Research article

Investigation of the efficiency of sorption-enhanced methanol synthesis process in circulating fast fluidized bed reactors

M.E.E. Abashar*, A.A. Al-Rabiah

Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

A B S T R A C T

The concept of circulating fast fluidization with in-situ water removal using zeolite-4A particles is introduced to the methanol synthesis process. The mathematical model of a circulating fast fluidized bed reactor (CFFBR) is validated by an actual industrial plant data. Also, the industrial plant feed data is used to test the performance of a bubbling fluidized bed reactor (FBR). The CFFBR with varying adsorbent compositions is investigated. The system exhibits optimum conditions at a low feed temperature of 201.75 °C due to water removal and thermodynamic equilibrium shift. The methanol production has substantially increased about 14-folds. The increase of the adsorbent mass concentration > 50.0% has a little effect on the maxima due to the total conversion of carbon. It is interesting to note that feeds rich in CO_2 and lean in CO are susceptible to a significant improvement of methanol production. The sensitivity analysis shows that the increase of H_2 in the feed decreases CO formation and consequently increases the carbon conversion to methanol. Moreover, the pressure is more effective at low ranges due to a high carbon conversion. The high efficiency shown by the CFFBR in this study suggests a promising application of these reactor generations in the methanol industry.

1. Introduction

Methanol (MeOH) is the simplest form of alcohol (CH_3OH). It is an oxygenated (50.0 wt% O_2) liquid fuel at room temperature with many desirable properties. Methanol can easily be transported and stored in a liquid form. It has lower carbon content and emissions compared to other liquid fuels. Methanol can be used as a direct fuel or blended with gasoline [1, 2]. It is also used to power reformed methanol fuel cells (RMFC) and direct methanol fuel cells (DMRC) [3–7]. As a source of carbon and hydrogen, methanol is considered as one of the most important feedstock for many basic industries such as: acetic acid, formaldehyde, MTBE, dimethyl ether (DME), dimethyl carbonate (DMC), gasoline and olefins (methanol-to-olefins, MTO) [8–17]. On the other hand, methanol is highly toxic and can cause blindness [17–19]. The compelling benefits and steady increase in methanol demand worldwide have imposed great challenges on academia-research and industry for continuous improvement with respect to catalysts, design, operation and control of methanol synthesis process.

Conventional processes such as ICI (synetix) and BASF have been used to produce methanol from syngas (H_2, CO_x) by gas phase heterogeneous catalytic reactions in fixed bed reactors over (Cu-ZnO/Al_2O_3, Cu-ZnO/Cr_2O_3) and ZnO-Cr_2O_3 (zinc chromite) catalyst, respectively. The ICI process is operated at a low pressure of 50–100 bar and a temperature of 200–250 °C, while the BASF process is operated at a high pressure of 250–350 bar and a temperature of 300–400 °C [9, 11, 20–26]. The ICI technology is implemented by different companies such Lurgi, Haldor Topsøe, Gas Chemicals, Mitsubishi and Davy Process Technology [8]. Methanol fixed bed reactors suffer from thermodynamic limitations, intra-particle diffusion limitations (low effectiveness factor), catalyst deactivation, large pressure drop, hot spots and runaway phenomena [9, 26–28]. Several studies dealing with methanol synthesis in different reactor configurations such as the slurry reactor, fluidized bed reactor and trickle bed reactor have been reported in the literature [8, 9, 12, 29, 30].

In the last few years, much attention has been paid to the role of selective water adsorbents and membranes for the displacement of thermodynamic barriers [11, 31, 32]. The pioneering work of Zhu et al. [33] has reported that zeolite-4A crystals have a high adsorption affinity and capacity of water (28.51 wt%). Moreover, the zeolite-4A crystals can be used at elevated temperatures (up to 800 °C), owing to their thermal stability. Bayat et al. [11, 13, 15] have published remarkable papers on the benefits that can be gained by in-situ removal of water by zeolite-4A for several configurations of sorption-enhanced methanol synthesis process.

