MODELING OF THREE-PHASE SINGLE PELLET STRING REACTOR. APPLICATION TO THE SELECTIVE HYDROGENATION

J.M. Schweitzer, A.Dandeu, A.I. Fernandes Hipolito
Institut Français du Pétrole, Chemical Engineering Department, PO Box 3 69390 Vernaison France

Summary

A new intensified pilot plant reactor has been proposed to test new catalyst for fast reaction processes: a string pellet reactor. The objective of this work is to characterise this new tool by studying mass transfer, hydrodynamics and allene hydrogenation kinetics to define the limit use of this reactor and design rules. A complete dynamic model of the three-phase system taking into account the measured mass transfer was developed and fitted on experimental data.

Keywords

Process intensification, micro reactor, hydrogenation

Introduction

For reactor scale up purpose, it is important to know the intrinsic kinetics of a reaction on the catalytic active sites. Generally, intrinsic kinetics is determined into small reactor where, mass transfer resistances are reduced, isothermal conditions are achieved and hydrodynamics is well controlled. Micro-reactors are alternative tools compared to conventional lab reactors because they allow to control the scales where transfers (mass and heat) are enhanced which leads to a decreasing or an elimination of these external resistances. Transfers are crucial for very rapid exothermic reactions like selective hydrogenations. It is necessary to ensure that the chosen reactor, where the intrinsic kinetics will be determined, is working near the chemical regime. A new intensified pilot plant reactor has been proposed to test new catalyst for fast reaction processes, the so-called Single Pellet String Reactor (SPSR). This reactor should help to access to real kinetic performances of the catalyst in isothermal conditions minimizing the number of experiments. The intrinsic kinetic parameters for steam reforming of n-heptane [1] and for olefin hydrogenation [2] were measured in this type of reactor. The objective of this work is to characterise this new tool in three phase G/L/S configuration by coupling mass transfer, hydrodynamics and allene hydrogenation kinetics to define the optimized operating conditions of this reactor corresponding to the chemical regime. A complete dynamic model of the three-phase system, taking into account measured mass transfer and hydrodynamic parameters, was developed and fitted on experimental data.

Experimental section

The reactor has been supplied by Erfheld Technology and the geometry corresponds to a series of six plate reactor modules. A squared channel of 4x4 mm² and 1.5 m long has been machined in a stainless steal plate to load the catalyst particles. This plate is inserted between two plates where a channel devoted to thermal fluid circulation has also been machined as shown in Figure 1. This thermal fluid flow is used to control the temperature of the reactive zone by both heating up the reactor and removing the reaction heat. The temperature is measured inside the catalytic channel at the inlet and outlet of each module.

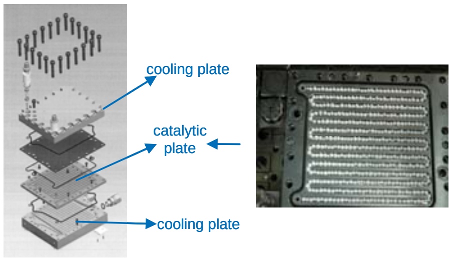

Figure 1: Catalytic module reactor

Selective hydrogenation reaction of allene has been studied. The commercial catalyst with real spherical shape has been loaded inside the six modules of the reactor. The liquid feed was composed of 3 % wt of allene and 97% of propene. The reaction scheme is presented in Figure 2. The objective of the allene selective hydrogenation is to produce propene by limiting the propane production.

$$C_3H_4 \quad + \quad H_2 \quad \rightarrow \quad C_3H_6 \qquad : reaction\ 1$$
$$C_3H_6 \quad + \quad H_2 \quad \rightarrow \quad C_3H_8 \qquad : reaction\ 2$$

Figure 2: Reaction scheme for allene hydrogenation

Hydrodynamic study

Single Pellet String Reactors present quite complex hydrodynamic patterns when there are used with two phase gas/liquid flows. That is why, an hydrodynamic study in single phase flow and two phase flow was carried out. The liquid residence time distributions (R.T.D.) and the pressure drop were measured and analysed [3], [4]. Gas/liquid and liquid/solid mass transfer were measured.

