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Process Intensification of Emulsion Polymerization in the Continuous *Taylor* Reactor

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Summary: Process intensification is investigated by the emulsion polymerization of styrene in the continuous *Taylor* reactor. The result is an increase in space time yield up to a factor 200 in comparison to a semi-batch polymerization process. This is obtained by a fast emulsion polymerization with a mean residence time, which is reduced to 60 seconds. The article presented the results of the process and the economical aspects of the *Taylor* reactor plant.

Keywords: economical aspects; fast emulsion polymerization; process intensification; *Taylor* reactor

Introduction

Process intensification is one important task for polymer reaction engineering. Emulsion polymerization is mainly performed in discontinuous stirred tank reactors of some tenth of metric tons, where the rate of polymerization and hence the heat production rate is controlled by semibatch-wise feeding of monomers or a pre-emulsion. Revolving cycle periods of production are in the range of several hours. Keeping a certain level of production rate process intensification implies a reduction in reactor volume and subsequently an increase in space time yield by at least two orders of magnitude.[6] In order to follow this concept the fast running emulsion polymerization is investigated in a continuous *Taylor* reactor. This special type of reactor consists of two coaxial concentric cylinders of which the outer one is fixed and the inner rotating one is used as a stirrer. The chemical reaction takes place in the gap volume. Due to the existing flow pattern, depending on the rotational speed of the inner cylinder and the viscosity of the reaction medium, the *Taylor* reactor can be used as a plug flow tubular reactor, a tank-in-series as well as a continuous stirred tank reactor.

The hydrodynamic behavior of the reactor is examined by measurements of residence time distributions in dependence on different axial *Reynolds* numbers and *Taylor* numbers.

The experiments are carried out with the monomer styrene and a recipe, which is assigned from a batch process. The fast emulsion polymerization is investigated and presented in this paper for mean residence times of one, five and ten minutes.

Experimental Part

The experimental investigation of the hydrodynamics was done by online conductivity measurements at the inlet and outlet of the *Taylor* reactor. De-ionized water was used as homogeneous Newtonian fluids and potassium chloride as tracer for pulse injection. Residence time distributions were obtained by normalizing measured data and after subsequent de-convolution, *Bodenstein* numbers were calculated on the basis of the dispersion model for a reactor

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Table 1.
Recipe of the continuous emulsion polymerization of styrene

Components	Weight fraction, %
Styrene	6.00
Water	92.16
SDS	1.50
n-Pentanol	0.20
PPS or VA-044	0.14

closed on both sides. Stirring speed and throughput, respectively, varied *Taylor* and axial *Reynolds* numbers.

The polymerization experiments were carried out with a free radical micro-emulsion recipe, which was assigned from an equivalent batch process according to Table 1.

Styrene as monomer (*BASF AG*), sodium dodecylsulfate (SDS) as emulsifier, n-pentanol as co-emulsifier, potassium persulfate (PPS) as initiator (all from *Merck*) and 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as a faster decomposing water soluble initiator (*Wako Chemicals*) were used without further purification. Three controlled feed lines supplied the *Taylor* reactor with the reaction mixture: an aqueous solution of the emulsifier and co-emulsifier, the pure monomer and an aqueous solution of the initiator (PPS or VA-044). The three feed lines were mixed and heated up to reaction temperature before entering the *Taylor* reactor. Samples were taken along the reactor and in the reactor outlet. The residual monomer content was analyzed by GC in order to determine the monomer conversion by the internal standard method. Mean latex particle diameter was measured by light scattering.

Fast Running Emulsion Polymerization in the Continuous *Taylor* Reactor

Fast running emulsion polymerization means to polymerize to almost complete conversion in less than 10 minutes. The experiments are carried out in a *Taylor* reactor, which is very flexible. The characteristic number for a *Taylor* reactor is the *Taylor* number *Ta* with the gap width *d*, the rotational speed ω, the inner cylinder radius r_i and the kinematical viscosity ν.

$$Ta = \frac{\omega \cdot r_{\mathrm{i}} \cdot \mathrm{d}}{\nu} \sqrt{\frac{\mathrm{d}}{r_i}}$$

At a very low rotational speed of the inner cylinder laminar flow, the so-called laminar *Couette* flow is observed. By increasing rotational speed and hence increasing *Taylor* number in excess of the critical *Taylor* number, $Ta_{crit} = 42$, the laminar *Taylor* vortex flow builds up in the gap.

