

# KINETICS OF VINYL ACETATE EMULSION POLYMERIZATION IN A PULSED TUBULAR REACTOR. COMPARISON BETWEEN EXPERIMENTAL AND SIMULATION RESULTS

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**Abstract** - A new reactor, the pulsed sieve plate column (PSPC), was developed to perform continuous emulsion polymerization reactions. This reactor combines the enhanced flexibility of tubular reactors with the mixing behavior provided by sieved plates and by the introduction of pulses that is important to prevent emulsion destabilization. The main objective of this work is to study the kinetics of vinyl acetate (VA) emulsion polymerization reactions performed in this PSPC. Therefore, both experimental studies and reaction simulations were performed. Results showed that it is possible to obtain high conversions with rather low residence times in the PSPC.

*Keywords:* pulsed tubular reactor, emulsion polymerization, VA, kinetics, modeling.

## INTRODUCTION

Continuous reactors present economic advantages for the production of large amounts of polymer and avoid product differences from batch to batch. Of the different types of continuous reactor, the CSTRs are the most commonly used. Nevertheless, tubular reactors present several advantages when compared to CSTRs, such as higher operational flexibility, reduced losses during start-up and shut-down due to their smaller volume, and easier temperature control. In order to prevent the emulsion destabilization and plugging of the tubular reactor, two approaches were presented in the literature: 1) usage of high recycle rates (loop reactors) and 2) introduction of pulses. In

this second approach good local agitation might be combined with little backmixing, resulting in much higher monomer conversions and particle concentrations than those obtained in single CSTRs (Mayer et al., 1996). In addition, sustained oscillations in those variables due to renucleations that are often observed in CSTRs (Greene et al. 1976; Kiparissides et al. 1980; Rawlings and Ray, 1988; Hoedemakers, 1990; Paquet and Ray, 1994; Ohmura et al., 1998) or in continuous loop reactors (Araújo et al., 2000) may be minimized or avoided.

The main objective of this work was to study the kinetics of vinyl acetate emulsion polymerizations carried out in a pulsed tubular reactor. Experimental

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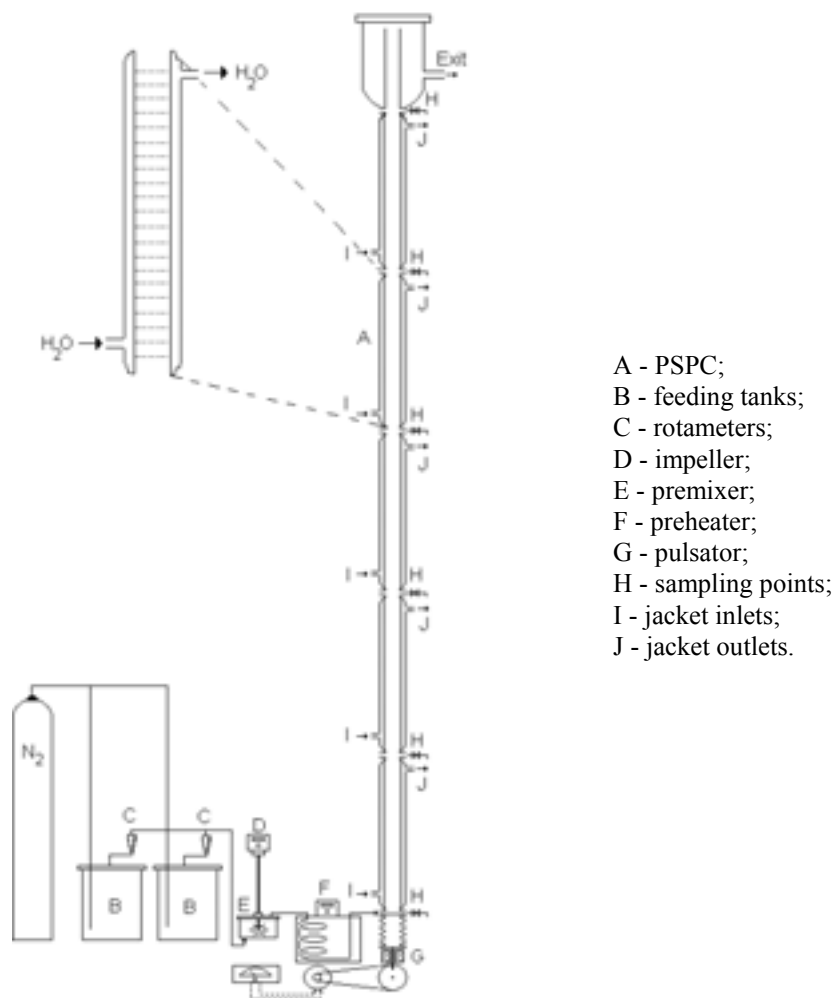
studies as well as reaction simulations were performed.