In recent years, the advantages and the potential industrial applications of circulating fast fluidized bed reactors (CFFBR) have been
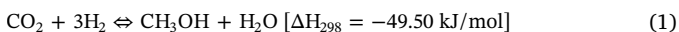
---

acknowledged by many investigators [34–37]. Among the advantages of the CFFBRs are: effective gas-solids contacting with less gas by-pass, reduced gas-solid backmixing, effective solids circulation, uniform solids and temperature distribution, allows high gas flowrate, negligible intra-particle diffusion resistances and efficient solid regeneration capability [38–40]. Surprisingly, the application potential of these versatile reactors in the methanol industry yet has received little attention and not an area of active research.

The purpose of this study is to implement a circulating fast fluidized bed reactor (CFFBR) in a methanol synthesis process and to explore and evaluate the performance of the reactor for efficient production of methanol. Furthermore, the impact of in-situ water removal by zeolite-4A particles on the thermodynamic constraints and reactor performance is thoroughly investigated. In this respect, a reactor bed of the catalyst and zeolite-4A particles with different compositions is employed. In addition, a parametric study is conducted to assess the influence of temperature, pressure and H_2/CO_x ratio on the performance of the reactor. In order to achieve these goals, the powerful mathematical modeling and simulation approach is considered. We hope through this approach more insight into the benefits of the CFFBRs in methanol production are gained.
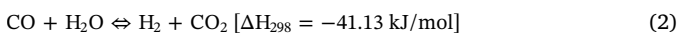
2. Reaction kinetics

A comprehensive summary of methanol kinetic models has been given by Bussche and Froment [41]. In general, three dependent chemical reactions involved in methanol formation:
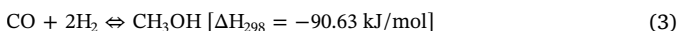
Hydrogenation of CO_2:

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \ [\Delta H_{298} = -49.50 \text{ kJ/mol}] \tag{1}$$

Water-gas shift reaction (WGS):

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \ [\Delta H_{298} = -41.13 \text{ kJ/mol}] \tag{2}$$

Hydrogenation of CO:

$$CO + 2H_2 \Leftrightarrow CH_3OH \ [\Delta H_{298} = -90.63 \text{ kJ/mol}] \tag{3}$$

Two different main views as bases for developing the kinetic models for methanol synthesis have been reported in the literature [41]. The first view claims that the main carbon source in methanol is CO, and CO_2 has a promotion effect and increases the catalyst activity in small concentrations due to its ability to oxidize Cu^0 to Cu^+. Moreover, CO_2 has an inhibitory effect and decreases the catalyst activity at high concentrations owing to its strong adsorption on the active sites [42]. The second view claims that the main carbon source in methanol is CO_2, and CO reacted to form CO_2 by the water-gas shift reaction. And, the excessive water formed at high concentrations of CO_2 has an inhibitory effect due to blockage sites by the water causing decrease in catalyst activity [41]. It is worth mentioning that the kinetic model supported this view able to predict satisfactorily the experimental data of the first view [41]. In this study, the kinetic model based on the second view is implemented; because the model is developed with a view backed by mechanisms and had a satisfactory predictive performance. Moreover, this model uses the common surface oxygen intermediate to couple overall rate of reactions, so it is quite different from some other kinetic models that have been published. Lei et al. [43] have implemented this kinetics to model an actual industrial quasi-isothermal Lurgi reactor satisfactorily. According to the kinetic model of Bussche and Froment [41], the rate expression for reaction (1) and (2) are given as follows:

$$R_1 = \frac{k_1 P_{CO_2} P_{H_2} \left[1 - \frac{(P_{H_2O} P_{CH_3OH})/(P_{H_2}^3 P_{CO_2})}{K_1^e}\right]}{[1 + K_1(P_{H_2O}/P_{H_2}) + K_2\sqrt{P_{H_2}} + K_3 P_{H_2O}]^3} \tag{4}$$

