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Dynamic modeling and operability analysis of a dual-membrane fixed bed reactor to produce methanol considering catalyst deactivation

M. Farsi, A. Jahanmiri *

Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

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ABSTRACT

The goal of this research is dynamic operability analysis of dual-membrane reactor considering catalyst deactivation to produce methanol. A dynamic heterogeneous one-dimensional model is developed to predict the performance of this configuration. In this configuration, a conventional reactor has been supported by a Pd/Ag membrane tube for hydrogen permeation and alumina–silica composite membrane tube to remove water vapor from the reaction zone. To verify the accuracy of the considered model, the results of conventional reactor are compared with the plant data. The main advantages of the dual-membrane reactor are: higher catalyst activity and lifetime, higher CO_2 conversion and methanol production.

1. Introduction

Methanol as the simplest aliphatic alcohols is a volatile, colorless, flammable and poisonous chemical component. It is completely miscible with water and organic solvents. It forms an explosive mixture with air and burns with a non-luminous flame. Methanol is one of the most important industrial petrochemical products that used as a fuel, solvent, antifreeze and intermediate to produce other components. It can be synthesized from different sources such as natural gas, coal, biomass and petroleum. The commercial method to synthesize methanol is the direct combination of carbon monoxide, hydrogen and carbon dioxide gases in the presence of a catalyst. Conventionally, the reactions occur in a shell and tube exchanger that catalyst pellets are packed in tubes. Saturated water is circulated in the shell side to cool the reactor. Since the methanol synthesis reactions are reversible, conversion in the reactor is low and the most of unreacted syngas should be recycled in the process.

There are several researches on the modeling and simulation of conventional methanol synthesis reactor in the literature. Graaf et al. modeled a commercial low pressure methanol synthesis reactor at the steady state condition [1]. They showed that the size of catalyst particles exhibits intraparticle diffusion limitations. Lange presented a good review of methanol synthesis technologies [2]. Jahanmiri and Eslamloueyan modeled a conventional methanol reactor at steady state condition and showed that the difference between one and two-dimensional simulation is negligible [3]. Velardi and Barresi proposed an auto thermal multi-stage reactor configuration to promote methanol production [4]. Kordabadi and Jahanmiri modeled and optimized a Lurgi type methanol reactor to enhance methanol production [5]. This optimization approach enhanced a 2.9% additional yield in the methanol production rate.

Catalyst deactivation is a common event in petroleum and petrochemical industries that has an important effect on the process performance and stability. In the methanol synthesis process, catalyst deactivation is a great problem in the practice that decreases the production rate and should be considered in the design stage. In the methanol process, deactivation of $Cu/Zn/Al_2O_3$ catalyst is caused by chemical poisoning and thermal sintering. Sintering is a solid state transformation which occurs at high temperatures and is promoted by water molecules. Sulfur compounds, chlorine and heavy metals act as methanol catalyst poisons. Deactivation of methanol synthesis catalyst has been discussed by researchers in various studies. The CuO/ZnO catalyst is deactivated very slowly with an estimated lifetime about 3–4 years [6]. Quinn et al. showed that synthesis gas contaminants lead to catalyst deactivation [7]. Jung et al. claimed that the reduction of ZnO in the methanol catalyst increases the deactivation rate [8]. They suggested oxygen injection into the reactant feed in order to regenerate the catalyst lifetime. Wu et al. suggested that addition of small amounts of silica in methanol catalyst increases the stability of the catalyst by suppressing the crystallization of Cu and ZnO [9]. Ladebeck showed that decreasing

* Corresponding author. Tel.: +98 711 6133088; fax: +98 711 6287294.
E-mail address: jahanmir@shirazu.ac.ir (A. Jahanmiri).

