical position ($D = 10.0$ cm and $H = 130.0$ cm), with a stirring system installed on its top. Two different stirring configurations were tested. The first one is a short shaft (40 cm length) with only one flat-bladed impeller body (Figure 1.a), while the second one is a long shaft (80 cm length) with two flat-bladed impeller bodies (Figure 1.b). Both of them were constructed in stainless steel. Depending on the selected holdup, one of the shafts was used to carry out the reaction in a stable way.

An electrical heater, connected to a control system, was installed in the bottom of the reactor to provide heat and maintain a constant reactor temperature throughout the reaction (Figure 2).

Styrene (from *Innova*, 20 ppm of p-terc buthyl catecol) was used as monomer (disperse phase), Dibenzoyl Peroxide – BPO (from *Akzo-Nobel*) as chemical initiator and poly(vinyl pyrrolidone) – PVP (from *Sul Polímeros*, $M_w = 360{,}000$ g/mol) as stabilizing agent. All the reactants were used as received. Nitrogen was fed into the reactor to avoid any inhibition by oxygen.

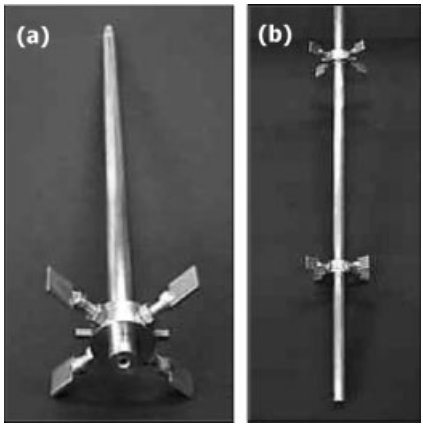

Figure 1.
Different shafts used: a) short (one impeller); b) long (two impellers).

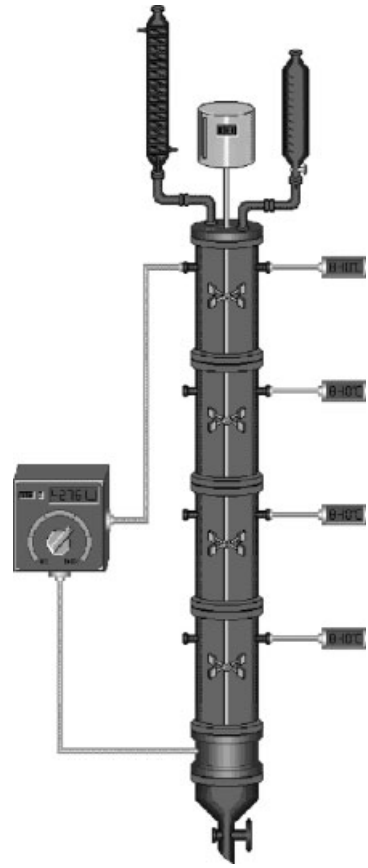

Figure 2.
Scheme of the vertical tubular reactor used in the experiments.

Table 1.
Basic reactions formulation.

Temperature (°C)	[PVP] (g/l)	[BPO] (% wt)	Impeler Type	Agitation Frequency
84.0	2.0	0.9101	Flat-Blade (4 blades)	350 RPM

Table 1 summarizes the basic reactions formulation adopted in the experiments.

Sieving (differential granulometric analysis), gravimetry and viscosimetry techniques were used to determine the polystyrene PSD, the final monomer conversion and the viscosimetric molecular weight, respectively.

Results and Discussion

In the first set of experiments, different holdup values were tested (0.10, 0.15 and 0.25) using the short shaft (Figure 1.a). According to Figure 3, the increase in the holdup value displaced the PSD histogram toward the higher sizes particles. This result was expected once the increase in the holdup leads to higher coalescence rates and less intense turbulent fields (turbulence damping).

Using the short shaft, only the superior part of the reactor is submitted to high intense turbulence levels (high shear stress zone), in which breakage predominates over coalescence. In this case, the dissipated turbulent energy presents a profile that decreases toward the bottom of the reactor, named circulation zone (low shear stress region). Through qualitative fluid dynamics tests, it was observed that raising the holdup there is an increase in the axial dispersion of the dispersed organic phase. Hence, the greater the number of drops in the low shear stress region, the greater should be the coalescence rate in this region, which contributes for the particles size growing.

From Figure 3, it is still possible to notice that the increase in the holdup provided wider PSD. According to the explanations given before, the greater the number o drops submitted to different shear intensity regions, the wider should be the expected PSD histogram.

