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Modeling and operability of DME production from syngas in a dual membrane reactor

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ABSTRACT

In this research, a conventional shell and tube reactor is supported by the hydrogen and vapor membrane tubes for water vapor removal and hydrogen permeation in the single step DME synthesis process. The proposed dual membrane structure is heterogeneously modeled based on the mass and energy conservation laws at steady state condition. To prove the accuracy of the developed model and assumptions, the simulation results of the conventional DME reactor are compared with the available data. Then, the performance and operability of the proposed structure is compared with the hydrogen membrane, water membrane and conventional reactors. The simulation results show that the DME production capacity in the dual membrane reactor is improved about 17.2% compared to the conventional process. Higher DME production rate due to shift the thermodynamic equilibrium limitations, and lower CO_2 production are the main advantages of the proposed reactor.

1. Introduction

Currently, the fossil fuels such as natural gas, coal, petroleum and derivatives are the main energy sources in the world, so the current century is called the era of fossil fuels (Arcoumanis et al., 2008). Dimethyl ether (DME) is one of the main derivatives from fossil fuels that it presents the excellent properties such as high cetane number, low volatility and low carbon dioxide and particulate matter emission (Ng et al., 1999). Currently, increasing environmental restrictions has created a good opportunity to introduce DME as a substitute for the diesel fuel and LPG (Alam et al., 2004; Fleisch et al., 1997; Rouhi, 1995; Song et al., 2004; Sorenson, 2001).

From industrial viewpoint, DME can be produced through the direct conversion of syngas or methanol dehydration. In the single step synthesis process, syngas is converted to the methanol as an intermediate component and then DME is produced through the methanol dehydration. Therefore, used catalyst in the direct method is a mixture of methanol synthesis and methanol dehydration catalysts. Currently, DME synthesis through CO_2 hydrogenation has been introduced as an effective process because of lower thermodynamic limitation, investment and operational costs compared to the syngas conversion (Bonura et al., 2014, Frusteri et al., 2015). In the indirect method, the produced methanol in the methanol plant is fed to the DME reactor. Since methanol synthesis reactions are equilibrium restricted and the equilibrium conversion of syngas is low, when the methanol dehydration reaction takes place simultaneously in the single step process, the syngas conversion increases considerably.

Many researchers have focused on DME synthesis from methanol and syngas (Nie et al., 2005). Brown et al. developed a slurry reactor to produce DME in the single-step process (Brown et al., 1991). The results showed that the single step DME production offers lower capital and operating costs compared to the indirect DME synthesis method. Omata et al. calculated the optimal temperature profile along a laboratory tubular reactor to produce DME from syngas to overcome the equilibrium limitations at high temperatures and catalyst activity restrictions at low temperatures (Omata et al., 2003).

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Moradi et al. studied DME synthesis through the single step process in a slurry reactor (G.R. Moradi, 2007). The catalyst was supplied by mixing of commercial grade of methanol synthesis and dehydration catalysts. Khandan et al. studied direct synthesis of DME over the modified zeolite by aluminum oxide in a three-phase slurry reactor (N. Khandan, 2012). The experimental results showed that the proposed multi-functional catalyst is a good candidate to produce DME through the single step process. Lu et al. studied the mechanism and kinetics of DME synthesis in a laboratory fluidized-bed reactor (Lu et al., 2004). The experimental results showed that the fluidized bed reactor results in higher CO conversion and DME production compared to the fixed bed or slurry reactors. Liu et al. studied DME production through the methanol dehydration in a fixed bed membrane reactor considering the gamma-alumina catalyst. The zeolite membrane was used to remove water vapor from the reaction zone and decreasing water concentration over the catalyst (Liu et al., 2011). Farsi et al. modeled and optimized methanol dehydration and cyclohexane dehydrogenation in a thermally coupled reactor (Farsi et al., 2010). The results showed that DME production capacity is improved about 2.8% in the proposed structure. Mardanpour et al. modeled DME production in a hydrogen permselective membrane fluidized bed reactor at steady state condition (Mardanpour et al., 2012). The simulation results showed that permeation of hydrogen could improve DME production and CO conversion in the single step DME synthesis process. Vakili et al. modeled DME synthesis from syngas in a membrane thermally coupled reactor. In the proposed configuration DME synthesis and cyclohexane dehydrogenation reactions occur in the tube and shell sides, respectively (Vakili et al., 2012). The results showed that DME production increases about 600 ton per year in the proposed configuration. Farsi et al. modeled DME production in a water vapor permselective membrane reactor (Farsi and Jahanmiri, 2011). The simulation results showed that the removal of water vapor from the reaction zone could shift the thermodynamic equilibrium limitation toward the DME production.

