# Interactions of gas and liquid phase with porous particles in the gas-phase catalytic polymerization of olefins

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## Introduction

The importance of sorption equilibria of monomer(s) and other low-molecular weight species in the polymer phase was already stressed out several times (Hutchinson and Ray, 1990; McKenna, 1998; Moore and Wanke, 2001). Reaction rates of propagation and other reactions depend on the actual concentration of reacting species at supported catalyst sites, which are permanently covered by a polymer phase (except of early stages of polymerization). The concentration of a species at catalyst sites is thus determined by the simultaneous action of reaction(s), transport through polymer phase and particle pores and by thermodynamics of sorption of reacting and non-reacting species in the polymer phase. Secondary processes, such as crystallization and swelling of polymer phase are also relevant in this respect. The combination of above-mentioned processes was already properly addressed in the literature, particularly in the framework of the multi-grain conceptual model, e.g., by Hutchinson et al (1992), Debling and Ray (1995) and others. The transport resistance in micro-grains caused by a slow diffusion in the polymer phase is somewhat compensated by the short diffusion length on the order of 1 μm or less.

Less attention has been paid to interactions of liquid phase with porous catalyst and polymer particles in gas-phase reactors for polymerization of olefins. Let us name at least following cases of these interactions:

a) supported porous catalyst particles can be injected into the reactor in the form of a slurry with the alifatic diluent, where the diluent is going to vaporize in the initial stage of particle growth and thus slows down the transport of monomer to the surface of catalyst particle,
b) growing polypropylene particles can be showered by the liquid monomer(s) in certain types of polymerization reactors,
c) in fluidized beds operated in condensed or super-condensed regimes, growing polyethylene particles come into contact with drops of liquid diluent used to remove excess of reaction heat.

Interactions described above could have important effects to the description of transport processes inside porous catalyst and polymer particles as well as to sorption equilibria.

## Description of experiments

The multi-purpose experimental apparatus aimed for various aspects of catalytic polymerization of olefins was designed and constructed in our research laboratory. This apparatus allows to investigate sorption and desorption processes in polymer phase and/or in porous particles. After its completion it will allow to study the growth of a set of polymer particles during polymerization under well-defined hydrodynamic conditions. The apparatus consists of: (i) a mini-reactor equipped with on-line gas composition control system utilizing the mass spectrometer, (ii) a magnetic suspension balance used for measurements of dynamic changes of a sample weight at elevated temperatures and pressures, (iii) a catalyst or particle injection system, (iv) a purification system for monomer(s) and other gases, (v) temperature and pressure control system and (vi) the industrial computer used for overall control and recording of measured data.

