CONDENSED MODE COOLING FOR PE: IMPORTANCE OF THERMODYNAMICS IN REACTOR AND PARTICLE MODELLING

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Heterogeneously-catalyzed gas-phase polymerization of ethylene in fluidized bed reactors (FBRs) is the single type of reactor used for polyethylene (PE) production. Due to an ever-increasing demand for PE, it is possible to substantially improve the heat removal efficiency, and consequently increase the production capacity of an FBR by exploiting the so-called condensed mode cooling method. In this method, compounds referred to as induced condensing agents (ICAs), typically C_3-C_8 alkanes, are added to the reactor recycle stream, (partially) liquefied in an external heat exchanger and then injected into the reactor in the form of small droplets along with the gaseous components. The fast evaporation of the liquid phase inside the reactor absorbs additional polymerization heat and thus enhances the production capacity of the unit.

ICAs are chemically inert in the sense that they do not have any influence on the behavior of the active sites. Nonetheless, recent papers from our group have clearly demonstrated that the rate of ethylene polymerization (R_p) increases in the presence of ICAs. As the partial pressure of the ICA in the gas phase increases, R_p also increases. The normalized rates of polymerization with the one without any *n*-hexane reveals that the increase in the R_p is more pronounced at the beginning of reaction and decreases as the reaction progresses, approaching a steady-state value at the later steps.

A new process model is developed based on the thermodynamics of sorption coupled with the dynamics of mass and heat transfer in a growing polymer particle. The thermodynamic simulations, performed by employing the Sanchez-Lacombe EoS, show that by increasing the partial pressure of *n*-hexane in the gas phase, the equilibrium concentration of ethylene in the amorphous phase of PE increases (cosolubility effect). However, at the beginning of the reaction, R_p is promoted much more strongly than would be expected from the cosolubility effect alone. According to the free-volume theory, in addition to the solubility, the diffusivity of ethylene in PE is also expected to increase by increasing the partial pressure of *n*-hexane (codiffusion effect). The simulations of polymer flow model (PFM), adapted to describe the dynamics of mass and heat transfer in a single growing particle, indicate that it is possible to appropriately describe the observed influence of *n*-hexane on R_p by taking into account the both cosolubility and codiffusion effects; during the early stages of the reaction, a specific magnitude of the enhancement in the ethylene diffusivity due to the codiffusion effect of *n*-hexane causes a more significant impact on the ethylene concentration gradient and therefore the efficiency (η) and overall rate of polymerization. Furthermore, the PFM simulations suggest that the addition of *n*-hexane has a negligible effect on the thermal behavior of the growing particles under the operating conditions used in the experiments.

The presented process model is a new development in the field of modeling the process of gas phase ethylene polymerization on supported catalysts. This framework not only enables us to describe the observed polymerization rates, but also serves as a useful intellectual tool to develop improved understanding about the dynamics of the polymerization reaction in the presence of *n*-hexane as the ICA compound.