MULTI-SCALE, MULTI-PHASE MODELLING OF A SERIES OF SLURRY-PHASE ZIEGLER-NATTA ETHYLENE POLYMERIZATION CSTRs

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ABSTRACT

Continuous slurry-phase polymerization, in the presence of a heterogeneous Ziegler–Natta catalyst, is one of the most commonly employed processes in the production of polyolefins, including high-density polyethylene (HDPE), isotactic polypropylene (IPP) as well as ethylene copolymers with α-olefins. Polymerization in a series of continuous stirred tank reactors is often employed to control the Molecular Weight Distribution (MWD), Copolymer Composition Distribution (CCD) of the copolymer chains, as well as the degree of crystallinity and density of the polymer which are strongly affect the final mechanical, physical, optical, rheological, etc. properties of the polyolefin resins.

The slurry-phase HDPE process technology employs two or three stirred-tank reactors in series and utilizes a Z-N catalytic system composed of a titanium chloride compound and an alkyl aluminum cocatalyst. The process uses hydrogen as a chain-transfer agent to control the molecular weight of the polymer and a comonomer (i.e., butene, hexene, etc.) to control the density and crystallinity of the polyethylene resin. Each unit in the cascade series of two or three reactors is commonly operated under different conditions (i.e., monomer, comonomer and hydrogen concentrations as well as temperature and pressure) to control the MWD (i.e., unimodal, bimodal, trimodal) and CCD.

In the present study, a comprehensive mathematical model is developed to simulate the dynamic operation of an industrial scale series of 2(or 3) slurry-phase olefin catalytic polymerization stirred tank reactors. A comprehensive multi-site, Z–N kinetic mechanism is employed to describe the molecular and compositional changes of the ethylene copolymer. The equilibrium species concentrations in the various phases (i.e., solid, liquid and gas) are calculated using the Sanchez–Lacombe Equation of State. Dynamic macroscopic mass species and energy balances are derived to calculate the time evolution of the concentrations of the various molecular species as well as the polymerization rate, heat removal rate, temperature and polymer molecular properties (i.e., number- and weight-average molecular weights, MWD and CCD). The effects of various operating conditions (i.e., temperature, pressure, catalyst and co-catalyst, ethylene comonomer, hydrogen and diluent mass feed rates, etc.) on the dynamic behavior of an industrial scale slurry-phase HDPE plant and molecular and rheological polymer properties are fully analyzed. It is shown that the proposed comprehensive model is capable of simulating the dynamic operation of an industrial scale HDPE slurry-phase plant under different operating modes (i.e., plant start-up, at steady-state and during a grade transition).

KEYWORDS: Ziegler-Natta olefin polymerization, Mathematical modelling of a series of stirred-tank slurry-phase reactors, Dynamic plant simulation, Polyolefin manufacturing.

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