Mathematical Modelling of Ziegler-Natta Catalyzed Polyethylene Production in a Fluidized Bed Reactor using the Probability Generating Function (PGF) Technique

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Abstract. Polyethylene is a versatile polymer widely produced via gas-phase fluidized bed reactors due to their efficiency and flexibility. This work presents a mathematical model of the linear low-density polyethylene production in a gas-phase reactor using 1-butene as the comonomer and Ziegler-Natta catalyst. Assuming perfect mixing, the model incorporates two types of active sites with distinct kinetic constants, leading to a set of population balance equations. Polymer molecular properties are calculated using the method of moments and the probability generating function technique. The model is implemented in Julia and validated with experimental data from an industrial reactor.

Keywords: Linear Low-Density Polyethylene, Gas-Phase Reactor, Mathematical Modelling.

Modelizado de la Producción de Polietileno en un Reactor de Lecho Fluidizado con Catalizador Ziegler-Natta Mediante la Técnica de las Funciones Generadoras de Probabilidad (PGF)

Resumen. El polietileno es un polímero versátil ampliamente producido mediante reactores de lecho fluidizado en fase gaseosa debido a su eficiencia y flexibilidad. Este trabajo presenta un modelo matemático para la producción de polietileno lineal de baja densidad en un reactor de fase gaseosa, utilizando 1-buteno como comonómero y un catalizador Ziegler-Natta. Asumiendo mezcla perfecta, el modelo incorpora dos tipos de sitios activos con constantes cinéticas distintas, a partir de los cuales se desarrollaron ecuaciones de balance poblacional. Las propiedades moleculares del polímero se calculan utilizando el método de los momentos y la técnica de modelado de las funciones generadoras de probabilidades. El modelo se implementa en Julia y se valida con datos experimentales de un reactor industrial.

Palabras clave: Polietileno Lineal de Baja Densidad, Reactor Fase Gas, Modelo Matemático.

1 Introduction

Linear low-density polyethylene (LLDPE) is a widely used thermoplastic polymer, especially used in packaging and construction applications, playing a key role in everyday life. Among the technologies used for its polymerization, fluidized bed reactors offer significant advantages, such as improved temperature control and efficient mass transfer (Ghasem,2024). In these reactors, ethylene is copolymerized with olefinic co-monomers to tailor copolymer final properties. However, the current understanding of the relationships between operating conditions and structural characteristics of LLDPE and their influence on final properties remains limited.

The most critical structural features include the molar mass distribution (MMD), comonomer composition distribution (CCD), and short-chain branching distribution (SCBD). These distributed molecular properties are key factors governing the end-use performance of LLDPE (Soares et al.,2019). Understanding and controlling these molecular properties as a function of process operating conditions is essential for producing polyolefins with tailored performance. In this context, the development of mathematical models of industrial processes has become a valuable tool to ensure safety, sustainability, and efficiency.

In this study, a mathematical model was developed to simulate the production of LLDPE in a fluidized bed reactor using ethylene as the main monomer, 1-butene as the comonomer, and the well-known Ziegler-Natta catalyst (Cecchin et al.,2000).

The remainder of this work is structured as follows: first, the mathematical model and its underlying assumptions are described in detail. Then, simulation results are presented and compared with experimental data. Finally, key conclusions and implications of the modeling approach are discussed.

2 Mathematical Modelling

The mathematical model presented in this work assumes a perfectly mixed reactor configuration, and the kinetic scheme incorporates two types of active catalytic sites, each characterized by distinct kinetic rate constants. It follows the conventional mechanism described in the literature, which includes catalyst activation, initiation, propagation, chain transfer, and deactivation steps (Alves et al.,2021). From this kinetic framework, population balance equations (PBEs) were derived to describe the dynamics of the reactive species. The method of moments was applied to the PBEs, enabling the calculation of number-average and mass-average molar masses (M_n and M_m). Additionally, the probability generating function (PGF) (Asteasuain et al.,2002) approach was employed to transform the PBEs and obtain the MMD. The model also predicts production rate and monomer conversion.

The model considers perfect mixing with a single phase present in the reactor. This represents the limiting case in which there are no differences between the temperatures and concentrations of the gas in the bubble and emulsion phases. Two distinct types of active sites are considered, for which mass balances are derived separately. Kinetic constants for each active site type were adjusted with experimental data from an industrial reactor. The mass balance equations include the corresponding balances for potential active sites, initiation sites, impurity-deactivated sites, ethylene and 1-butene monomers, hydrogen, and catalyst, and PBEs of living polymer chains having ethylene or 1-butene as the terminal monomer and of dead polymer chains. In addition, the model equations include the calculation of the volumetric polymer production rate, the volume of the polymer phase, the total bed volume, the molar flow rate of potential active sites entering the reactor, and the energy balance. The model also includes equations for the total moments of order 0, 1, and 2 of living and dead polymer chains. The average molar masses M_n and M_m are computed as a function of the total moments.

The MMD is calculated using the pgf modelling technique. This technique is easy to implement. In a first step, the PBEs are transformed to the pgf domain, yielding balance equations for the pgf transform of the corresponding MMDs (Asteasuain, Sarmoria et al.,2002). The pgf values obtained by solving the pgf balances are inverted using a suitable inversion method to obtain the MMDs. In this model, the IFG inversion method (Asteasuain,2003) is used.