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Nomenclature

a_v	specific surface area of catalyst pellet ($m^2\ m^{-3}$)
A_c	cross section area of each tube (m^2)
C_i	molar concentration of component i ($mol\ m^{-3}$)
C_p	specific heat of the gas at constant pressure ($J\ mol^{-1}$)
dp	particle diameter (m)
D	tube diameter (m)
D_{ij}	binary diffusion coefficient of component i in j ($m^2\ s^{-1}$)
D_{im}	diffusion coefficient of component i in the mixture ($m^2\ s^{-1}$)
E_p	activation energy of permeability ($kJ\ mol^{-1}$)
F	total molar flow rate ($mol\ s^{-1}$)
f_i	partial fugacity of component i (bar)
h_f	gas–solid heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
k_1	reaction rate constant for the 1st rate equation ($mol\ kg^{-1}\ s^{-1}\ bar^{-1/2}$)
k_2	reaction rate constant for the 2nd rate equation, ($mol\ kg^{-1}\ s^{-1}\ bar^{-1/2}$)
k_3	reaction rate constant for the 3rd rate equation ($mol\ kg^{-1}\ s^{-1}\ bar^{-1/2}$)
L	reactor length (m)
P	total pressure (bar)
P_i	partial pressure of component i (bar)
P_0	pre-exponential factor of hydrogen permeability, ($mol\ m^{-2}\ s^{-1}\ Pa^{-1/2}$)
r	rate of reaction ($mol\ kg^{-1}\ s^{-1}$)
r_1	rate of reaction for hydrogenation of CO ($mol\ kg^{-1}\ s^{-1}$)
r_2	rate of reaction for hydrogenation of CO_2, ($mol\ kg^{-1}\ s^{-1}$)
r_3	reversed water–gas shift reaction ($mol\ kg^{-1}\ s^{-1}$)
R	universal gas constant ($J\ mol^{-1}\ K^{-1}$)
Re	Reynolds number
Sc_i	Schmidt number of component i
T	temperature (K)
t	time
u	superficial velocity of fluid phase ($m\ s^{-1}$)
U	overall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
y_i	mole fraction of component i ($mol\ mol^{-1}$)
z	axial reactor coordinate (m)

Greek letters

α_H	hydrogen permeation rate constant, ($mol\ m^{-1}\ s^{-1}\ Pa^{-1/2}$)
μ	viscosity of fluid phase ($kg\ m^{-1}\ s^{-1}$)
ρ	density of fluid phase ($kg\ m^{-3}$)
π_w	water vapor permeation rate constant, ($mol\ m^{-2}\ s^{-1}\ Pa^{-1}$)
ε	bed void fraction

Superscripts

g	in bulk gas phase
s	at surface catalyst

Subscripts

0	inlet conditions
i	chemical species
1	water membrane side
2	reaction side
3	hydrogen membrane side

CO_2 concentration over the methanol synthesis catalyst surface increases catalyst activity and lifetime [10].

Process intensification consists of development novel equipments and integration of conventional processes to create dramatic improvements in manufacturing and processing. Process integration offers many advantages compared to the conventional processes, particularly in the reaction–separation systems. Although integration can increase production and decrease capital and operating costs, the integrated processes exhibit some disadvantages compared to conventional processes. The operability and controllability of integrated processes are very complex and should be investigated using dynamic simulation. Membrane reactors as an integrated process combine a catalytic reactor with a membrane to add reactants or remove products from reaction. Product removal from the reaction environment increases the residence time in the reactor and shifts equilibrium toward completion.

Rahimpour et al. improved methanol production in an industrial methanol reactor by a Pd/Ag based hydrogen-permselective membrane tube [11]. Gallucci et al. showed that higher CO_2 conversion, higher selectivity and methanol yield are advantages of novel membrane methanol reactor compared to the traditional reactor [12]. Farsi and Jahanmiri modeled a dual-membrane reactor for methanol production at steady state condition [13]. The dual-membrane reactor consists of water and hydrogen membrane tubes for simultaneous hydrogen permeation and water vapor removal from the reaction zone. This configuration enhanced about 10% additional yield compared to conventional process in the same operating conditions.

There is no work about dynamic modeling of dual-membrane reactor in the literature. In this paper, a dual-membrane reactor to produce methanol is modeled and the effect of long term catalyst deactivation on the production rate has been investigated. Also, the operability of the considered dual-membrane reactor is analyzed and compared to the conventional reactor at dynamic condition. This configuration can increase methanol production by shift the thermodynamic equilibrium limitation. However, the effect of temperature and concentration on the catalyst deactivation rate can change the efficacy of membrane reactor during the operational time. Thus, the main goal of this study is the performance investigation of dual-membrane reactor configuration to produce methanol during 1200 days of operation. To verify the accuracy of the considered model, the simulation results for conventional reactor are compared with the plant data.

2. Process description

2.1. Conventional methanol reactor

Commercially, the methanol synthesis process from natural gas consists of synthesis gas preparation, methanol synthesis and methanol separation sections. First, methane is mixed with steam and reformed to carbon oxides and hydrogen over nickel catalyst. In the methanol synthesis section carbon oxide and hydrogen reacts to form methanol and water mixture. One of the most widely used commercial isothermal methanol reactors is the Lurgi Methanol Converter. This reactor operates at pressures of 50–100 bar and temperatures between 230 and 265 °C and uses a