A comparison of homogeneous and heterogeneous dynamic models for industrial methanol reactors in the presence of catalyst deactivation

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Abstract

Dynamic simulation of a Lurgi type industrial methanol reactor has been studied in the presence of long term catalyst deactivation. The performance of the reactor was investigated using two different dynamic models: (a) a simple homogeneous model, and (b) a heterogeneous model. The models were validated against measured daily process data of a methanol plant recorded for a period of four years. Good agreements were achieved and both models were found to predict almost identical results under industrial operating conditions. The high velocity of the reactant stream was found to be the most important reason for this phenomenon. The simple model represents a useful tool for dynamic simulation, optimization and control of methanol synthesis. Introducing such a simple model reduces the number of typical states to half, and this in itself will significantly reduce the level of computation in the model base estimators.
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1. Introduction

The extreme complexity of the processes involved in the methanol synthesis justify the computer simulation of such processes in order to get further understanding of the system without the need for conducting costly and time-consuming experiments. The dynamic simulation of methanol synthesis processes, in particular, has a wide range of applications including; the start-up and shut-down investigations, system identification, safety, control, optimization, and transient behavior and operability studies. The dynamic simulation is preferred to steady-state simulations in operability studies since the former provides a realistic description of the transient states of the reactor owing to the fact that the numerical solution strategies employed in dynamic models are more robust than the solution of a typical steady-state model. Thus,

it allows for safe and trustworthy studies of the control and optimization of the reactor [1,2].

Quasi-steady-state models of multiphase methanol reactors have been the subject of extensive studies and a summary of these works has been presented in several reviews [3–5]. However, a critical examination of the literature reveals that there is no information available regarding the use of dynamic models for industrial methanol synthesis in the face of long term catalyst deactivation. Therefore, we decided to thoroughly study the phenomenon of methanol synthesis in the presence of catalyst deactivation by a dynamic simulator. It is clear that several key aspects of this problem require research including a comparison of the homogeneous and heterogeneous treatment of the catalytic reaction at industrial operating conditions. In this way the validity of using simple homogeneous dynamic models for optimization and control purposes can be investigated.

This work reviews a hierarchy of dynamic mathematical models for industrial methanol synthesis along with the corresponding class of spatiotemporal patterns that may emerge

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in this high-pressure catalytic reactor. It must be highlighted that in high-pressure reactors the interactions between the catalyst and the fluid flow result in the formation of the so called thermal patterns [6]. These thermal effects are responsible for providing positive-feedback and long-range communication among various sub-processes involved. Thus, we study non-isothermal models of such reactors. Our current understanding of the reactor performance suggests that they are governed by the interaction of a fast and long-range autocatalytic-variable (typically, the temperature) with a slow and localized change in the catalytic activity. Such one-dimensional systems are excitable but are unlikely to exhibit sustained spatiotemporal patterns in the absence of global-interaction or flow. This work focuses, therefore, on the interaction of the fluid-phase, through which the reactants are supplied, and the reactive solid-phase. This interaction may produce patterns under conditions that in the absence of such interaction induce homogeneity in the system. Experimentalists had tried to minimize this interaction by increasing the fluid flow-rate into the reactor, or by applying control to the gas-phase concentration.

We describe below two fixed-bed dynamic models, differing in the number of phases they account for: in the homogeneous model, gradients between the solid and fluid-phases are neglected and the rates are expressed in terms of the fluid-phase concentration and temperature, while in the heterogeneous model which accounts for both phases and their heat and mass exchange, the rates are expressed in terms of the solid-phase temperature and concentration profiles. Both models are analyzed under realistic conditions and employ a slow process of changes in activity.

The objective of current work is to investigate the behavior of industrial methanol reactors and offer a simple model as a starting point for further studies on the system identification, optimization and control of such reactor.

2. Reactor models

A typical methanol reactor handles the process of conversion of synthesis gas (CO_2, CO and H_2) to form methanol. Such a reactor usually resembles a vertical shell and tube heat exchanger. The tubes are packed with catalyst pellets and boiling water is circulating in the shell side to remove the heat of exothermic reactions.

In this study, two different one-dimensional models have been considered, the homogeneous and heterogeneous models. The basic structure of both models is composed of heat and mass balance conservation equations coupled through thermodynamic and kinetic relations, as well as, auxiliary correlations for predicting physical properties.

2.1. Heterogeneous model

Methanol reactors are traditionally modeled by a heterogeneous model, which is a conventional model for a catalytic

reactor with heat and mass transfer resistances. The balances typically account for accumulation, convection, and transport to the solid-phase. The axial dispersion is neglected here while the heat loss by a coolant is considered. The mass and energy balances for the solid phase are expressed by:

$$\varepsilon_s c_t \frac{\partial y_{is}}{\partial t} = k_{gi}(y_i - y_{is}) + \eta r_i \rho_B a, \quad i = 1, 2, \ldots, N - 1 \tag{1}$$

$$\rho_B c_{ps} \frac{dT_s}{dt} = a_v h_f(T - T_s) + \rho_B a \sum_{i=1}^{N} \eta r_i(-\Delta H_{f,i}) \tag{2}$$

where y_{is} and T_s are the solid-phase mole fraction and temperature, respectively. The following two conservation equations are written for the fluid phase:

$$\varepsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{F_t}{A_c} \frac{\partial y_i}{\partial z} + a_v c_t k_{gi}(y_{is} - y_i),$$
$$i = 1, 2, \ldots, N - 1 \tag{3}$$

$$\varepsilon_B c_t c_{pg} \frac{\partial T}{\partial t} = -\frac{F_t}{A_c} c_{pg} \frac{\partial T}{\partial z} + a_v h_f(T_s - T)$$
$$+ \frac{\pi D_i}{A_c} U_{shell}(T_{shell} - T) \tag{4}$$

where y_i and T are the fluid-phase mole fraction and temperature, respectively.

The boundary conditions are as follows:

$$z = 0, \qquad y_i = y_{i0}, \qquad T = T_0 \tag{5}$$

while the initial conditions are:

$$t = 0, \qquad y_i = y_i^{ss}, \qquad y_{is} = y_{is}^{ss},$$
$$T = T^{ss}, \qquad T_s = T_s^{ss}, \qquad a = 1 \tag{6}$$

where y_i^{ss}, y_{is}^{ss} are the steady-state profiles of the mole fraction and T^{ss}, T_s^{ss} are the steady-state profiles of temperature along the reactor. The values of , T^{ss}, T_s^{ss} are determined from a steady-state simulation.

For both homogeneous and heterogeneous models, several auxiliary correlations for estimation of mass and heat transfer coefficients are used. These auxiliary correlations are given in Appendix A.

2.2. Homogeneous model

In this simple model we assume that gradients of temperature and concentrations between the phases can be ignored and the equations for the two phases can be combined. The general fluid-phase balance is a model with the balances typically account for accumulation, convection, and reaction. In the current work, axial dispersion of heat is neglected and the heat loss by a coolant is considered as we study a realistic