MULTI-SCALE, MULTI-PHASE MODELLING OF A SLURRY-PHASE CATALYTIC ZIEGLER-NATTA HDPE CONTINUOUS PROCESS

Costas Kiparissides, Chemical Process & Energy Resources Institute, Centre for Research and Technology Hellas and Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece
costas.kiparissides@cperi.certh.gr
Prokopios Pladis, Chemical Process & Energy Resources Institute, Centre for Research and Technology Hellas, Greece

Key Words: Catalytic polymerization, multi-scale model, slurry-phase, mass transfer limitations.

Continuous slurry-phase polymerization, in the presence of a heterogeneous Ziegler–Natta (Z–N) 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 their copolymers with higher olefins. Polymerization in a series of reactors is often employed to control comonomer distribution, which is important for resin grades such as pipe applications that require excellent environmental stress crack resistance. The slurry HDPE process technology employs two or more stirred-tank reactors in series and utilizes a Z-N catalyst system composed of a titanium chloride compound and an alkyl

Figure 6 – The slurry Polymerization Process

aluminum cocatalyst. The process uses hydrogen as a chain-termination agent to control the molecular weight of the product and a comonomer to control the density of the polyethylene grade. The process operates in a continuous mode in a cascade of two or three autoclave-type vessels. Each reactor can operate under a different hydrogen partial pressure, thereby allowing the control of the molecular weight distribution. Typical reaction operating conditions are temperature 70 - 90 °C and a pressure less than 10 bar with a residence time 45 min per reactor.
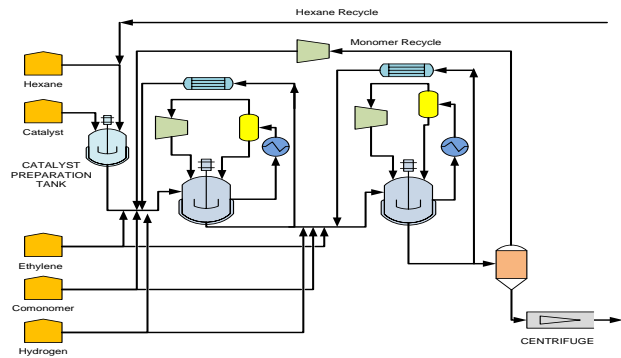
Despite the number of experimental kinetic studies that have enhanced our knowledge on the mechanism of Ziegler-Natta olefin polymerization, most of the previous kinetic modeling studies employ simplified polymerization kinetics to describe the catalytic polymerization of ethylene-a-olefin of Ziegler-Natta catalysts. In the present study, a comprehensive mathematical model is developed to simulate the dynamic behavior of a slurry-phase catalytic olefin polymerization industrial process in a series of continuous stirred tank reactors. A detailed kinetic mechanism is proposed to describe the molecular and compositional developments of ethylene copolymerization in the presence of a multi-site Ziegler-Natta catalyst.

Dynamic macroscopic mass species and energy balances are derived to calculate the dynamic evolution of the various molecular species concentrations as well as the polymerization rate, temperature and heat removal rate in each reactor of the multi-reactor configuration. The equilibrium species concentrations in the various phases
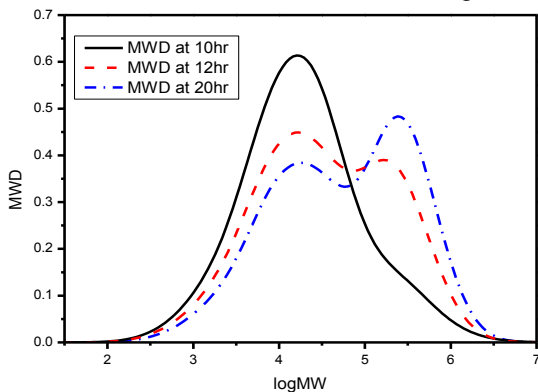

Figure 2 – Evolution of the MWD at the end of the second reactor

(i.e., solid, liquid and gas) are calculated using the Sanchez–Lacombe Equation of State. Gas-to-liquid and liquid-to-solid mass transfer limitations are also included in the comprehensive dynamic process model. The effects of process operating conditions (i.e., temperature, monomer and co-monomer partial pressures, catalyst to co-catalyst molar ratio, hydrogen and diluent concentrations, etc.) on the dynamic plant behavior as well as on the molecular (i.e., molecular weight and copolymer composition distributions) and viscoelastic properties of polyolefins are fully assessed. It is shown that the proposed comprehensive model is capable of simulating the dynamic operation of a slurry-phase series of stirred tank reactors under different plant operating policies for the production of polyolefins with desired multimodal MWD and CCD.