### EXPERIMENTAL PROCEDURE

The experimental setup comprises a pulsed sieve plate column (PSPC) composed of five stainless steel sections, each one with a 1000 mm length and a 40.0 mm internal diameter and its own independent jacket. The plates are stainless steel disks, each one with 39 holes of 3 mm in a triangular arrangement, resulting in a free area of 22.3% on each plate. Plate spacing is 50 mm, resulting in a free volume of 95.7% of the reactor. The pulsator is positioned at the bottom of the column and stroke length and frequency can be adjusted within the ranges 5 to 25 mm and 0.2 to 3.5 Hz, respectively. Figure 1 shows a schematic presentation of the continuous reactor used in this experimental procedure.

The start-up procedure in the reactions comprised filling the reactor with water and heating until reaction temperature was reached. The reactants were fed in two different streams: 1) an aqueous solution of emulsifier (SLS), initiator ( $\text{Na}_2\text{S}_2\text{O}_8$ ) and pH buffer ( $\text{Na}_2\text{CO}_3$ ) and 2) the organic phase, composed of the commercial grade monomer vinyl acetate (VA). In order to remove traces of dissolved oxygen, nitrogen was continuously fed into both feed tanks. Table 1 shows the experimental conditions and Table 2, the composition of each feed stream; these two streams were pre-emulsified together before entering the reactor.

In order to allow a better understanding of the complex mechanisms involved in this kind of reactions, samples were taken both at the reactor outlet and at five other sampling points distributed throughout the reactor. Monomer conversion was measured by gravimetry and particle diameter was measured by photon correlation spectroscopy (Malvern -Zetasizer S).



**Figure 1:** Schematic presentation of experimental setup

**Table 1: Experimental conditions – VA emulsion polymerization reactions.**

Variable	Value
Temperature (°C)	55.0
Residence time (min)	30.0
Stroke length (mm)	5.0
Pulsation frequency (Hz)	3.5
Peclet number*	92.0

\*Peclet number from pulse tracer studies (Palma and Giudici, 2001).

**Table 2: Formulation of VA emulsion polymerization reactions.**

	Stream 1 (g)	Stream 2 (g)
Vinyl Acetate	-	7922
H <sub>2</sub> O	34000	-
SLS	122.58	-
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	101.19	-
Na <sub>2</sub> CO <sub>3</sub>	29.76	-

## MODEL DEVELOPMENT

The kinetic mechanism used in this work to represent emulsion polymerizations includes the following reactions: initiation, propagation, transfer to monomer and polymer and termination by disproportionation, as well as micellar and homogeneous nucleation mechanisms and particle coalescence. The following assumptions were made in deriving the model equations:

1. Monomer concentrations in polymer particles, monomer droplets and aqueous phase are at thermodynamic equilibrium.
2. Total mass of polymer produced in the aqueous phase is negligible.
3. Particle nucleation occurs through micellar and/or homogeneous mechanisms.
4. Polymer particles are spherical and monodisperse.
5. The pseudo steady-state assumption is valid for polymer radicals.
6. Kinetic constants do not depend on chain length.
7. Kinetic constants in the aqueous and polymer phases are the same.
8. Radicals that enter polymer particles are of length 1.
9. Radicals generated by initiation or chain transfer to monomers have the same reactivities.
10. Reactions are performed at constant temperature.
11. Radial mixing is perfect.
12. Axial velocity is constant.

13. Axial mixing is represented by an axial dispersion coefficient.

Besides the population and mass balance equations, the model is composed of a significant number of algebraic equations. These algebraic equations are used to describe the monomer partition among monomer droplets, polymer particles and aqueous phase; the emulsifier partition among aqueous phase, micelles and polymer particles; the computation of the average number of radicals per polymer particle; radical concentration in the aqueous phase; rates of micellar and homogeneous nucleation; particle coalescence; radical desorption, etc. . .

