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Sorption-enhanced methanol synthesis in a dual-bed reactor: Dynamic modeling and simulation

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ABSTRACT

This work considers a dynamic mathematical model of a dual-bed multifunctional methanol reactor (DMMR) in the face of long term catalyst deactivation. A configuration of two catalyst beds instead of one single bed with selective adsorption of water inside the first bed is developed for methanol production. Synthesis gas and flowing adsorbents are both fed to the first reactor of DMMR. Contact of gas and fine solid particles inside packed bed results in the selective adsorption of water from the methanol synthesis system which increases temperature and methanol production. This reactor functions at a higher than normal operating temperature and at very high yield. In the second converter, the heat of reaction is used to pre-heat the synthesis gas to the first bed. Thus, a more favorable temperature profile is observed in DMMR compared to single-bed multifunctional methanol reactor (SMMR), and conventional methanol reactor (CMR). This way, the catalysts are exposed to less extreme temperatures and hence, declining the catalyst deactivation *via* sintering. Moreover, a differential evolution (DE) algorithm as a robust method is applied to optimize the reactors length ratio. The results of this study show a higher methanol production and longer catalyst lifetime for DMMR.

1. Introduction

Methanol is a clear biodegradable liquid petrochemical that is manufactured on a large scale in the world. It is utilized as fuel, solvent, and building block to produce chemical intermediates [1] and made from synthesis gas in a series of three reactions [2–5].

As a consequence of thermodynamic limitations of methanol synthesis process, only certain per-pass reactant conversions can be achieved in the reactor units. So, it is a common practice to introduce product separators and reactant recycle loops to obtain a reasonable degree of reactant utilization in such a reactor unit. These methods are usually complicated and expensive [6]. A practical solution to by-pass the thermodynamic limitation of many processes is to use a sorption-enhanced reaction process in a multifunctional reactor. In this equipment, an additional phase, flowing solids which are selective adsorbents, is introduced to the reaction zone and the equilibrium is shifted toward the formation of more products. These fine solid particles (adsorbents) and gas flow co-currently (or counter-currently) through the column packed with other solid phase (catalysts). Multifunctional reactor can be considered as two-phase or three-phase system [7]. The idea of contacting gas and fine solid particles (flowing solids) inside a packed bed was patented nearly sixty years ago [8]. Westerterp et al. [9], Nikacevic et al. [10], and Iliuta et al. [11] performed various studies to evaluate the performance of different sorption-enhanced reaction processes.

Recently, a novel idea is proposed for methanol synthesis based on a sorption-enhanced reaction process with zeolite 4A as the water adsorbent which is flowing in a single-bed multifunctional methanol reactor (SMMR) [2,3]. *In situ* H_2O removal in this reactor leads to the displacement of water gas-shift equilibrium and subsequently, enhances CO_2 conversion into methanol using sorption-enhanced reaction process [11]. Fig. 1 shows a 7 m long SMMR and a heat exchanger as the feed gas pre-heater.

The main subject of this paper is to boost the efficiency of methanol synthesis process at low price and in large quantities in a dual-bed multifunctional methanol reactor (DMMR) by means of *in situ* water adsorption. A DMMR consists of shell and tube heat exchanger reactors in which the first reactor, water-cooled reactor, is combined in series with the second reactor, gas-cooled reactor.