Julia was chosen for model implementation due to its high-performance capabilities, particularly suited for numerical computing and scientific simulations. As an open-source programming language specifically designed for technical applications, Julia offers speed while maintaining simplicity and readability. Its native support for parallel computing and just-in-time (JIT) compilation enables efficient handling of large-scale population balance equations and complex kinetic models. These features make Julia especially advantageous for simulating polymerization processes where computational efficiency and accuracy are critical.

The model was implemented using the Differential Equations package to solve a stiff system of ordinary differential equations, including mass balances, energy balance, moment, and pgf equations for both living and dead polymer chains. The implementation is organized around a central function that defines dynamic state variables representing concentrations of monomers, hydrogen, catalyst, different types of active sites, polymer moments, and additional variables required for the pgf formulation. The pgf method is incorporated by including real and imaginary components of the zeroth, first, and second-order pgf transforms of both living radicals and dead polymer chains for each type of active site. This enables the transformation of PBEs and later inversion of the PBE transforms to reconstruct the MMD using the IFG method. To enhance performance, the simulation exploits Julia's distributed standard library to allow parallel computation. The modular structure of the code facilitates adjustments in reaction conditions and kinetic parameters, supporting its application for industrial-scale simulations.

In addition to the full Julia model described above, a simplified version of the model was implemented in gPROMS® for parameter estimation purposes. This software is well known for its robust capabilities in parameter estimation for highly complex processes. The simplified model focuses solely on the calculation of M_n and M_m applying the method of moments. Experimental data of M_n and M_m from an industrial reactor was used to estimate the kinetic parameters.

3 Results and Discussion

The main operating conditions of each case are summarized in Table 1. For both scenarios, simulations start from a reactor with ethylene, 1-butene, and hydrogen concentrations as given in Table 1; all other reactants have 0 initial concentrations. Fig. 1 compares M_n and M_m calculated with the fitted model and the experimental data of two operating scenarios, showing good agreement. Fig. 2 shows the MMDs at the final reaction time for the two operating cases.

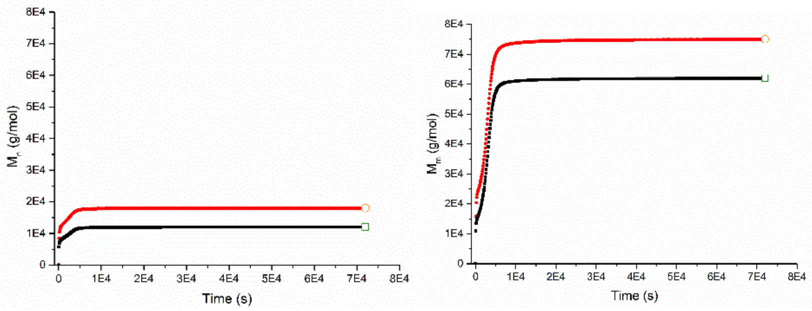

Fig. 1. Comparison between experimental (○ for Case A and □ for Case B) and predicted (● for Case A and ■ for Case B) M_n and M_m as a function of time for two different operating conditions.

Table 1. Operating conditions of cases A and B.

Operating Conditions	**Case A**	**Case B**
Initial Temperature (K)	313	311
Initial ethylene concentration (mol/dm^3)	0.343	0.286
Initial 1-butene concentration (mol/dm^3)	0.132	0.119
Initial hydrogen concentration (mol/dm^3)	0.211	0.281
Steady state temperature (K)	359	359
Catalyst feed (g/s)	1.16	1.50
Ethylene feed (g/s)	87000	79816
1-butene feed (g/s)	67592	67041
Hydrogen feed (g/s)	3915	5735

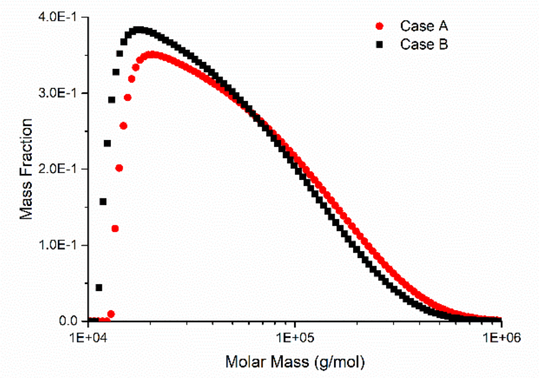

Fig. 2. Calculated MMDs at final reaction time for cases A and B.

4 Conclusion

A comprehensive mathematical model of the LLDPE production in an industrial fluidized bed reactor using 1-butene as comonomer and a Ziegler-Natta catalyst was developed. The model incorporates a detailed kinetic mechanism with two types of active catalytic sites and considers all relevant polymerization steps. A full version of the model was implemented in Julia, which predicts key polymer characteristics such as M_n, M_m, and MMD. Besides, a simplified version of the model that only computes M_n and $M_m$was implemented in gPROMS® to estimate kinetic parameters using experimental data from an industrial reactor. A very good agreement between model predictions and experimental data was achieved. Overall, the developed model provides a valuable tool for understanding the relationships between reactor operating conditions and LLDPE properties and serves as a foundation for process optimization and control.

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