DEVELOPMENT OF A TUBULAR REACTOR FOR CONTINUOUS EMULSION COPOLYMERIZATION

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Summary

This contribution describes the development of a tubular reactor for continuous emulsion copolymerization processes. Special features of this reactor includes the use of oscillatory (pulsed) flow and internals (sieved plates) to prevent polymer fouling and promote good radical mixing along with a controlled amount of axial mixing. Jacket temperatures can be controlled independently along the five reaction sections. The copolymer system studied (butyl acrylate and vinyl acetate) is strongly prone to composition drift due to very different reactivity ratios. A mathematical model was developed and used to successfully optimize the lateral feeding profile in order to reduce compositional drift.

Keywords

Process Intensification, Novel Reactor Technologies, Emulsion Polymerization, Tubular Reactor, Continuous Pulsed Sieved Plate Column.

Introduction

The aim of this work is to report the optimization of a continuous emulsion copolymerization of vinyl acetate (VAc) and butyl acrylate (BuA) in a pulsed sieve plate column (PSPC). In order to improve its operational flexibility, the column is divided in five sections, each one presenting independent lateral feed and temperature controls. This flexibility allows the control of the copolymer composition by feeding the more reactive monomer along the column. An energy balance was included and an optimization procedure was implemented in a mathematical model developed in a previous work [1] considering axial dispersion model of copolymerization reactions conducted in a pulsed sieve plate column reactor. Details about this model can be found in references [6, 7, 8]. Figure 1 represents the experimental unit used in this work Table 1 describes the recipe. A pulsator is located at the bottom of the reactor and the adequate choice of stroke length and pulsation frequency provides a combination of good local agitation with little backmixing, preventing deemulsification and reactor clogging [2, 3, 4, 5] and reducing radial temperature and concentration gradients. The amplitude of pulses was kept in 18 mm and the frequency was set to 2.1 Hz. In all sections, the same inlet cooling jacket temperature was kept constant ranging from 56 to 57^{o}C. The flow rates of all monomer and aqueous phase feed streams were also maintained constant for a residence time of 30 minutes and using a PID controller system. In this case, metering pumps were controlled according to the weight decrease of monomer and aqueous phase feeding tanks. The operational conditions described in Table 2 are the same considered in simulations performed with the mathematical model.

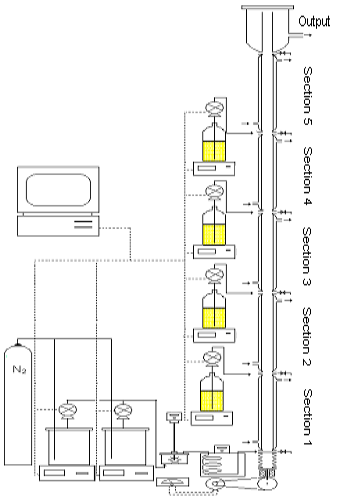

Figure 1 – Continuous Pulsed Sieve Plate Column

Table 1. Copolymerization Recipe.

Reactants	Weight Fraction
Vinyl Acetate (VAc)	0.1574
Butyl Acrylate (BuA)	0.0279
Water (H_2O)	0.7958
Sodium Lauril Sulfate (SLS)	0.0119
Sodium Persulfate ($Na_2S_2O_8$)	0.0057
Sodium Carbonate (Na_2CO_3)	0.0014

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Table 2. Operational Conditions.

Peclet Number	61
Amplitude	18 mm.
Frequency	2.1 Hz.
Cooling Jacket Temperature	56-57 (°C)
Residence time	30 min.

Results

Continuous emulsion polymerization presents many advantages in comparison to the same process performed in batch or semi-batch stirred tanks. Continuous reactors are smaller, so that temperature control can be improved, and provide a better product quality control by the reduction of the variations among consecutive batches. The PSPC, used as a continuous one pass tubular reactor, may also avoid periodical self-sustained oscillations observed in continuous stirred tank reactors and in loop reactors [9]. In this work, emulsion copolymerizations of VAc with BuA are performed in the PSPC because of the commercial significance of this system and also due to the differences in the aqueous phase solubility and in the reactivity ratio of these monomers. Both differences between these monomers contribute to a large composition drift with conversion when this reaction is carried out, not only by batch emulsion copolymerization, but also in the PSPC without lateral monomer feed. As a consequence, the copolymer chains formed in the beginning of reaction present more repeated units of the more reactive monomer than at the end of reaction. Thus, in order to prevent this compositional drift, the more reactive monomer (BuA) is added in the bottom of the column, as well as in lateral feed streams. The best distribution of BuA among the lateral feeding points was optimized using the mathematical model and then tested experimentally to validate the optimization result. Two different runs are represented in Figures 1 and 2. In both reactions the total amount of each monomer consumed is the same. Thus, the final copolymer composition achieved is the same (85% of VAc and 15% of BuA).