According to the benefits of the single step DME synthesis process over the methanol dehydration and advantages of membrane reactors against the conventional processes to shift the thermodynamic equilibrium limitations, in this research a dual membrane reactor is proposed to produce DME from syngas. Generally, increasing hydrogen and decreasing water vapor concentration over the catalyst in the single step DME process can shift the reactions toward DME production. The main aim of the present study is modeling and simulation of the proposed dual membrane reactor based on the mass and energy conservation laws at steady state condition. Then, operability and feasibility of the proposed structure is proved compared to the conventional process.

2. Reaction scheme and kinetics

In this section the rate and kinetic of DME synthesis reactions are presented. The used catalyst to convert syngas to methanol and methanol to DME are $CuO/ZnO/Al_2O_3$ and δ-Al_2O_3 that are packed in the reactor simultaneously. The single step DME synthesis reactions are as:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad H_{298K} = -90.56\,kJ/mol \tag{1}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad H_{298K} = -49.43\,kJ/mol \tag{2}$$

Table 1 – Reaction rate constant for DME synthesis from syngas.

$k = A\exp(B/RT)$	A	B
k_1	1.828×10^3	−43.723
k_2	0.4195×10^2	−30.253
k_3	1.939×10^2	−24.984
k_4	9.64	−152.900
K_{CO}	8.252×10^{-4}	30.275
K_{CO2}	2.1×10^{-3}	31.846
K_{H2}	0.1035	−11.139
K_{CH3OH}	1.726×10^{-4}	60.126

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad H_{298K} = -23.56\,kJ/mol \tag{3}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad H_{298K} = +41.12\,kJ/kmol \tag{4}$$

The rate of reactions is selected from literature (Nie and Fang, 2004):

$$r_1 = \frac{k_1 f_{CO} f_{H_2}^2 \left(1 - \frac{f_{CH_3OH}}{K_{f1} f_{CO} f_{H_2}^2}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2}\right)^3} \tag{5}$$

$$r_2 = \frac{k_2 f_{CO_2} f_{H_2}^3 \left(1 - \frac{f_{CH_3OH} f_{H_2O}}{K_{f2} f_{CO_2} f_{H_2}^3}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2}\right)^4} \tag{6}$$

$$r_3 = \frac{k_3 f_{CH_3OH} \left(1 - \frac{f_{DME} f_{H_2O}}{K_{f3} f_{CH_3OH}^2}\right)}{\left(1 + \sqrt{K_{CH_3OH} f_{CH_3OH}}\right)^2} \tag{7}$$

$$r_4 = \frac{k_4 \left(f_{CO} f_{H_2} - \frac{f_{H_2O} f_{CO}}{K_{f4}}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}\right)\left(f_{H_2}^{1/2} + \frac{K_{H_2O} f_{H_2O}}{K_{H_2}^{1/2}}\right)^3} \tag{8}$$

The reaction rate constants are selected from literature and tabulated in Table 1 (Song et al., 1988; Zhang et al., 2001).

3. Mathematical modeling

3.1. *Reactor modeling*

In this research, a one-dimensional heterogeneous model is developed to simulate the proposed structure at steady state condition. The proposed reactor consists of a number of three coaxial tubes. The inner tube is water permselective membrane and it is surrounded by reaction zone. The produced water vapor is permeated from the reaction zone to the sweep gas in the inner tube. The reaction zone is an annulus space between the inner and second tubes, that packed by DME synthesis catalysts. The second tube is hydrogen permselective and hydrogen is transferred from sweep gas to the reaction zone through the considered membrane layer. Indeed, the sweep gas flows along an annulus space between second and third tubes. The third tube is surrounded by the boiling water to remove the reaction heat from the reaction zone. Fig. 1 shows the schematic diagram of the proposed dual membrane reactor.