



Membrane/sorption-enhanced methanol synthesis process: Dynamic simulation and optimization



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ABSTRACT

In this study, a dynamic mathematical model of a Membrane-Gas-Flowing Solids-Fixed Bed Reactor (Membrane-GFSFBR) with in-situ water adsorption in the presence of catalyst deactivation is proposed for methanol synthesis. The novel reactor consists of water adsorbent and hydrogen-permselective Pd-Ag membrane. In this configuration feed gas and flowing adsorbents are both fed into the outer tube of the reactor. Contact of gas and fine solids particles inside packed bed results in selective adsorption of water from methanol synthesis which leads to higher methanol production rate. Afterwards, the high pressure product is recycled to the inner tube of the reactor and hydrogen permeates to the outer tube which shifts the reaction towards more methanol production. Dynamic simulation result reveals that simultaneous application of water adsorbent and hydrogen permeation in methanol synthesis process contributes to a significant enhancement in methanol production. The notable advantage of Membrane-GFSFBR is the continuous adsorbent regeneration during the process. Moreover, a theoretical investigation has been performed to evaluate the optimal operating conditions and to maximize the methanol production in Membrane-GFSFBR using differential evolution (DE) algorithm as a robust method. The obtained optimization result shows there are optimum values of inlet temperatures of gas phase, flowing solids phase, and shell side under which the highest methanol production can be achieved.

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1. Introduction

As a result of increasing rate of the world oil consumption, pollutant emission from diesel engines, and global warming, the development of alternative clean energy sources such as alcohols and ethers has attracted a great deal of attention. These alternative fuels and fuel additives are less polluting and present good burning characteristics.

1.1. Methanol

Methanol, also named as methyl alcohol or wood alcohol, is a multipurpose base chemical with a simple molecular structure which can be derived from abundant energy resources, predominantly natural gas. Thermodynamic equilibrium limitations and catalyst deactivation are factors affecting the methanol production rate in an industrial reactor [1]. This alcohol and its derivatives are important in several industrial processes and useful in the production of fuels, pesticides, and drugs [2]. Hence, there have

been numerous studies conducted to develop the efficiency of the industrial methanol synthesis reactor [3–6].

Hydrogenation of CO, hydrogenation of CO₂, and reversed water-gas shift (WGS) reaction caused by presence of water which makes the reaction of CO with H₂O happen and converts CO to CO₂ [7], are three overall reactions involved in the methanol synthesis process (see Table 1).

(r_1)–(r_3) are not independent accordingly, (r_2) is a linear combination of the others. In this study, the kinetic rate expressions have been adopted from Graaf et al. [8].

1.2. Mechanism

A great deal of researches has been carried out to understand the mechanism of methanol synthesis reaction for a wide variety of catalysts under different operating conditions. It is assumed that the primary source of carbon in methanol is CO₂ [9]. Accordingly, the mechanistic details of the hydrogenation of CO₂ into methanol on a Cu surface can be summarized as the elementary reaction steps presented in Table 2.

Among these elementary reactions, steps (c)–(g) comprise the major steps in methanol synthesis. An illustration of the proposed mechanism by Hu et al. [9] is also depicted in Fig. 1.

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Table 1
Reactions involved in methanol synthesis.

Hydrogenation of CO (r_1):	$\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$	$\Delta H_{298} = -90.55 \text{ kJ mol}^{-1}$
Hydrogenation of CO_2 (r_2):	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	$\Delta H_{298} = -49.43 \text{ kJ mol}^{-1}$
Reversed WGS reaction (r_3):	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$	$\Delta H_{298} = +41.12 \text{ kJ mol}^{-1}$

Table 2
Elementary reaction steps of the hydrogenation of CO_2 into methanol on a Cu surface [9].

$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{a})^{\text{a}}$	(a)
$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{a})$	(b)
$\text{CO}_2(\text{a}) + 2\text{H}(\text{a}) \rightarrow \text{HCOO}(\text{a}) + \text{H}(\text{a})$	(c)
$\text{HCOO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{H}_2\text{COO}(\text{a})$	(d)
$\text{H}_2\text{COO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{H}_2\text{CO}(\text{a}) + \text{OH}(\text{a})$	(e)
$\text{H}_2\text{CO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{H}_3\text{CO}(\text{a})$	(f)
$\text{H}_3\text{CO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{CH}_3\text{OH}$	(g)
$\text{OH}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{H}_2\text{O}$	(h)

^a H(a): adsorbed hydrogen.

The results showed that chemisorbed CO_2^- , formate, dioxomethylene, formaldehyde, and methoxy are the main intermediates in methanol synthesis [9].