Finally the wavy *Taylor* vortex will develop if the quotient of outer to inner cylinder radius is more than 1.4. At high rotational speed the flow pattern changes to a turbulent *Taylor* vortex flow. If a continuous medium flows through the reactor the hydrodynamics will correspond with the different *Taylor* vortex flow patterns and change from tubular reactor behavior over tank-in-series to continuous stirred tank reactor characteristics. The *Taylor* reactor is therefore a very flexible device with adjustable residence time distributions.[5]

The reactor used is a horizontal *Taylor* reactor with dimensions shown in Table 2.

In Figure 2 the different curves according to different axial *Reynolds* numbers are shown. The definition of the axial *Reynold* is given by the gap width, the kinematical viscosity ν of the fluid, the mean axial velocity of the fluid which can be expressed by the volume flow V, the length l and the reactor volume V_R.

$$\mathrm{Re}_{\mathrm{ax}} = \frac{2\mathrm{d} \cdot \bar{\mathrm{u}}_{\mathrm{ax}}}{\nu} = \frac{2\mathrm{d}}{\nu} \cdot \frac{V \cdot \mathrm{l}}{V_{\mathrm{R}}}$$

The dimensionless *Bodenstein* number is a characteristic value and gives a relation between the convective mass transport and the axial dispersion of the liquid system and is defined by the mean velocity, the length of the reactor and the dispersion coefficient D_{ax} below.

$$Bo = \frac{\overline{u} \cdot L}{D_{ax}}$$

An infinite *Bodenstein* number is typical for a system without back mixing like an

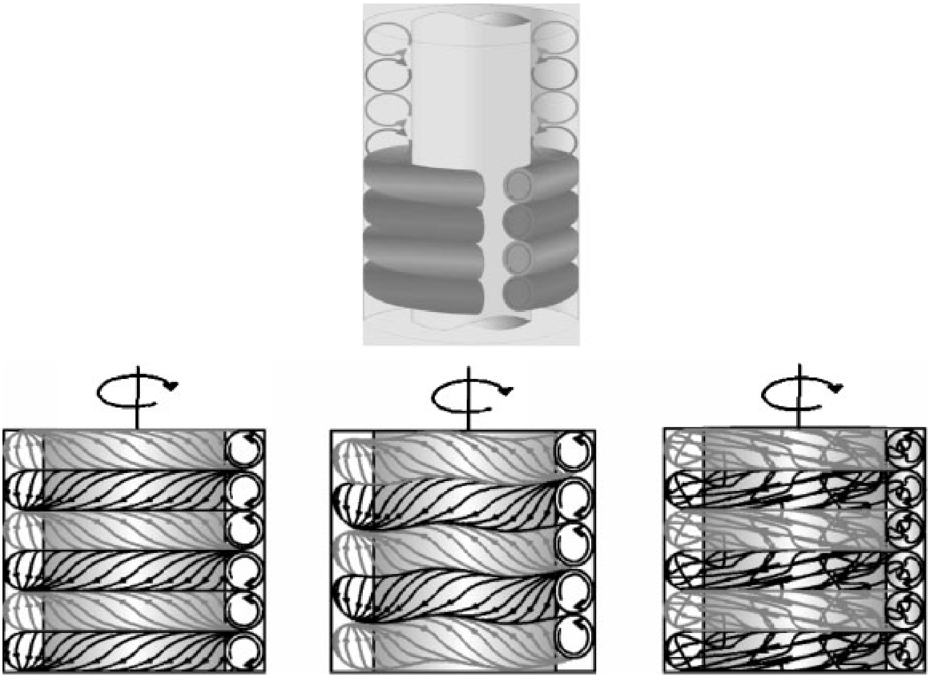

Figure 1.
Taylor reactor and different flow patterns: laminar, wavy and turbulent *Taylor* vortex flow from left to right.

ideal plug flow tubular reactor. A value nearly zero characterizes a system with complete backmixing like a continuous stirred tank reactor.

