



Investigation of thermally double coupled double membrane heat exchanger reactor to produce dimethyl ether and methyl formate



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ABSTRACT

Owing to concerns associated with energy consumption and energy intensive methods in the chemical industries, the present study aims to investigate production of some downstream products of natural gas in a recuperative configuration. Accordingly, simultaneous production of dimethyl ether from methanol and syngas and also methyl formate from methanol is investigated in a catalytic heat-exchanger reactor assisted with water perm-selective membranes. Dimethyl ether synthesis from methanol and syngas are exothermic reactions supplying required energy for the methanol dehydrogenation reaction. Produced waters in both exothermic sides are eliminated from reaction media by permeation through the perm-selective membranes equipped on the inner and outer surfaces of the reactor. A feasibility study is implemented through a mathematical model based on mass and energy balance. Genetic algorithm as a powerful method in nonlinear optimization problems is applied to obtain optimum operating conditions. 97% methanol conversion to dimethyl ether, 66% methanol conversion to methyl formate and 17% hydrogen conversion are the advancements of the proposed thermally double-coupled double-membrane reactor working under optimum conditions.

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1. Introduction

Currently, increasing energy consumptions in domestic and industrial applications is a global concern. Regarding environmental problems and limited sources of fossil fuels, investigating clean sources of energy and reducing energy consumptions are vital. Actually, the main energy challenge is reducing energy consumption with no decline in efficiency of the process and quality of the products. Chemical processes as a cornerstone in economy of governments, are one of the main consumers of energy. Fossil fuels such as natural gas, liquefied petroleum gas (LPG) and natural gas liquid (NGL) are mainly used as energy sources in the chemical industries (Ross, 1981). Fossil fuels supply more than 80% of the energy requirement in household and industrial parts. Environmental problems such as global warming, climate change and defects in biodiversity are some harmful effects of fossil fuels emissions (Nigam and Singh, 2011). These issues leads to researchers and concerned industries to investigate clean sources of energy. Chemical and petrochemical industries that are the largest energy consumers among industries are responsible for exploring

clean and renewable sources of energy. One of the reasonable solutions to overcome the problems of fossil fuels is introducing new fuels, which are green or at least are less harmful for environment. Dimethyl ether (DME) is one of the suggested compounds. DME (which is also known as methoxymethane) is the isomer of ethanol and the simplest ether. With ignition properties similar to those of butane and propane, DME is classified as liquefied petroleum gas (LPG) (Zhang et al., 2010). It exists in liquid form when subjected to the pressures higher than 0.5 MPa (Aziz et al., 2014). Hence, it does not require high-pressure containers for storage and transport. Followings are some advantages of DME that make it an alternative energy resource meeting strict standards of emissions (Aziz et al., 2014):

- Lack of explosive peroxides leading to easy and safe transport and storage
- Lack of carbon-carbon bonds leading to lower carbon monoxide emission than natural gas
- High cetane number without NO_x

Potentially DME could be used as a suitable hydrogen carrier in the fuel cells and an intermediate in producing dimethyl sulfate, methyl acetate and lower olefins. The aforementioned advantages and applications of DME are attractive for researchers and

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industries (Raouf et al., 2008; Chen et al., 2012; Ladera et al., 2012; Tokay et al., 2012; Hayer et al., 2013; Faungnawakij et al., 2007).

DME is produced both directly and indirectly from syngas. In the single-step production of DME (i.e. direct synthesis of DME), both syngas to methanol and methanol dehydration reactions occur simultaneously in a single reactor filled with bi-functional catalyst (Ren et al., 2006; