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Sorption-enhanced methanol synthesis: Dynamic modeling and optimization

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ABSTRACT

Owing to the global energy concerns in today's world, alternative fuels such as methanol have become an increasingly attractive option to meet the growing power demand. This work considers a dynamic mathematical model of a gas-flowing solids-fixed bed reactor (GFSFBR) with in situ water adsorption for methanol synthesis in the face of long term catalyst deactivation. Contact of gas and fine solid particles inside packed bed results in the selective adsorption of water from the methanol synthesis that leads to higher methanol production compared to the conventional methanol reactor (CMR). Moreover, a theoretical investigation has been performed in order to evaluate the optimal operating conditions and maximize the methanol production in a GFSFBR using differential evolution (DE) algorithm as a robust method. Dynamic optimization result has shown that under optimum values of inlet temperature of gas phase, inlet temperature of flowing solid phase, and inlet temperature of shell side the highest methanol production can be achieved during the operating period.

1. Introduction

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

1.1. Methanol

Methanol, also called methyl alcohol or wood alcohol, is a multipurpose base chemical that has a simple molecular structure. It can be made from many plentiful energy resources, predominantly natural gas. Thermodynamic equilibrium limitations and catalyst deactivation are parameters that affect the rate of methanol production in an industrial reactor [1]. This alcohol and its derivatives are important in numerous industrial processes and useful in production of fuels, pesticides, and drugs [2]. Hence, there have been a lot of studies conducted to improve the efficiency of the industrial methanol synthesis reactor [3–6].

Hydrogenation of CO, hydrogenation of CO_2, and reversed water–gas shift (WGS) reaction due to the presence of water that makes the reaction of CO with H_2O happen and converts CO to CO_2 [7], are the three overall reactions involved in the methanol synthesis process (see Table 1).

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

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

Using the idea of sorption-enhanced reaction in a gas-flowing solids-fixed bed reactor (GFSFBR) is a practical solution to by-pass the thermodynamic limitation of several processes. In these systems, flowing solids, as the additional phase with the selective adsorption capability, are introduced to the reaction zone in order to shift the equilibrium toward more products formation. Gas phase along with these 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 [9].

In the case of methanol synthesis, a novel idea is proposed in the 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 $Na_{12}(Si_{12}Al_{12}O_{48})\cdot 27H_2O$ and high water adsorption affinity which makes it favorable for water removal or separation [10]. In situ water removal in a gas-flowing solids-fixed bed methanol synthesis reactor contributes to the displacement of water gas-shift equilibrium which increases CO_2 conversion into methanol through a sorption-enhanced reaction process [11].

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Table 1
Reactions involved in methanol synthesis.

Hydrogenation of CO (r_1):	$CO + 2H_2 \leftrightarrow CH_3OH$	$\Delta H_{298} = -90.55$ kJ/mol
Hydrogenation of CO_2 (r_2):	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	$\Delta H_{298} = -49.43$ kJ/mol
Reversed WGS reaction (r_3):	$CO_2 + H_2 \leftrightarrow CO + H_2O$	$\Delta H_{298} = +41.12$ kJ/mol

Low pressure drop, low axial dispersion of flowing phases, high mass and heat transfer rates, and application of regenerable adsorbents are the favorable characteristics of GFSFBR. A dominant problem involved in the conventional sorption-enhanced reaction process is the discontinuous operation of the reactor. Since the effects of separation are lost at the equilibrium state of the adsorbent, it is essential to perform a cyclic regeneration of solids during the whole process [11]. In order to overcome this predicament, a continuous regeneration of zeolite 4A is carried out in GFSFBR based on desorption of water vapor. In most cases, dehydration of zeolites is carried out under vacuum or by a flow of carrier gas, with a simultaneous rise in temperature to 300–400 °C [12]. Zeolite 4A crystal has a relatively good thermal stability and the change of its structure accompanied by the decrease in its water capacity takes place only at temperatures higher than 1073 K [10].

1.3. Dynamic simulation

Dynamic modeling of processes has gained much more attention to describe a wide range of applications including: start-up and shut-down investigations, system identification, safety, control, optimization, transient behavior, and operability studies. In operability studies, due to the application of more powerful numerical strategies in the solution of dynamic models compared to the steady-state ones, the realistic description of the transient states obtained through dynamic simulation are more trustworthy than the steady-state solution. As a result, it is more secure and reliable to study the optimization and control of methanol synthesis reactor by a dynamic simulator [13,14].

1.4. Optimization

Dynamic optimization has its particular jargon to address specific features of the problem. Most of the optimization problems in the process industry can be broken down into non-linear, non-convex, and constrained optimization problems [15]. The important plant parameters which are chosen for optimization are equipment size, recycle flows, and operating conditions such as concentration, temperature and pressure. An optimum design is based on the best or the most favorable conditions. Almost always, these optimum conditions can eventually be reduced to a consideration of profits or costs. Consequently, an optimum economic design could be achieved based on conditions giving the highest profit per unit of production or the lowest cost per unit of time. When one design variable is changed, it is frequently found that some costs rise and the others reduce. Under these circumstances, the total cost can be achieved with minimum amount at one value of the specific design variable, and this value would be considered as an optimum.

Common optimization techniques have limited applications. The main difficulty in using these techniques is the feasibility of identifying the local optimum instead of global one owing to their sensitivity to initial guess. Considering this fact, it is essential to develop more useful optimization techniques based on natural phenomena (evolutionary computation), including: simulated annealing (SA) [16], evolution strategies (ESs) [17], genetic algorithms (GAs) [18,19] and differential evolution (DE) algorithm [20].

1.5. Literature review

The concept of contacting gas and fine flowing solid particles within a packed bed was proposed about sixty years ago [21]. Kuczynski et al. [22] investigated an experimental study of methanol synthesis in a counter-current gas–solid–solid trickle flow reactor and considered amorphous LA-25 low-alumina cracking as methanol adsorbent. The obtained result indicated a higher conversion of the reactants for the situation of removing product from the reactor. In 1988, Westerterp et al. [23] compared the intensified process with the conventional methanol synthesis in a highly optimized Lurgi process. They reported a considerable energy saving in the synthesis loop as a result of reduction in the recirculation rate and pressure drop inside the reactor. A steady-state mathematical model for ammonia synthesis with in situ adsorption in a co-current gas-flowing solids-fixed bed reactor was developed by Nickacevic et al. [24]. Modeling result showed that the conversion stays higher than those in the conventional reactor even if the reactor performs at much lower temperatures and pressures. In order to evaluate the performance of sorption-enhanced dimethyl ether (DME) synthesis reactor, Iliuta et al. [11] recommended an isothermal, unsteady-state model of the process. The yields of methanol and DME as well as DME selectivity were favored and a reduced fraction of unconverted methanol was observed under H_2O removal conditions. On the other hand, there have been a lot of studies on the optimization of methanol synthesis in the literature. A novel radial-flow spherical-bed methanol synthesis reactor was optimized by Rahimpour et al. [25] using DE algorithm to maximize the overall methanol production. Parvasi et al. [15] simulated and optimized methanol synthesis loop with membrane reactor. Dynamic optimization of temperatures was implemented for improving the overall methanol production using DE method. Networks (NTWs) of four catalytic reactors with periodically switched inlet and outlet sections for reversible exothermic reactions of methanol synthesis were studied by Mancusi et al. [26,27] and Altimari and Mancusi [28]. They analyzed the effects of various switching strategies on the NTW stability and performance. Recently, Bayat et al. [29] proposed a steady-state mathematical model of a gas-flowing solids-fixed bed reactor (GFSFBR) for methanol synthesis and a multi-objective optimization of GFSFBR operating conditions with the purpose of maximizing methanol production rate and selectivity using NSGA-II algorithm. They also proposed a multifunctional reactor (MR) for simultaneous production of hydrogen and methanol with the application of GFSFBR in the exothermic side of this novel configuration. Then, they performed an optimization of MR using DE algorithm, in order to maximize both hydrogen mole fraction and methanol yield [30].

1.6. Objective

The presence of flowing adsorbents inside the methanol synthesis packed bed reactor results in the significant changes in transport characteristics of GFSFBR along with a more complex flow pattern and solving procedure. Besides, it is functionally more demanding to apply a GFSFBR with continuous adsorbent regeneration than a conventional reactor [31]. Dynamic modeling of a gas-flowing solids-fixed bed methanol synthesis reactor considering the simultaneous effects of water vapor adsorption and catalyst deactivation as well as optimization of GFSFBR operating conditions using DE algorithm is the goal of the present study. A critical examination of the literature reveals that there is no information available regarding the use of GFSFBR with in situ

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