Increasing axial *Reynolds* number shifts the maximum of *Bodenstein* number toward higher values of *Taylor* number. That shows the variance of given conditions, which can be adjusted for the *Taylor* reactor.

The recipe of the system shown in Table 1 is a good example for the experiments with regard to process intensification. Styrene has a chain propagation rate constant of $k_p = 460\,\mathrm{L\,mol^{-1}\,s^{-1}}$ at 70 °C. At this temperature the conversion reaches a level of about 82% ± 3% at a mean residence time of 10 minutes (Figure 3). Increasing the temperature up to 85 °C and reducing the mean residence time to 5 minutes promote conversion toward a level of 87% ± 2%. At this mean residence time a conversion of styrene up to 95% can be achieved by an increase in temperature to 110 °C. The high conversion rates are achieved by different reaction conditions. One possibility is to increase the parameters temperature and/or pressure. This leads to conversion rates up to 95%. The average particle diameter is 45 nm.

A further reducing of mean residence time to only 60 seconds is actually the fastest emulsion polymerization. The recipe is the same as shown in Table 1, only the initiator was changed from PPS to VA-044, a faster decomposing one. The conversion of styrene reaches 70% at a temperature of 75 °C and decreases to 60% at 65 °C, while the temperature of the reactor is decreasing from 110 °C at the beginning of the experiment and finally ends at a value of

Table 2.
Dimension of the continuous laboratory *Taylor* reactor

Volume	700 ml	Gap width	5.2 mm
Pressure limit	9 bar	Radius inner cylinder	16 mm
Length	1100 mm	Radius outer cylinder	21 mm

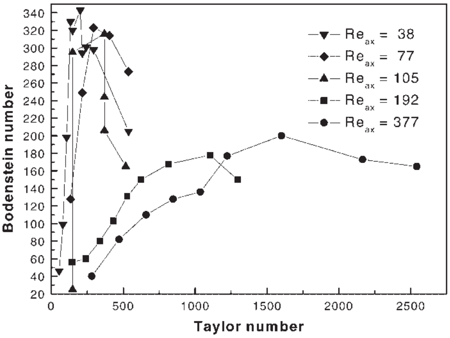

Figure 2.
Bodenstein number in dependence of the *Taylor* number for different axial *Reynolds* numbers Re_{ax}.

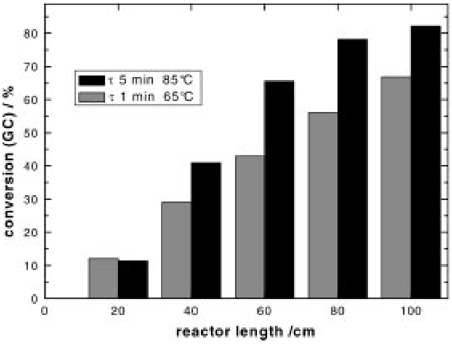

Figure 4.
Conversion in dependence of reactor length for mean residence time 5 min and 1 min.

65 °C after 25 mean residence times. This is caused by the heat exchanger that is supposed to heat up the reaction mixture just before entering the *Taylor* reactor. But, the heat exchanger was originally designed for a volumetric flow rate of about 4 l/h. It does not cover a throughput of more than 42 l/h and so the power input is not high enough to hold the emulsion at 75 °C.

Figure 4 presents the conversion in dependence on the reactor length for mean residence times of one and five minutes, respectively.

Economical Aspects

In the current economical context, which is very dynamic and competitive – partly due to globalization –, industry is forced to develop new reactor concepts in order to provide high performance at lower costs.

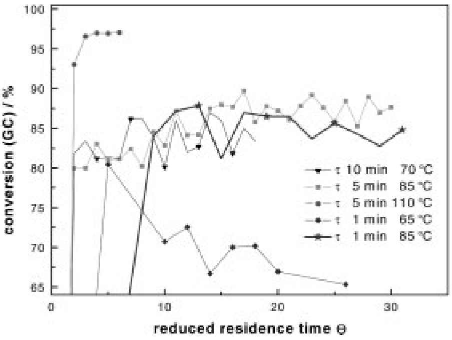

Figure 3.
Conversion of styrene emulsion polymerization in the continuous *Taylor* reactor at different reaction conditions and mean residence times of 1, 5 and 10 min.