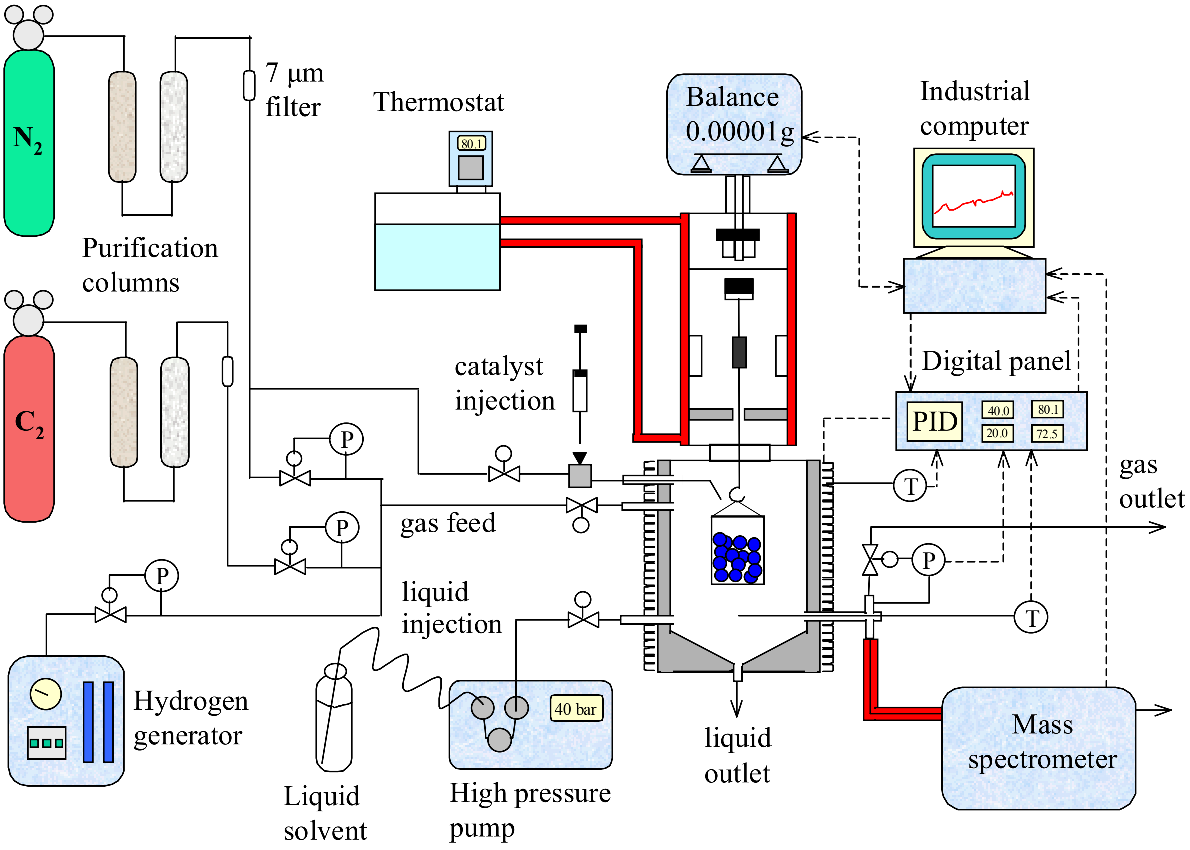

**Figure 1.** The schema of the experimental equipment.

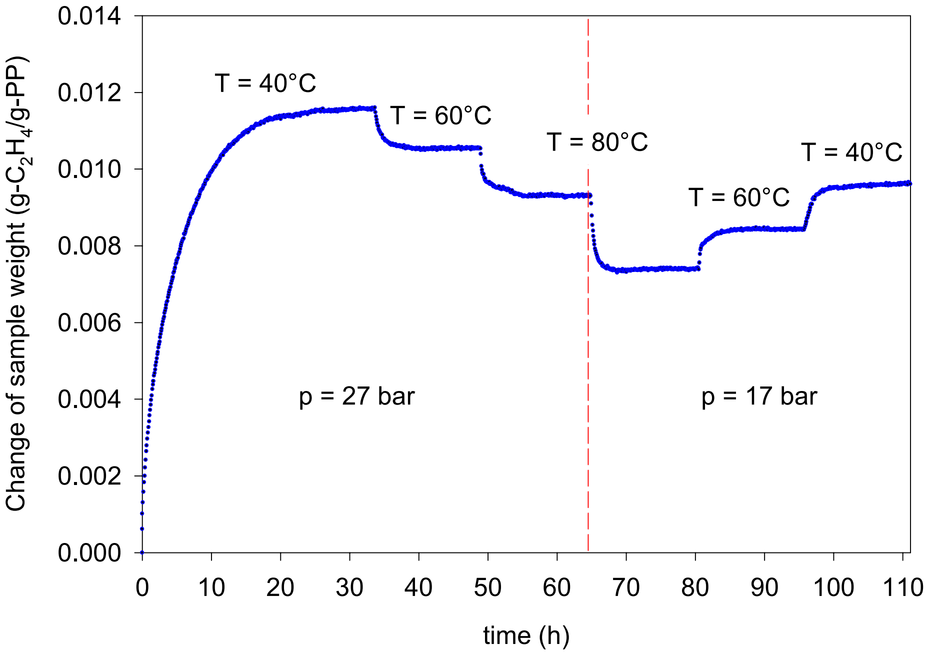

**Figure 2.** Dynamic evolution of a sorbed amount of ethylene in polypropylene in a typical sorption experiment.

This experimental equipment was initially tested on sorption experiments, i.e., the sorption of monomers (ethylene, propylene), co-monomers (e.g., 1-hexene, 1-butene, 1-octene) and various solvents/diluents (e.g., n-pentane) in polymer particles at various process conditions (temperature, pressure, fluid phase composition).

The sorption equilibria and the kinetics of sorption-desorption processes in the system of polymer particles – gas phase was measured for several industrially important polymers (polyethylene, polypropylene) with grades that differ in the size of particles, copolymer composition, crystallinity, tacticity, particle porosity etc. An example of the dynamics of a typical sorption experiment is displayed in Figure 2. Both equilibrium sorption data and transport properties of species in the polymer phase can be estimated from these experiments, cf. Figure 3.