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

Application of Gas-Flowing Solids-Fixed Bed Reactor (GFSFBR) using the concept of sorption-enhanced reaction is a practical solution to by-pass the thermodynamic limitation of several processes. In order to shift the equilibrium toward more product formation in these systems, flowing solids with the selective adsorption capability are introduced to the reaction zone as the additional phase. Gas phase along with fine adsorbent particles is flowing through the packed bed of catalyst in a co-current or counter-current operation. Two phase or three phase system can be considered in this type of equipment [10].

In the case of methanol synthesis, a novel idea is proposed in current study based on the sorption-enhanced reaction process, considering zeolite 4A as the water adsorbent. Zeolite 4A is a solid particle with the composition of $\text{Na}_{12}(\text{Si}_{12}\text{Al}_{12}\text{O}_{48}) \cdot 27\text{H}_2\text{O}$ and high water adsorption affinity that makes it desirable for water removal or separation [11]. In-situ water removal in a gas-flowing solids-fixed bed methanol synthesis reactor contributes to the displacement of WGS equilibrium which enhances CO_2 conversion into methanol via a sorption-enhanced reaction process [12]. Fig. 2 presents the three-phase methanol synthesis system consisting of synthesis gas and solids trickle flow over the catalyst packed bed.

Low pressure drop, low axial dispersion of flowing phases, high mass and heat transfer rates, and application of regenerable

adsorbents are the favorable features of GFSFBR. The discontinuous operation of the reactor is the principal problem involved in the conventional sorption-enhanced reaction process. Since the effects of separation are lost at the equilibrium state of the adsorbent, it is very important to execute a cyclic regeneration of solids during the whole process [12]. To overcome this predicament in GFSFBR, a continuous regeneration of zeolite 4A is performed based on desorption of water vapor. In most cases, dehydration of zeolites is carried out under vacuum or in a flow of carrier gas, with a simultaneous rise in temperature up to 300–400 °C [13]. Zeolite 4A crystal has a relatively good thermal stability and only at temperatures higher than 1073 K, the change in its structure accompanied by the decrease in its water capacity takes place [11].

1.4. Palladium-based membrane reactors

A membrane reactor combines a membrane separation process with a chemical reaction in one system. Membrane reactors have been applied to most common types of catalytic reactions, including dehydrogenation, hydrogenation as well as partial and total oxidation reactions [14]. The prevailing advantages of membrane reactors are: (1) improving the reaction rates, (2) declining the byproduct formation, (3) lowering the energy needs, and (4) the possibility of heat integration. These benefits potentially lead to the compact equipment requirements that can be operated with a high degree of flexibility [15]. Palladium-based membranes are utilized commercially to purify hydrogen and dehydrogenate organic molecules. The catalytic ability of the membrane surface in conjunction with the selectivity of hydrogen permeation makes it feasible to selectively shift the chemical equilibrium towards the product side [16]. Many investigations have been carried out, concerning the application of Palladium-based (Pd-Ag) membrane reactors for the methanol synthesis [17–23].

1.5. Process deficiencies and modifications

Owing to the thermodynamic limitations of methanol synthesis process, only specific per-pass reactant conversions can be obtained in the reactor units. Consequently, it is a prevalent practice to introduce product separators and reactant recycle loops

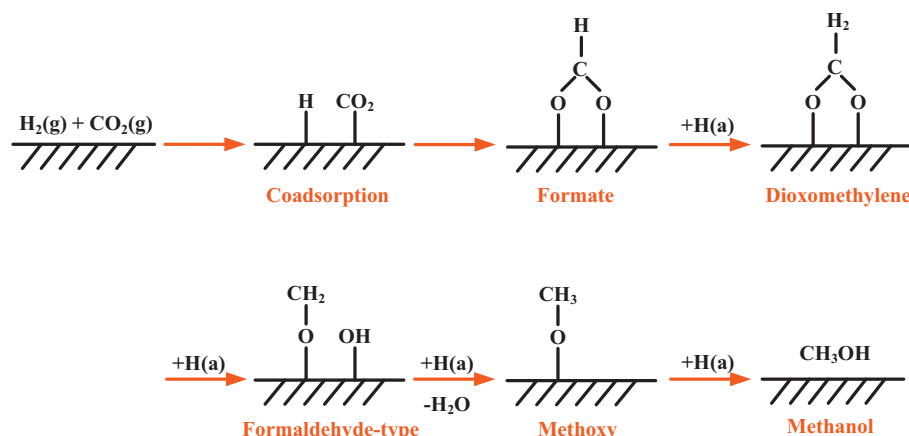


Fig. 1. Summary of methanol synthesis mechanisms [9].

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