Meanwhile it is proven that continuous operations have more advantage over batch operations, because of constant polymer quality and lower variable costs: as there are none periodical starting and stopping operations or dead time periods necessary, less labor is required, due to a simplified control of the equipment and grade of final product. The fixed costs for batch processes are in general still lower, however, for high volume lines continuous processing is becoming much more economical.[1,2]

Emulsion polymerization is predominantly performed in semi batch stirred tank reactors. An important challenge for industry therefore is to change these processes from large-scale batch to small-scale continuous operation.

In case of emulsion polymerization, the *Taylor* reactor may turn out to be an adequate continuous alternative. This reactor type can easily be automated and this implies less operating labor. Along with reduced dimensions it offers a high processing capacity just as well.

For an economical comparison between the *Taylor* reactor and a standard semi batch stirred tank reactor, a scale-up from lab to industrial plant is needed, unavoidable, without accessing the geometrically similarity theory. The attempt to keep the ratio between length and gap length constant results in an extremely long and

Table 3.
Dimensions of the continuous *Taylor* reactor

Dimension	Laboratory scale	Industrial scale
Volume [l]	0.673	100.2
Length [mm]	1107	5867
Gap length [mm]	5.2	27.56
Length/Gap length	213	213

inefficient reactor, as shown in Table 3 below.

For reducing the risks associated with the construction of large process plants it is recommended a pilot plant between lab and industrial plant. Even if the appropriate costs for this intermediate step amount at minimum 10% of those for the entire industrial plant.[3]

The pilot plant for the *Taylor* reactor will not be considered for the economical comparison with the standard semi-batch reactor, because this comparison will be performed directly between industrial plants. Therefore, no effort will be invested in this.

To estimate the investment costs for a *Taylor* reactor, the following costs have to be determinated:

a) Costs of the apparatus and equipment from published data
b) Direct and indirect costs
c) Costs for off-site installations
d) Costs for capital equipment

In order to prevent under- or over- cost estimations, for each cost segment a range is used. The estimation is based on real data, gained from industry. A value outside its range will stand for an estimation error. A summary is presented in the Table 5 below.

Table 5.
Typical percentages of fixed-capital investment values for direct and indirect cost segments

Fixed-capital	Range, %
Direct costs	
Purchased equipment	15–40
Purchased equipment installation	6–14
Instrumentation and controls (installed)	2–8
Piping (installed)	3–20
Electrical (installed)	2–10
Buildings (including services)	3–18
Yard improvements	2–5
Service facilities (installed)	8–20
Land	1–2
Indirect costs	
Engineering and supervision	4–21
Construction expense	4–16
Contractor's fee	2–6
Contingency	5–15

The costs for apparatus and machines can be estimated also on their weight, so-called "prices per kilogram".[4]

Conclusion

It is possible to decrease the mean residence time to 60 seconds in fast runs of continuous emulsion polymerization in order to enhance the space-time yield by a factor of 200 in comparison to a standard semi-batch process. Increasing the reaction temperature improves the efficiency of the process, and further experiments will show whether it is possible to improve conversion even up to more than 90%.

Furthermore, process intensification will be promoted by optimization of the follow-

Table 4.
Factors in equipment scale-up and design

Type of equipment	Is pilot plant usually necessary?	Major variables for operational design (other than flow rate)	Major variables characterizing size or capacity	Maximum scale-up ratio based on indicated characterizing variable	Approximate recommended safety or over-design factor
Batch reactors	Yes	Reaction rate Equilibrium state	Volume Residence time	>100:1	20%
Continuous reactors	Yes	Reaction rate Equilibrium state	Flow rate Residence time	>100:1	20%

ing process parameters: Temperature, pressure and mean residence time with an increasing content of monomer.

The economic benefits of the *Taylor* reactor are evaluated in context of all these process improvements, which provide a substantially higher space time yield, considering the costs of the equipment needed in order to assure such process intensification.

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