Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Investigation of the Phase Separation Process of Polymer-Monomer Mixtures II



Project Manager
Anne Rott

Principal Investigator
Prof. Markus Busch

Project Term
2023 - 2024

Clusters
Lichtenberg II Cluster Darmstadt

Software
LAMMPS

Institute
Ernst-Berl-Institut für Technische und Makromolekulare Chemie

University
Technische Universität Darmstadt

Introduction

The polymerization of low-density polyethylene takes place at high temperatures and pressures up to 3000 bar. Under these conditions, modeling provides an important tool for investigation and improvement of the process. Hereby, not only the polymerization itself but also the separation process is of importance. The separation process of the LDPE polymerization process is comprised of two consecutive flash separator vessels. In 1these separators, the pressure is reduced from reaction pressure to a pressure between 300 and 200 bar (high-pressure separator, HPS) and then further reduced to ambient pressure (low-pressure separator, LPS). These pressure reductions induce phase separation between polyethylene and ethene. It has been observed that the high-pressure separator operates outside of thermodynamic equilibrium conditions. Therefore, when modeling this separator, a time-dependent approach has to be taken. In this work, molecular dynamics simulations are used. To accurately represent an experimental molecular weight distribution, a large number of polymers and therefore also a large number of monomers have to be simulated.

Methods

The separation process can be divided into different phases (formation of polymer droplets, formation of monomer bubbles inside polymer droplets, coalescence and growth of monomer bubbles and coalescence of polymer droplets to a polymer-rich phase), which can be described using molecular dynamics (MD).

The focus hereby is on the formation and growth of monomer bubbles during the pressure drop between reactor and high-pressure separator. MD is hereby applied to model the phase separation process time- and space resolved by reducing the pressure applied on the simulation box. The obtained positions of the atoms are then used to determine the phase of every monomer molecule.

Results

As molecular dynamics simulations are quite time-consuming and therefore not applicable in daily use, the focus of this work was to establish a correlation to calculate the amount of ethene after the separator based on the conversion inside the reactor and the pressure of the separator. Since depending on the polymerization conditions, different polymeric structures and different amount of branching can be observed in the polymer, a usable correlation needs to be capable to depict multiple branching densities. Therefore, the simulation was performed using polymers with different branching densities. It was found that the branching density, as long as it is in an experimentally obtainable range, has no impact on the separation depicted by the simulation. It was also shown that the separation between polymer and monomer itself occurs in a timescale which can be depicted by the simulation, leading to the conclusion that the deviations from thermodynamic equilibrium in the high-pressure separator are due to transport of the monomer bubbles inside the polymer network. Additionally, since most processes include comonomers, a simulation for the separation of ethene-vinyl acetate-copolymer, ethene, and vinyl acetate was performed. However, no conclusion could be made on the impact of the comonomer on the separation process.

Discussion

The separation between polymer and monomer in the high-pressure separator of the LDPE polymerization process has been successfully modeled. Hereby, a correlation to calculate the amount of ethene in the polymer phase after the high-pressure separator based on the conversion inside the reactor and the separator pressure was obtained. However, no comparison between the determined correlation and industrial data has been performed yet. Additionally, the influence of polymer branching and comonomers on the separation process was looked upon. While no influence of the branching density on the process could be observed, the simulations including comonomers did not yield any conclusive results.

Last Update: 2025-04-23 11:24