

Propylene polymerization: comparison between batch and continuous operation using process simulation

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Highlights

- Polymers obtained in batch mode can be very different from those in continuous mode.
- The recycle ratio strongly impacts the conversion and polymer properties.
- Process simulation support for both scale-up and scale-down is imperative to understand the main adjustments needed.

1. Introduction

In process and polymer development, the research typically starts in the laboratory scale, then to pilot and then, industrial scale. In bench scale, to reduce the use of reactants, to ensure safety and for practical operation, batch reactors are commonly used^[1]. In the opposite direction, for industrial plant support, ideally, the scale-down of the unit in pilot scale is preferred. However, having a pilot unit imply several costs, large volumes of waste and resources to carry on the tests. Consequently, depending on the process, it is not possible to have a dedicated pilot unit.

In this way, it is necessary to have the laboratory supporting plant troubleshooting. Then, the challenge is to extract most of the value from bench scale and understand the trade-offs and impacts of extrapolating results. Some drawbacks of operating in bench scale, specifically for polymerization reactions, is the high exothermicity of the reactions. In batch reactors it is difficult to properly control the medium temperature due to the fast behavior of the reaction. Changes in temperature directly affect the quality of the polymer and should be accounted for. In this context, the utilization of mathematical models for both scale-up and down is fundamental^[1,2]. In this work, the comparison between producing polypropylene in batch and continuous reactors are presented and discussed in terms of molecular weight, polydispersity index and conversion. It is noted that a direct correlation between the polymer obtained in batch mode and continuous mode is absent. To ensure reproducibility for both scale-up and scale-down processes, adjustments become imperative to achieve identical polymer characteristics.

2. Methods

Three case studies were evaluated: (i) batch reactor, (ii) continuous stirred tank reactor and (iii) continuous stirred tank reactor with recycle stream, containing the monomer and the polymer. To compare the three configurations of reactors, simulations in Aspen Plus were carried out. Initially, the kinetics of propylene polymerization with Ziegler-Natta catalyst was implemented using kinetic constants from the literature, considering 4 sites-based types and five main steps: activation of the potential site, chain initiation, chain propagation, chain transfer and site deactivation. Regarding the thermodynamic property method, PC-SAFT method was used. For the operational conditions, all reactors were considered isothermal at 70°C and 32 bar.

3. Results and discussion

The simulate results for the three case studies (i) batch reactor (Batch), (ii) continuous stirred tank reactor (Rec =0) and (iii) continuous stirred tank reactor with recycle stream (Rec = recycle/feed = 0.16 to 0.80) are presented in Figure 1. For the conversion plots, Figure 2(a), as expected, the increase in the conversion can be attained increasing the recycle ratio to the feed, Rec. However, changes in the recycle to feed ratio affect the bulk reactor composition, which has an impact in the polymer molecular weight (Mn and Mw). Looking at the polydispersity index plots, Figure 2(b), It is possible to observe that the increase in the recycle ratio changes the PDI of the polymer obtained, when compared to the polymer obtained in the batch reactor. This occurs due to the mass of polymer formed that is recirculated to the reactor, also due to the increase in the conversion in the continuous reactor. Regarding the polymer

molecular weight (M_n and M_w), Figures 2(c) and (d), one can observe that it can vary drastically from one case to another.

Regarding residence time, it is clear that for the same value, the continuous mode results in higher conversion than the batch, which is desired for the process. However, in terms of polymer properties (M_n , M_w and PDI), there is an impact, showing that keeping the same residence time is not an interesting strategy to the scale up/down.