An axial dispersion model with Danckwerts's (1953) boundary conditions was used in the dynamic modeling of the PSPC. The method of lines was used to discretize the second-order partial differential equations in the axial direction. The resulting system of algebraic-differential equations was implemented in FORTRAN and solved with the numerical integrator DASSL (Petzold, 1982). A detailed description of the mathematical model developed can be found in Sayer (2000).

## RESULTS AND DISCUSSION

The following figures present the results of two replicate reactions, Runs 6 and 6a.

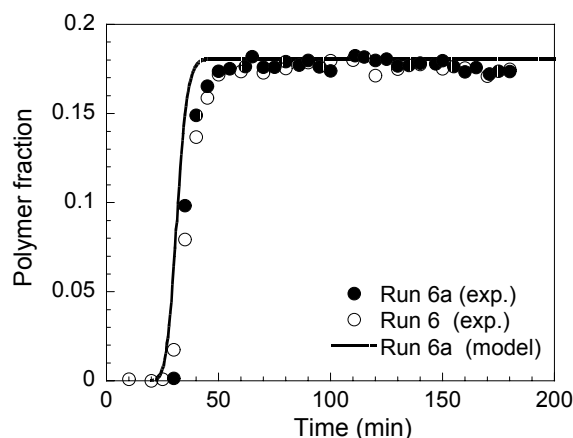
Figure 2 shows the dynamics of reactor start-up, comparing experimental and simulation results. In Fig. 2a it might be observed that the polymer fraction in the reactor increases quite abruptly and that less than two residence times are required to reach steady-state conditions (residence time = 30 minutes). This behavior is in accordance with the low axial dispersion conditions of this reaction (axial Peclet number = 92). A good agreement between experimental and simulated results is observed. Experimental particle concentration, Fig. 2b, presents a quite complex behavior during reactor start-up. At first particle concentration increases drastically and then it decreases due to particle coagulation mechanisms until the steady-state is reached after approximately 2.5 residence times. Despite its consideration of micellar and homogeneous nucleation and particle coalescence mechanisms, the dynamic model was not able to represent such a complex dynamic behavior. This is probably due to the monodisperse particles assumption, as observed by Araújo et al. (2000). Some slight deviations can also be observed between experimental and simulation steady-state results, but taking into account that particle concentration is computed from conversion and particle diameter data, adding measurement errors from both variables, these deviations are not significant. Figure 2c shows a comparison of experimental and simulated average particle diameters; the measurement error of this variable was  $\pm 3$  nm.

Figure 3a shows the evolution of monomer conversion and average particle diameter along the fractional reactor length under steady-state conditions. A very good reproducibility is observed and results show that it is possible to achieve high

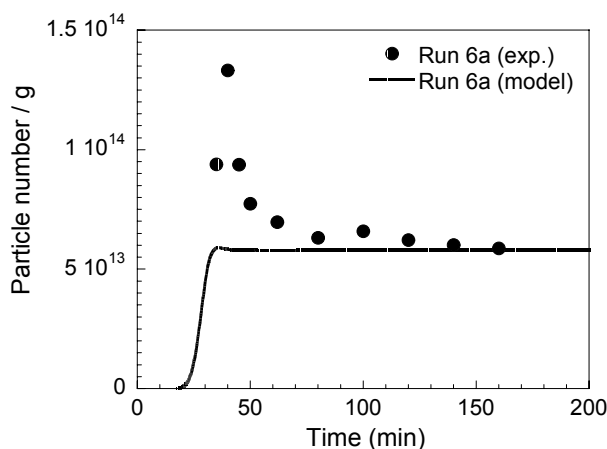
conversions in short residence times (30 minutes) in the PSPC. Agreement between experimental data and simulation results is quite good.

