The Wicker Tube Reactor – Characterization and Modeling

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Abstract: A new type of reactor for continuous emulsion polymerization was characterized by measurements of the residence time distribution in water and during a chemical reaction. These measurements show nearly plug flow behavior even in the laminar flow region. The thermal behavior was modeled with respect to temperature, monomer and initiator concentration. Continuous emulsion polymerization can be run inherently safe and with remarkable high space time yield in the new wicker tube reactor.

Keywords: Continuous emulsion polymerization · Hydrodynamics · Residence time distribution · Tube reactor

Introduction

The wicker tube reactor was developed for continuous emulsion polymerization [1][2]. Due to long mean residence times, axial flow in this tubular reactor is in the laminar region. However, secondary flow phenomena like Dean vortices and turning back movements narrow the residence time distribution towards plug flow behavior. Therefore, a more uniform product may be possible. Additionally, the cooling capacity is very high because of the very large ratio of surface area to volume of the reactor. In order to determine the suitability of the wicker tube reactor for emulsion polymerization, residence time measurements were carried out in water and during a chemical reaction with an increasing dynamic viscosity.

Experimental

The reactor consists of a 100 m tube (inner diameter: 1 cm), coiled around

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seven cores (diameter 7 cm) that form a regular polygon. It has a constant circle of curvature along the whole tube and may be used with pigs for cleaning and separating polymerization runs with different recipes. In order to determine the residence time distribution, conductivity measurements in water were carried out using potassium chloride as tracer. With a chemical reaction potassium chloride was substituted by potassium thiocyanate. The output and input signals were detected photometrically after the reaction. By reaction of the thiocyanate with iron(III) chloride, red brown iron thiocyanate was formed.

Due to the fact that, in practice, the input injection does not fit the ideal Dirac pulse signal, special treatment of the experimental data is necessary and deconvolution technique is applied. To extract the input signal from the response signal in the reactor outlet both signals are transferred into the Fourier domain where they are divided. The resulting frequency function is transferred back into the time domain to yield the real reactor transfer function, the residence time distribution.

Results

In comparison with common continuous reactor types such as the laminar flow tubular reactor this new coiled tube reactor has significantly narrower residence time distributions. For the quantitative

description of the nonideal hydrodynamics the dispersion model is applied. Its characteristic parameter is the dimensionless ratio of the rate of mass transport by convection to the rate of mass transport by diffusion or axial dispersion, the so-called Bodenstein number, Bo [3]. According to the dispersion model the Bodenstein number was determined in dependence of the Reynolds number:

$$Bo = \frac{u_z L}{D_{ax}}$$

Fig. 1 shows Bodenstein *versus* Reynolds numbers for water at ambient temperature. Absolute values of Bodenstein numbers obtained indicate almost plug flow behavior of the wicker tube reactor. The resulting residence time distributions are comparable with the behavior of a cascade of 600 to 1500 continuous stirred tank reactors (CSTRs). Furthermore, Bodenstein number is approximately proportional to Reynolds number with a significant change in slope around a Reynolds number of 2500, which is interpreted with the transition from laminar flow into the transient flow regime. This transition point changes from 2300 for straight empty pipes to higher Reynolds numbers for coiled tubes.

In order to simulate the residence time behavior during an emulsion polymerization a moderate increase in dynamic viscosity of about 50 mPas was realized by the catalytic crosslinking reaction of partly hydrolyzed polyvinyl alcohol in aque-
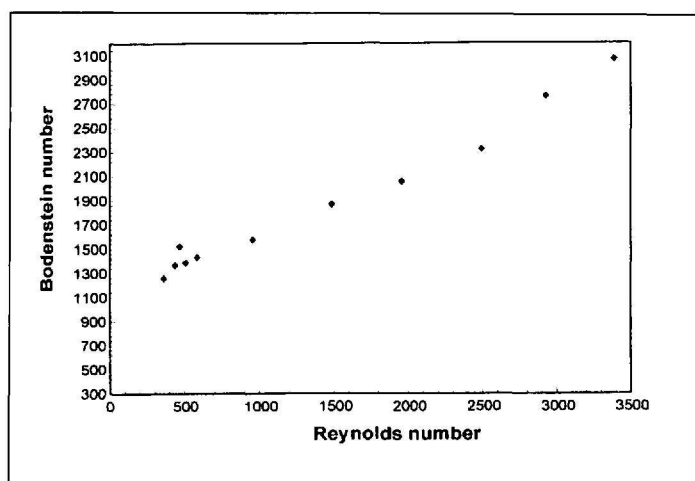
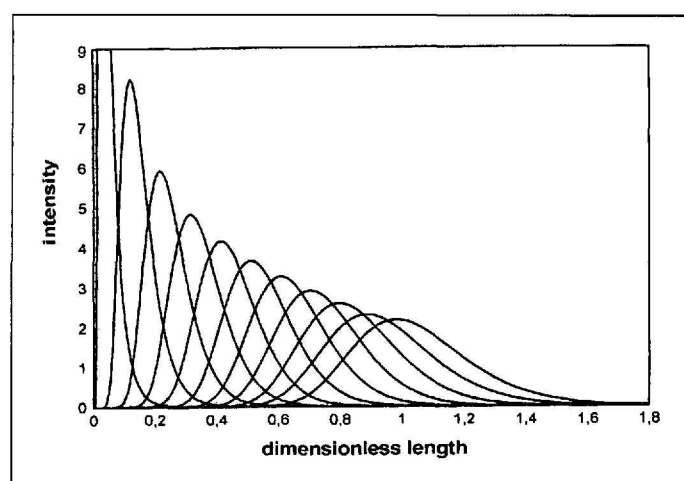Fig. 1. Bodenstein number *versus* Reynolds number.

