Polymer fouling in tubular reactors for radical polymerizations

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Highlights

- Modeling and predicting of wall-layer formation
- Process intensification in polymerization processes
- Hydrophobic coatings for fouling reduction
- Residence time distribution in tubular reactors while polymerization

1. Introduction

Tank reactors, either operated in batch or semi-batch mode, serve as the primary means for producing specialty polymers such as Polyvinylpyrrolidone (PVP). This process type boasts high flexibility, but while continuously operating reactor systems are considered for process intensification due to improved controllability, energy efficiency, and heat transfer, the production of low-volume products like PVP necessitates the use of tubular reactors with mixing elements. Unfortunately, fouling deposits in continuously operating mixer-reactors present a significant challenge, leading to blockages and shutdowns during the polymerization of N-vinylpyrrolidone (NVP).

Fouling arises from side reactions that produce large molecular weight, branching, or crosslinked polymer chains. The presence of dead zones with sluggish flow and increased local residence time exacerbates the formation of a polymer network [1]. Understanding the causes of deposit formation and developing a model to describe deposit layer growth are crucial for optimizing process conditions and predicting fouling during reactor scale-up.

Extensive research on NVP polymerization kinetics has identified terminal double bonds (TDBs) as the primary cause of long chain branching. Models quantifying TDBs, validated in a CSTR reactor, were extended to describe branching point distribution in subsequent studies [2].

Hydrophobic films with low surface energy are well suited to reduce the formation of fouling deposits. Several polymerization experiments under varying process conditions were carried out in a lab-scale reactor with coated and uncoated surfaces [3].

2. Methods

To gain insight into the mechanism of the formation of fouling, we need to determine the buildup of the wall layer. A reaction system with capillary tubular reactors has been set up, where the residence time distributions at different reaction times can be recorded.

Hydrophobic coatings were applied by a project partner to various surfaces of polymerization reactors and were subsequently tested by measuring pressure loss.

The kinetic model, transport model for polymers, and viscosity model are integrated into an in-house developed CFD solver. This CFD model describes the formation of wall layers and is subsequently validated using experimental data from the capillary reactor across a wide range of concentrations.

3. Results and discussion

Figure 1 demonstrates that hydrophobic coatings on stainless steel mixing elements significantly reduce the amount of fouling in the reactor. This reduction is further confirmed through pressure measurements. Unfortunately, coatings cannot completely prevent fouling but only diminish it.

Figure 1. Stainless steel mixing element after polymerization: Left without coating, right with hydrophobic coating.

Figure 2 compares residence time distributions (RTD) in experiments and simulations for various monomer concentrations. In Figure 2A (20 wt.% monomer), breakthrough time shortens with time, and tailing increases due to the formation of a viscous wall layer. Simulations mirror these trends. In Figure 2B (5 wt.% monomer), the trends are less pronounced but still visible, with simulations aligning well with experimental data. Figure 2C (initiator concentration 10 times lower) shows faster tracer breakthrough and less pronounced tailing. Simulations consistently match experimental results, although experimental tailing is more pronounced, attributed to estimated transport properties of the tracer in the wall layer.
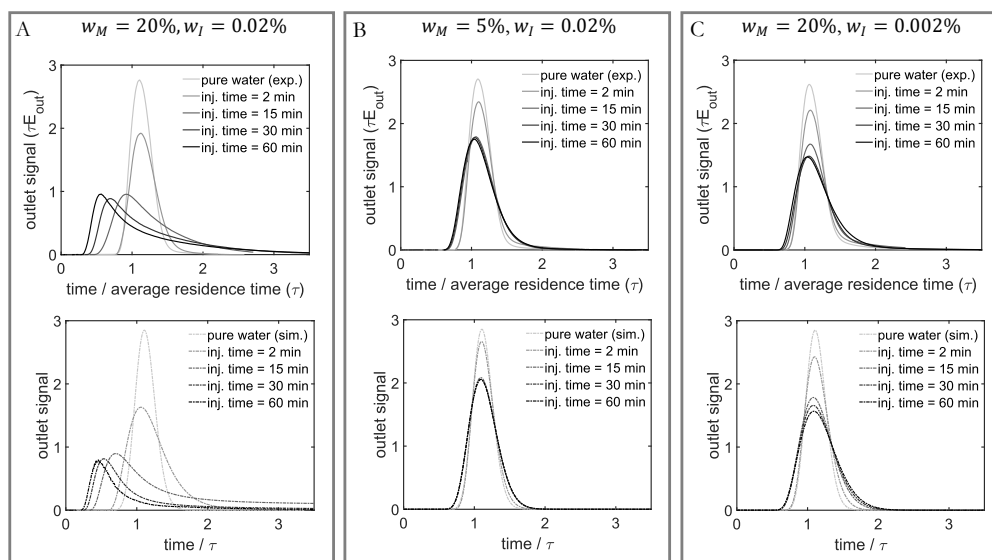

Figure 2. Residence time distributions for experiments (top) and simulations (bottom) for different monomer and initiator concentrations.

4. Conclusions

A Computational Fluid Dynamics (CFD) model was developed to simulate the formation of a viscous wall layer during free radical polymerization of N-vinylpyrrolidone. The model incorporates reaction kinetics, a viscosity correlation dependent on concentration and molecular weight, and a novel mass transport model for statistical polymer moments. Validation of the CFD model was achieved by setting up a capillary reactor to monitor wall layer formation through residence time measurements. The simulations align well with experimental results across a broad range of operating conditions.

Hydrophobic coatings were identified as effective in significantly reducing fouling; however, complete prevention remained elusive. These coatings proved to mitigate adhesion forces, making polymer removal more manageable while acknowledging that a residual adhesion persists.

References

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