Figure 3b shows the evolution of particle concentration along the fractional reactor length under steady-state conditions. The mathematical model is able to represent the trends of the experimental results; only some slight deviations might be observed between experimental and simulation steady-state particle concentrations. An interesting aspect observed in this figure is that, despite the relatively low emulsifier concentration used in these runs ( $\sim 1.24 \times 10^{-5}$  mol / cm<sup>3</sup> water), particle concentration increases along almost the whole reactor length. As shown by the simulation results in Fig. 3b, this increase might be attributed to significant homogeneous nucleation occurring along almost the whole reactor length due to the high solubility of the vinyl acetate in the aqueous phase. Therefore particle nucleation is not limited to the proximity of the reactor entrance, where the emulsifier concentration is above the critical micellar concentration (CMC).

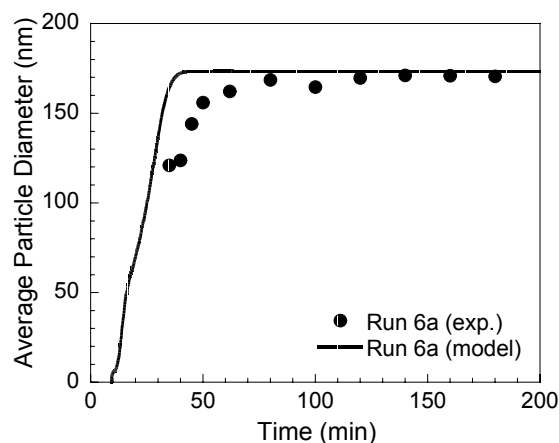
Figure 4a shows the simulated emulsifier concentration in the aqueous phase during reactor start-up along the fractional reactor length. It might be observed that the emulsifier concentration in the aqueous phase reaches the CMC only at the reactor entrance. Beyond the reactor entrance the emulsifier concentration in the aqueous phase increases during start-up, reaching a maximum that is below the CMC, and then decreases as the emulsifier is used to stabilize polymer particles. Figure 4b shows that under steady-state conditions the micellar nucleation mechanism is limited to the reactor entrance and the homogeneous nucleation mechanism is active along almost the whole reactor length.



(a)

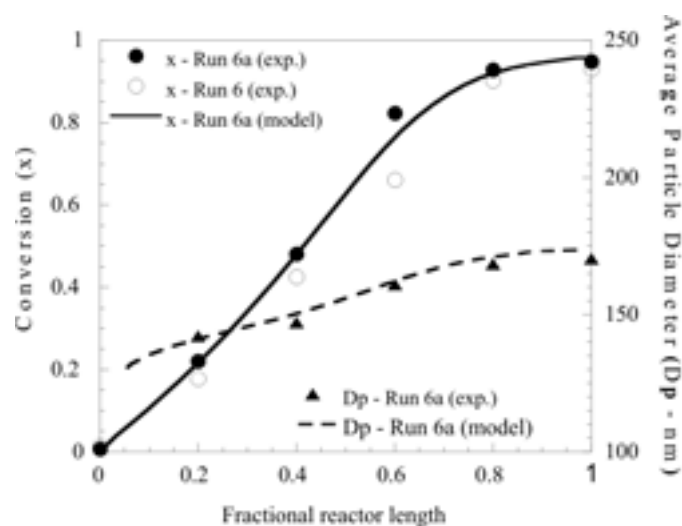


(b)

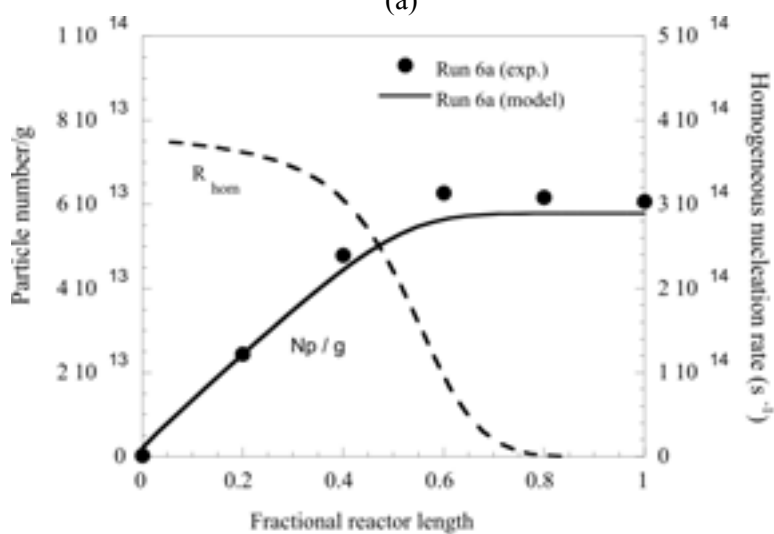


(c)

**Figure 2:** Dynamic behavior during VA emulsion polymerization reactions in a PSPC – comparison between experimental and simulation results. (a) Polymer fraction; (b) Particle concentration and (c) Average particle diameter.