Fig. 2. Local residence time distributions.

ous solution with glutardialdehyde. Even if the initial viscosity is ten times higher than the viscosity of water a rather narrow residence time distribution is obtained characterized by a Bodenstein number of 60, which is approximately equivalent to a train of 30 CSTRs.

Due to the change in viscosity during the reaction the Reynolds number varies as well. For the mathematical description of this behavior the reactor is divided into 20 segments of a length of 5 m. Each one is characterized by a special Bodenstein number. The profile of the viscosity is transferred from the time axis of the batch reaction in a stirred tank reactor to the length axis of the tubular reactor for the continuous reaction. For each tube segment the outlet signal of the previous segment represents the input signal of the following. It is assumed that the Bodenstein number is inversely proportional to the viscosity. Consequently, the characteristic Bodenstein number is determined for each segment and the corresponding distribution function can be calculated. Fig. 2 represents the residence time distributions of every second segment.

For scale up considerations careful analysis of the reactor safety is necessary. Hence, an additional model was developed in order to simulate hazardous scenarios. Fig. 3 shows the temperature profile for different times and reactor segments in the event of a cooling failure when the monomer and initiator feed is stopped but water is fed instead.

For the simulation of the thermal reactor behavior a set of kinetic parameters was selected based on an emulsion polymerization of MMA at a temperature of 80 °C. The average residence time was 30 min and the cooling failure happened after 2500 s.
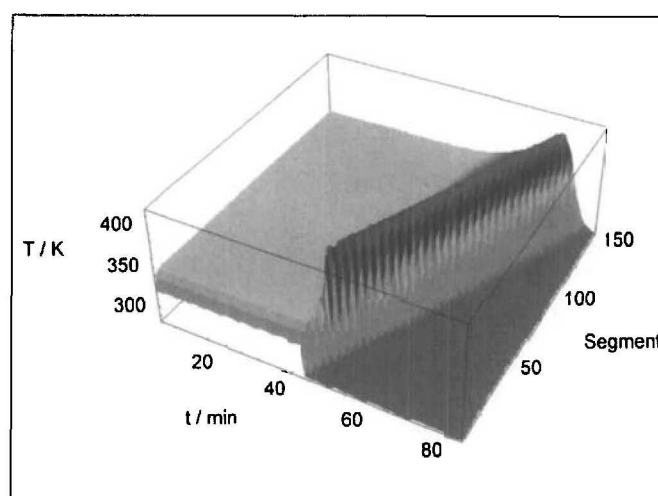

Fig. 3. Temperature profile for a cooling failure with continuous dosing of water.

The increase in temperature during a cooling failure in any simulation does not exceed 400 K. This will produce a pressure of approximately 2.5 bar, which is within the safety limits of the steel tube.

Conclusions

The large specific cooling area of the new wicker tube reactor of up to 400 m^2/m^3 enables to run exothermic emulsion polymerization continuously at remarkable high space time yield. Consequently, this reactor can be designed significantly smaller than a batch or semibatch reactor for the same production rate. Subsequently, the reactor inventory and the latent heat of unreacted monomers can be reduced by orders of magnitude. Inherently safe reactor operation becomes possible. However, polymer wall fouling is still a problem. To prevent the reactor from frequent shut downs, the reactor design allows cleaning with pigs.

Symbols

Bo Bodenstein number
u_z axial velocity
L reactor length

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