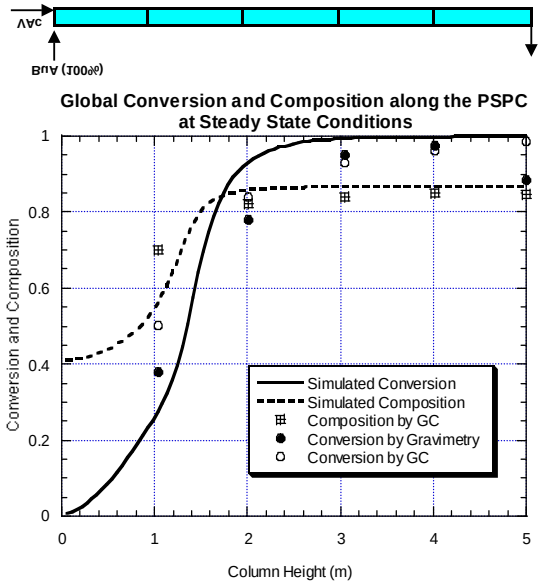

Figure 1 - Reaction carried out without lateral feed.

Figures 1 and 2 represent the global conversion and the composition, in VAc fraction, along the reactor length at steady state conditions. One can note that the strong compositional drift observed in Figure 1 can be avoided using the lateral feeding distribution shown in Figure 2. In all cases, the model predictions (curves) are in good agreement with the experimental data (symbols). Particle size and temperature (not shown) are also reasonable represented by the developed mathematical model for this reactor.

Conclusions

The developed model can predict with sufficient accuracy the effect of lateral monomer feed streams over the copolymer properties. The PSPC is a suitable reactor to solve the problem of composition drift for emulsion copolymerization reactions, which nowadays are performed in semi-batch processes in industrial scale.

References

(1) C. Sayer, R. Giudici, *Braz. J. Chem. Eng.* **2002**, 19, 89.
(2) D. Doormalen; D. Thoenes, *Chem. Engng. Sci.* **1992**, 47, 2603-2608
(3) J. Meuldijk; C.J.G Van Strein; F.A.H.C Van D.A. Paquet; W.H. Ray *AIChE J*. **1994**, 40. N° 1, 73-87.
(4) M. Palma; R. Giudici, *Chem. Eng. J.*, **2003**, 94, 189-198.
(5) C.A. Scholtens, J. Meuldijk, A.A.H. Drinkenburg, *Chem. Eng. Sci.* **2001**, 56, 955.
(6) C. Sayer, M. Palma, R. Giudici. *Ind. Eng. Chem. Res.* **2002**, 41, 1733.
(7) C. Sayer; R. Giudici, in proceedings of Congresso Brasileiro de Engenharia Química, Natal, **2002**, Vol. 14.
(8) A.C. Sallares; C. Sayer; R. Giudici, DECHEMA Monographs, **2004**, vol. 138, 231-237.
(9) P.H.H. Araújo; C. Abad; J.C. de la Cal; J.M. Asua; J.C. Pinto, DECHEMA Monographs, **1998**, Vol. 1334, 439-447.

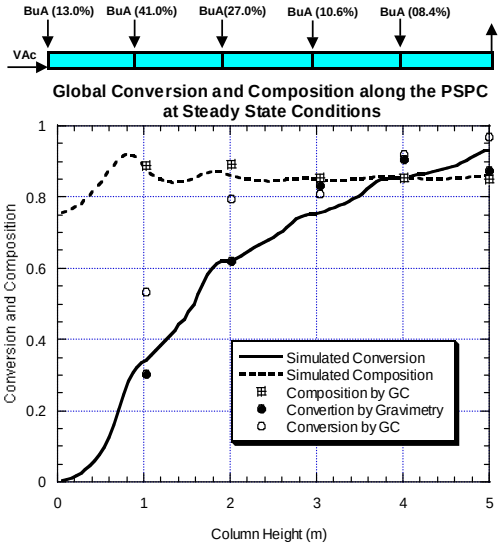

Figure 2 – Reaction carried out with optimized lateral feeds.