Methanol synthesis via sorption-enhanced reaction process: Modeling and multi-objective optimization

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ABSTRACT

Since liquid hydrocarbon fuels dominate the transportation sector for the foreseeable future, methanol could potentially be used as a much cleaner fuel than conventional petroleum-based fuels. Thus, development of methanol synthesis process to improve the methanol productivity has attracted increasing attention. This paper describes a steady-state mathematical model of a gas-flowing solids-fixed bed reactor (GFSFBR) with in situ water adsorption for methanol synthesis. Simulation result demonstrates that selective adsorption of water from methanol synthesis in GFSFBR leads to a significant enhancement in methanol production compared to zero solids mass flux condition. The remarkable advantage of GFSFBR over the conventional sorption-enhanced reaction process is the continuous adsorbent regeneration in this system. In the next step, a multi-objective optimization of GFSFBR is performed in order to maximize the methanol production rate and selectivity. Consequently, non-dominated sorting genetic algorithm-II (NSGA-II) is applied as a powerful method to optimize the GFSFBR. Optimization result has shown that there are optimal values of inlet temperature of gas and flowing solid phases, mass flux of flowing solids, flowing solid diameter, and pressure under which the highest methanol production rate and selectivity can be achieved. This paper shows how the concept of in situ water adsorption could be feasible and beneficial for methanol synthesis.

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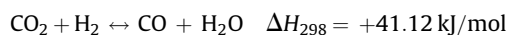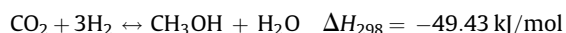
1. Introduction

Rising energy prices and global warming increases the attention to use of alternative fuels. The viability of alcohol as a fuel is a debatable issue owing to the requirement of other energy sources for production. Methanol has been considered as a fuel due to its physical and chemical properties and it has demonstrated to be an attractive automotive fuel.

1.1. Methanol

Methanol is one of the essential building blocks of the chemical industry and one of the highest volume commodity chemical produced in the world today. It is widely used as a primary raw material in many chemical processes such as formaldehyde and acetic acid production. Methanol is produced commercially by catalytic conversion of synthesis gas (H_2, CO_2, and CO) over $CuO/ZnO/Al_2O_3$ catalyst. In general, a minor improvement in production efficiency of important chemicals such as methanol may lead to remarkable profit increase, energy

conservation, and environmental protection [1]. Consequently, numerous studies have been conducted in an attempt to improve the efficiency of industrial methanol synthesis reactor [2–5].

In the conversion of synthesis gas to methanol, three overall reactions are mainly involved: hydrogenation of CO, hydrogenation of CO_2, and reversed water-gas shift (WGS) reaction due to the presence of water that causes the reaction of CO with H_2O and converts CO to CO_2 [6], which represented as follows:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H_{298} = -90.55\,kJ/mol$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{298} = -49.43\,kJ/mol$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298} = +41.12\,kJ/mol$$

The aforementioned reactions are not independent so, hydrogenation of CO_2 is a linear combination of the others. In the current study, the rate expressions have been selected from Graaf *et al.* [7].

As a consequence of thermodynamic limitations of methanol synthesis process, only certain per-pass reactant conversions can be achieved in the reactor units. Hence, it is a common practice to

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Nomenclature

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_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 per tube (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 solid (−)
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 solid (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)
ug	superficial gas velocity (m/s)
u_r	relative velocity for co-current flow of gas and flowing solid, ($= U_g - u_s'$) (m/s)
u_s'	real flowing solid 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 letters

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'	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	catalytic bed density (kg/m^3)
ρ_g	gas density (kg/m^3)
ρ_S	catalyst density (kg/m^3)
ρ_S'	flowing solids density (kg/m^3)

introduce product separators and reactant recycle loops to obtain a reasonable degree of reactant utilization in such a reactor unit. These methods are usually cumbersome and expensive [8].

1.2. Gas-flowing solids-fixed bed reactor (GFSFBR)

A practical solution to by-pass the thermodynamic limitation of many processes is using a sorption-enhanced reaction process in a gas-flowing solids-fixed bed reactor (GFSFBR). 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). GFSFBRs can be considered as two phase or three phase systems [9].

In this work, a novel idea is proposed for methanol synthesis based on sorption-enhanced reaction process with zeolite 4A as the water adsorbent. Zeolite 4A is a solid particle, with the composition of $Na_{12}(Si_{12}Al_{12}O_{48})\cdot 27H_2O$. Its high water adsorption capacity makes it interesting in water removal or separation [10]. The three phase system consists of synthesis gas and solids trickle flow over catalyst packed bed for methanol synthesis is illustrated in Fig. 1.

During methanol synthesis in GFSFBR, in situ H_2O removal could lead to the displacement of water gas-shift equilibrium and subsequently, enhances CO_2 conversion into methanol using sorption-enhanced reaction process [11]. GFSFBR has favorable properties such as low pressure drop, high mass and heat transfer rates, low axial dispersion in both flowing phases, and regenerability of the adsorbent. The practical issue involved in