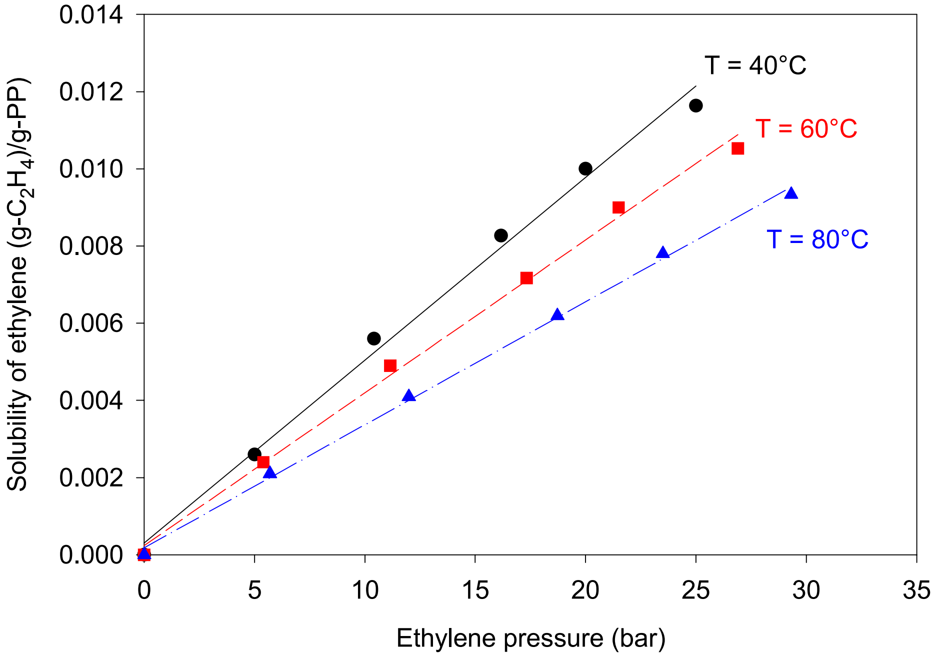

**Figure 3.** Sorption isotherms describing the solubility of ethylene in the sample of polypropylene.

We also plan to investigate the possible use of the direct gravimetric observations for the measurement of the kinetics of polymerizations. At the start of the experiment the supported catalyst particles are fed into the weighing basket inside the pressure cell of the mini-reactor. Then we record the course of the increase of a sample weight during the polymerization as well as all relevant process conditions.

## Modeling of interactions of liquid phase with porous particles

The modeling part of this study will include investigations of the behavior of a liquid phase in porous growing particles of polymer. Parametric studies will be based on the expanded dusty fluid model (Kosek et al, 2001) considering the presence of both the liquid and the gas phase in particle pores, the evaporation and condensation of a liquid phase, the permeability of the pore phase and the convective flow resulting from the evaporation and from the consumption of monomer by the polymerization reaction. Experimental observations suggest that the presence of liquid species in condensed regimes in fluidized beds affects the properties of the formed polymer phase. Furthermore, the evaporation of a liquid from catalyst particle pores could absorb a part of reaction heat at the critical stage of particle growth, where the particle is susceptible to overheating. A systematic study of the condensation and evaporation of a liquid phase in the porous material based on the reconstructed 3D porous media was performed by Štěpánek et al (1999).

## Conclusions

The results obtained in this work could be used for:

a) transfer of kinetic data corresponding to the catalyst into the system with reaction conditions substantially different from original reaction conditions (e.g., transfer from slurry to gas phase reactors),
b) degassing of the final product, i.e., desorption of the monomer from polymer particles,
c) differentiation between kinetic and thermodynamic effects w.r.t. kinetics of the polymerization, for example, between Arrhenius temperature dependence of rate constant versus the decreasing sorption capacity of polymer at higher temperatures.

There are number of experimental studies of sorption equilibria in polyolefins, cf. (Castro et al, 1987; Doong and Ho, 1991; Moore and Wanke, 2001 ). However, more extensive studies are still required to systematically comprehend all relevant effects, such as effects of polymer chain branching, composition and co-solvent effects. Systematic studies of diffusion processes in polymer phase are scarcer (Kulkarni and Stern, 1983; Aminabhavi et al, 1996). However, the knowledge of the dynamics of the establishing of sorption equilibria (which is limited by transport in polymer) could become attractive for particles exposed to regions of different temperature along their trajectories in fluidized beds or to areas of different composition in multi-zone circulating beds. The studies of desorption processes from polymer particles are also scarce (Le Blévec, 2000).

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