Reactor model and comparison with experimental data

A dynamic three phase reactor model was developed using a dispersed-plug flow description for the liquid and the gas phase. To check isothermal conditions inside the module, three-dimensional simulations of one module have been performed with a standard one phase exothermic reaction for the catalytic plate with reaction enthalpy close to the real system. Figure 3 shows a simulated temperature profile inside the catalytic channel. Simulations were carried out with an inlet cooling temperature of 20°C. Only 1°C of maximum temperature difference was calculated which confirms that isothermal conditions are achieved in this reactor.

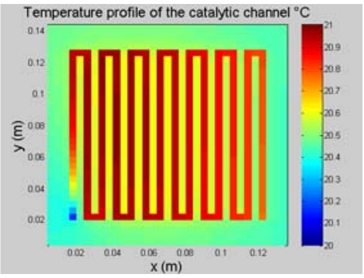

Figure 3: Temperature profile of the catalytic channel

A first model was developed taking into account gas/liquid and liquid/solid mass transfer phenomena. Henry coefficients were calculated using the Grayson-Streed method. Gas/liquid and liquid/solid mass transfer coefficients were measured in the hydrodynamic study. As a first approximation, no diffusionnal limitations have been considered inside catalyst grains. Indeed, if the catalyst particle size does not change between the Single Pellet String Reactor and the industrial reactor, the same apparent kinetics can be used in both cases for scale-up purpose.

Experiments were carried out at different residence time, flow velocities, and hydrogen flowrates. Experimental results were compared with the simulations.

This first approach does not fit well the experimental data. Simulations underestimate the experimental conversion even if we increase numerically the catalyst activity. The model indicates that there is a strong external liquid-solid mass transfer limitation which is not seen experimentally. To reach experimental conversion, it is necessary to multiply by ten the external liquid-solid mass transfer coefficient. Of course, this is not feasible because the uncertainty in the determination of this coefficient by cold flow experiments, is less than 20%. However, partial wetting of the particle could explain this behaviour. Indeed, when partial wetting occurs, the liquid-solid transfer film is partially destroyed and the access to the catalytic active sites is then favoured. Numerous studies have shown that in empty tubes of few millimetres in diameter, mass transfer between phases was greatly enhanced because of the segmented flow (Taylor flow) resulting in thin films between the bubbles / droplets and the walls. To interpret the high value for hydrogen mass transfer through liquid film, a second model was developed in order to take into account a partial wetting of the catalytic particle. The partial wetting of the catalyst is modelled as described in Figure 4. Liquid/solid mass transfer was considered only for the wetted fraction ß.

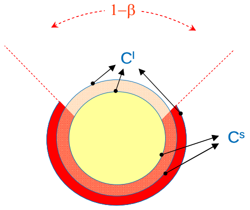

Figure 4: Schematic representation of partial wetting

The second model is in good agreement with experimental data as shown in Figure 5. To check the assumption of partial wetting, a transparent mock-up filled with glass beads was built. Figure 6 shows that in a certain range of operating conditions, stratified flow can be reached.

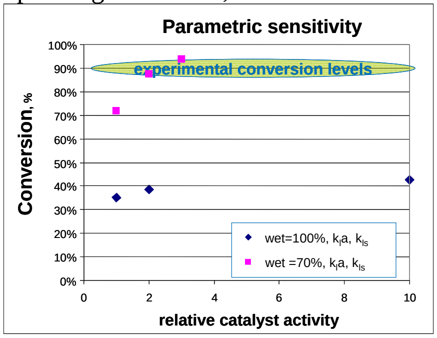

Figure 5: Effect of the partial wetting on conversion

Figure 6: Flow regime observation

Wetting efficiencies are measured for different operating conditions, and the second model was used to determine the intrinsic kinetic parameters.

References

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