It is important to point out that the existence of a holdup and shear stress profiles along the reactor are merely qualitative once these results were obtained through visual observation. Although the broadening of the PSD due to the increase of the system holdup, the histograms can still be considered narrow and apparently monomodals.

Using the same reaction system, it was not possible to carry out the styrene suspension polymerization in a stable way

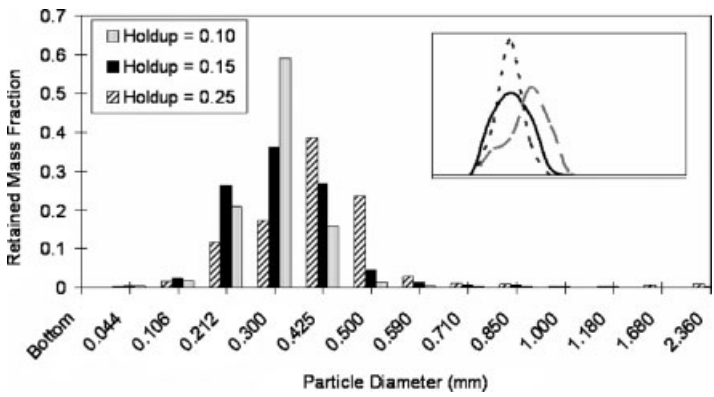

Figure 3.
Polystyrene PSD histograms obtained using the short shaft and different holdup values (0.10, 0.15 and 0.25).

Table 2.
Polystyrene particle properties using the short shaft.

Holdup	Dispersion	Sauter Mean Diameter (mm)
0.10	0.336	0.335
0.15	0.521	0.339
0.25	0.635	0.414

Table 3.
Polystyrene particle properties using the long shaft.

Holdup	Dispersion	Sauter Mean Diameter (mm)
0.35	0.682	0.446
0.40	0.838	0.422

considering holdup values higher then 0.25. In this way, the longest shaft with two impeller bodies (Figure 1.b) was used to overcome the lack of enough turbulent energy in the system. The agitation frequency was maintained at 350 RPM to carry out the reactions with holdup values of 0.35 and 0.40. Figure 4 presents the PSD histograms obtained for these situations and Table 3 contain the particle properties calculated from these histograms.

From Figure 4, it is possible to notice that, even raising the holdup from 0.35 to 0.40, the obtained PSD curves presented practically the same shape. Besides, according to the results presented in Table 3, the measured mean particle sizes were also almost the same. On the other hand, the particles sizes dispersion suffered an increase. Therefore, even raising the shaft length and the number of impeller bodies as an attempt to reduce the holdup and shear stress profile in the axial direction, the increase in the system holdup led to a broadening of the PSD histograms.

The reactions carried out considering high holdup values (0.35 and 0.40) proved that the reactor, even with no cooling jacket, is capable to adequately remove the heat generated by the reaction and, consequently, promote a very good temperature control of the reaction.

Conclusions

Despite the widening of the PSD curves and increasing of the mean particle size when the holdup was raised, the results can still be considered quite good because the PSD are reasonably narrow and apparently monomodal.

The use of the longest shaft provided enough turbulent energy to carry out the batch suspension reactions in a stable way even considering a relatively high holdup value (0.40). Although the high solid content produced and even with no an external jacket, the vertical tubular reactor was capable to efficiently release the heat generated by the reaction and, consequently, allow an adequate and stable temperature control of the reaction. Although the increased internal surface area, when

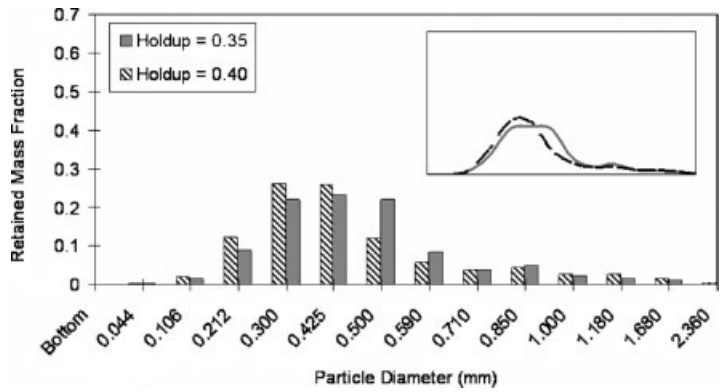

Figure 4.
Polystyrene PSD histograms obtained using the long shaft and different holdup values (0.35 and 0.40).

compared to the traditional low H/D reactors used to carry out suspension polymerizations, no significant fouling was verified inside the vertical tubular reactor. Therefore, the reactor showed to be a promising alternative for the batch production of suspension polystyrene particles with narrow PSD.

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