$$R_2 = \frac{k_2 [K_2^e (P_{H_2O} P_{CO}/P_{H_2}) - P_{CO_2}]}{[1 + K_1(P_{H_2O}/P_{H_2}) + K_2\sqrt{P_{H_2}} + K_3 P_{H_2O}]} \tag{5}$$

where:

$$k_1 = 1.07 \times 10^{-3} \exp\left(\frac{36.696 \times 10^3}{RT}\right) \quad , \frac{kmol}{kg_{cat}\,s\,bar^2} \tag{6}$$

$$k_2 = 1.22 \times 10^7 \exp\left(-\frac{94.765 \times 10^3}{RT}\right) \quad , \frac{kmol}{kg_{cat}\,s\,bar} \tag{7}$$

$$K_1 = 3453.38 \quad , [-] \tag{8}$$

$$K_2 = 0.499 \exp\left(\frac{17.197 \times 10^3}{RT}\right) \quad , bar^{-1/2} \tag{9}$$

$$K_3 = 6.62 \times 10^{-11} \exp\left(\frac{124.119 \times 10^3}{RT}\right) \quad , bar^{-1} \tag{10}$$

$$\log_{10} K_1^e = \frac{3066}{T} - 10.592 \tag{11}$$

$$\log_{10} 1/K_2^e = -\frac{2073}{T} + 2.029 \tag{12}$$

3. Mathematical modeling

Models are developed for a circulating fast fluidized bed reactor (CFFBR) and a freely bubbling fluidized bed reactor (FBR).

3.1. Circulating fast fluidized bed reactor (CFFBR) model

Fig. 1 shows a schematic diagram of the circulating fast fluidized bed reactor (CFFBR). A reactor model is developed with the following basic assumptions: steady state conditions, negligible axial and radial dispersion, uniform water adsorption, negligible interphase and intraparticle diffusion resistances due to the fine particles used.

The material balance equations for the components (CO_2, H_2, CO, CH_3OH, H_2O) are given by:

$$\frac{dF_{CO_2}}{dz} = (1 - \phi_2)\rho_s \varepsilon_{sd} A H [-R_1 + R_2] \tag{13}$$

$$\frac{dF_{H_2}}{dz} = (1 - \phi_2)\rho_s \varepsilon_{sd} A H [-3R_1 + R_2] \tag{14}$$

$$\frac{dF_{CO}}{dz} = (1 - \phi_2)\rho_s \varepsilon_{sd} A H [-R_2] \tag{15}$$

$$\frac{dF_{CH_3OH}}{dz} = (1 - \phi_2)\rho_s \varepsilon_{sd} A H [R_1] \tag{16}$$

$$\frac{dF_{H_2O}}{dz} = (1 - \phi_2)\rho_s \varepsilon_{sd} A H [R_1 - R_2] - \phi_2 \varepsilon_{sd} A G_s q \tag{17}$$

The energy balance can be written as:

$$\frac{dT}{dz} = \frac{\sum_{j=1}^{2} (1 - \phi_2)\rho_s \varepsilon_{sd} A H (-\Delta H_j) R_j - U\pi D (T - T_{sh}) H}{\sum_{i=1}^{n} F_i C_{Pi}} \tag{18}$$

where ε_{sd} is the average solids holdup at the dense region, and ρ_s is average solids density. ϕ_j is the mass fraction of particle j and given by:

$$\phi_j = \frac{mass\ of\ particle\ j}{total\ mass\ of\ solids} \quad , j = 1, 2 \tag{19}$$

and j = 1 and 2, refer to catalyst and adsorbent particles, respectively. G_s is the solid circulating rate given by:

$$G_s = U_s^o \rho_s \tag{20}$$

where U_s^o is the superficial solids velocity.

Collado [44–46] developed a new global momentum balance equation for vertical one-dimensional gas-solids flow based on