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Nomenclature

Symbol	Definition
A_c	cross section area of each tube (m^2)
A_i	inner area of each tube (m^2)
A_o	outside are of each tube (m^2)
Ar	Archimedes number for flowing solid particles ($= d_p^3\rho_g(\rho_p-\rho_g)g/\mu^2$)
a	activity of catalyst
a_s	specific surface area of catalyst pellet (m^2/m^3)
a'_s	specific surface area of flowing solid (m^2/m^3)
C_d	drag coefficient
Cp_g	specific heat of the gas at constant pressure (J/(mol K))
Cp_s	specific heat of the catalyst at constant pressure (J/(mol K))
Cp'_s	specific heat of the flowing solid at constant pressure (J/(mol K))
c_t	total concentration (mol/m^3)
D_i	tube inside diameter (m)
D_{ij}	binary diffusion coefficient of component i in j (m^2/s)
D_{im}	diffusion coefficient of component i in the mixture (m^2/s)
D_o	tube outside diameter (m)
d_{eq}	equivalent diameter of packing particles ($= 6(1-\varepsilon)/(a_s + (4/D))$) (m)
d_s	catalyst diameter (m)
d'_s	flowing solid diameter (m)
F_i	molar flow of species i (mol/s)
F_t	total molar flow (mol/s)
F^{Tube}	total molar flow per tube (mol/s)
F^{shell}	total molar flow per shell (mol/s)
G	mass flux of gas (kg/(m^2 s))
ΔH_{ads}	specific heat of adsorption (J/mol)
$\Delta H_{f,i}$	enthalpy of formation of component i (J/mol)
ΔH_{298}	enthalpy of reaction at 298 K (J/mol)
h_f	gas-catalyst heat transfer coefficient (W/(m^2 K))
h'_f	gas–solid heat transfer coefficient (W/(m^2 K))
h_i	heat transfer coefficient between fluid phase and reactor wall (W/(m^2 K))
h_o	heat transfer coefficient between coolant stream and reactor wall (W/(m^2 K))
K	conductivity of fluid phase S (W m/K)
k_{gi}	gas-catalyst mass transfer coefficient for component i (m/s)
k'_g	gas–solid mass transfer coefficient (m/s)
L	length of reactor (m)
M_i	molecular weight of component i (g/mol)
N	number of components used in the model ($N = 7$)
P	total pressure (bar)
q	concentration of water adsorbed in flowing solids (mol/kg)
q_e	equilibrium concentration of adsorbed water (mol/kg)
R	universal gas constant (J/(mol K))
Re_s	Reynolds number of packing elements
Re'_s	Reynolds number of flowing solids
r_i	reaction rate of component i (mol/(kg s))
S	mass flux of flowing solids (kg/(m^2 s))
T_g	bulk gas phase temperature (K)
T_s	temperature of catalyst phase (K)
T'_s	temperature of flowing solids (K)
T_{shell}	temperature of coolant stream (K)
U_{shell}	overall heat transfer coefficient between coolant and process streams (W/(m^2 K))
U_g	real gas velocity ($= G/\rho_g\varepsilon'$) (m/s)
u_g	superficial gas velocity (m/s)
u_r	relative velocity for co-current flow of gas and flowing solids ($= U_g - u'_s$) (m/s)
u'_s	real flowing solids velocity ($= S/\rho'_s\beta$) (m/s)
y_i	mole fraction of component i in the fluid phase (mol/mol)
y_{is}	mole fraction of component i in the catalyst phase (mol/mol)
z	axial reactor coordinate (m)

Greek letter

β	flowing solids holdup ($= \beta_d + \beta_s$)
β_d	dynamic flowing solids holdup
β_s	static flowing solids holdup
ε	void fraction of catalytic bed (m^3/m^3)
ε_s	void fraction of catalyst
ε'	void fraction corrected due to presence of the flowing solids ($= \varepsilon - \beta$) (m^3/m^3)
ϕ	sphericity of packed bed element
η	effectiveness factor
μ	dynamic viscosity (pa s)
ρ_B	void fraction corrected due to presence of the flowing solids ($= \varepsilon - \beta$) (m^3/m^3)
ρ_g	gas density (kg/m^3)
ρ_s	catalyst density (kg/m^3)
ρ'_s	flowing solid density (kg/m^3)

Superscripts

ss	initial condition (*i.e.*, steady-state condition)

A multifunctional concept is used in the water-cooled reactor that would be an effective way to by-pass the thermodynamic limitations of methanol synthesis. Besides, the outlet of this reactor is routed to the gas-cooled reactor where the cold feed synthesis gas for the first reactor flows in counter-current mode with the reacting gas mixture. This configuration permits a high temperature in the first bed and a low temperature in the second bed. It also results in a no longer needing of a pre-heater for the feed gas and a continuous reduction in the reaction temperature across the whole catalyst bed of the gas-cooled reactor, in order to sustain the equilibrium driving force for the reaction [1]. Both SMMR and first reactor of DMMR are of the same configuration with the exception of being 4.9 m long in the water-cooled reactor. The first reactor of DMMR length is 2.1 m less than that in SMMR, consequently a lower amount of adsorbent is required in this reactor. During the whole process, a continuous regeneration of zeolite 4A is carried out in a solids regenerator. In addition, pre-heating the cold feed gas inside the shells of second reactor is another advantage of this design.

Lately, Bayat et al. conducted a variety of studies on sorption-enhanced reaction process, including: a steady-state modeling and multi-objective optimization of methanol synthesis *via*