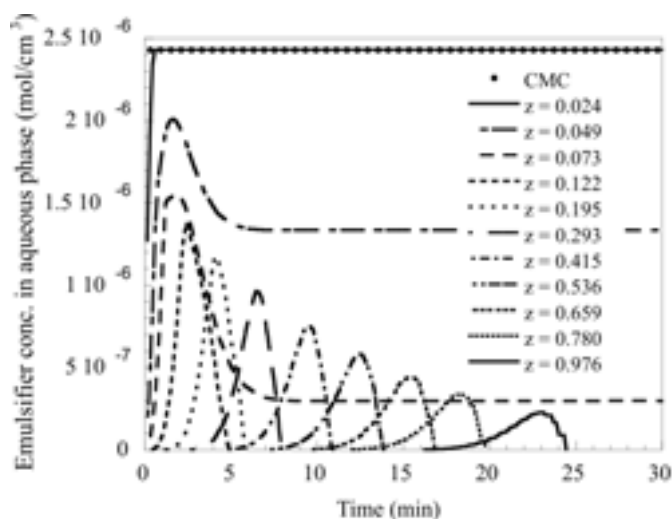


(a)

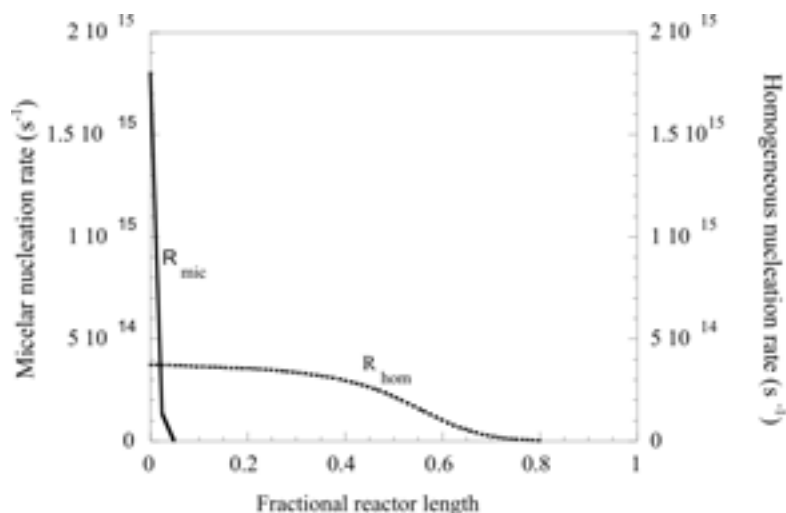


(b)

**Figure 3:** Evolution of process variables along the reactor length during VA emulsion polymerization reactions in a PSPC – comparison between experimental and simulation results. (a) Conversion and average particle diameter; (b) Particle concentration and homogeneous nucleation rate.



(a)



(b)

**Figure 4:** Nucleation behavior during VA emulsion polymerization reaction in a PSPC – simulation results. (a) Emulsifier concentration in the aqueous phase and (b) Micellar and homogeneous nucleation rates.

## CONCLUSIONS

A new reactor, the pulsed sieve plate column (PSPC), was developed to perform continuous emulsion polymerization reactions. Results showed that it is possible to achieve high conversions in rather low residence times in the PSPC, attesting to the economic viability of this kind of reactor to perform emulsion polymerization reactions. An interesting aspect observed in these reactions is that, due to the high solubility of vinyl acetate in the

aqueous phase, homogeneous nucleation is significant and particle nucleation is not limited to the proximity of the reactor entrance, where the emulsifier concentration is above the CMC. Consequently, the particle number increases along almost the whole reactor length. The dynamic model was able to represent the experimental results properly and allowed a better comprehension of the complex phenomena involved in these reactions.

## ACKNOWLEDGMENTS

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