Determination of kinetic parameters within laboratory scale for polypropylene process modelling.

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Highlights
- The determination process for the kinetic parameters is broken down into several steps.
- With help of experimental results, the kinetic parameters are fitted.
- Feasible solutions can be derived for polymerisation outcomes in lab-scale.

1. Introduction

Polypropylene (PP) is a typical mass plastic with wide fields of application in everyday life as well as in industrial areas. Due to the continuing demand on the market, it is necessary to further develop and optimize the manufacturing processes. One of the industrial processes to produce PP is a bulk technology process, where the polymerisation of the monomer propylene takes place with a Ziegler-Natta catalyst in bulk phase in several successive loop reactors. In order to predict the properties of the polymer produced in industrial set-ups at process conditions, it is possible to model and simulate the process using process simulation software. However, this requires precise knowledge about the polymerisation mixture, occurring reactions and thermodynamic behavior. Since it is not economically or ecologically viable to investigate the behavior of reaction mixtures on large-scale set-ups, experiments are carried out on a lab-scale.

2. Methods

To obtain simulation-based predictions for the industrial bulk polymerisation process, the reaction kinetics for the polymerisation of propylene with a Ziegler-Natta catalyst are developed in the lab-scale model. The laboratory set-up is a semi-batch stirred tank reactor, in which both the pre-polymerisation and the following main polymerisation step are taking place. Whereas in the industrial model, there are subsequent loop reactors for continuous operation. In lab-scale, nitrogen is used as an atmosphere. Therefore, additionally to the liquid phase of the monomer and the solid phase of the polymer, a gas phase must be taken into account. The pre-polymerisation step is carried out under moderate conditions without the chain transfer agent hydrogen present. Subsequently, the reactor is heated to process temperature of about 70 °C, so that the main polymerisation step can take place.

For the first modelling approach, the polymerisation system is kept as simple as possible. Therefore, the pre-polymerisation is excluded from the fitting process and considered as a fixed starting point. Additionally, influences of the heating processs between pre-polymerisation and main polymerisation will be neglected.

For the first approach, a single-site catalyst model and a reduced reaction mechanism are chosen. This is shown in Table 1.

Table 1. Considered polymerisation reactions.

Name	Reaction
Initiation	$C^* + C3 \rightarrow P_1^*$
Propagation	$P_1^* + \text{n C3} \rightarrow P_{n+1}^*$
Chain transfer	
to hydrogen H_2	$P^* + H_2 \rightarrow P + C^*$
to monomer C3	$P^* + C3 \rightarrow P + C^*$
to cocatalyst CoCat	$P^* + CoCat \rightarrow P + C^*$
spontaneous	$P^* \rightarrow P + C^*$
Deactivation of	
active polymer P^*	$P^* \rightarrow P + C$
active catalyst site C^*	$C^* \rightarrow C$

The kinetic parameters are then adjusted to match the experimental results, like yield and melt flow rate. An overview about the fitting process used to determine the kinetic parameters for the defined reactions is shown in the figure below.
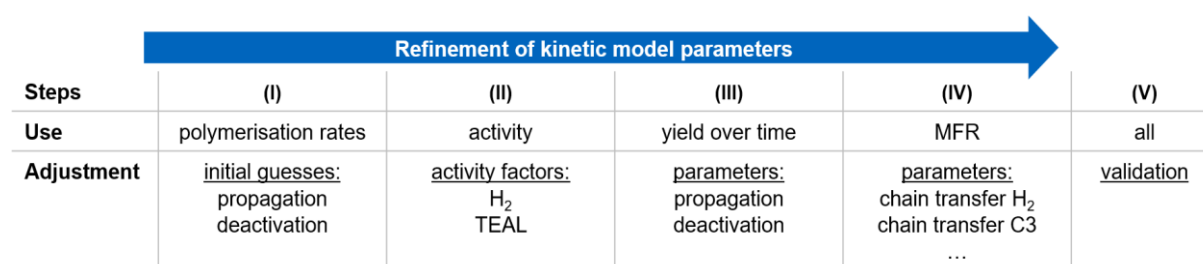

	Refinement of kinetic model parameters				
Steps	(I)	(II)	(III)	(IV)	(V)
Use	polymerisation rates	activity	yield over time	MFR	all
Adjustment	initial guesses: propagation deactivation	activity factors: H_2 TEAL	parameters: propagation deactivation	parameters: chain transfer H_2 chain transfer C3 …	validation

Figure 1. Schematic overview about the process to determine the kinetic model parameters based on lab-scale.

The set-up is modelled with the process simulation software gPROMS by Siemens.

3. Results and discussion

Since most of the parameters, which should be correctly predicted by the model, are dependent on more than one reaction within the polymerisation mixture, the adjustment of the parameters is not a straightforward way. Even though, it is possible to get feasible solutions for the different reaction parameters for prediction of polymer yield and properties within laboratory scale.

4. Conclusion

The reaction kinetics obtained for the lab-scale model can then be transferred to the industrial process model. It should be validated with available plant data, if this way of kinetic model scale-up is working for the polymerisation system at hand.