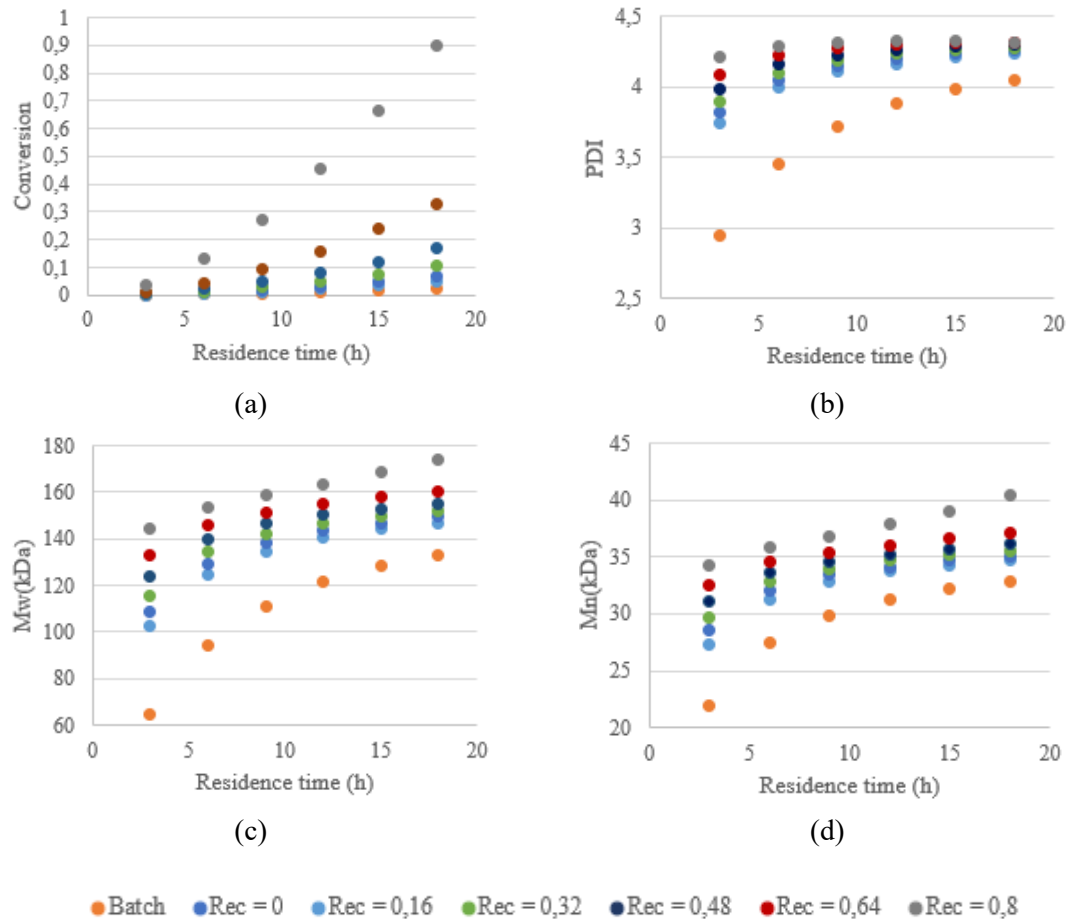


Figure 1. (a) Polymer conversion, (b) polydispersity indices (c) molecular mass M_w (kDa), and (d) M_n (kDa) as a function of residence time. The results are presented for the case studies (i) batch reactor (Batch), (ii) continuous stirred tank reactor (Rec = 0) and (iii) continuous stirred tank reactor (Rec = 0.16 to 0.80).

4. Conclusions

The simulations reveal the impossibility of achieving identical polymers in batch and continuous reactors while solely preserving the residence time and feed ratio. When contemplating scale-up and scale-down scenarios, due consideration must be given to these disparities, particularly in instances like copolymerization where additional phenomena, such as composition drift, may arise. Essential for comprehending the requisite adjustments, process simulation support proves imperative for both scale-up/down endeavors. In fact, more in deep studies must be done to improve the understanding of how the operational conditions can impact the polymer properties.

References

- [1] Ilare, J., Manfredini, N., Sponchioni, M., Storti, G., & Moscatelli, D., *Chemical Engineering and Processing-Process Intensification*, 165 (2021), 108440.
- [2] Ilare, J., & Sponchioni, M., *Advances in Chemical Engineering*, 56(1) (2020), 229-257.

Keywords

Polymerization, kinetics, scale-up, modeling, polypropylene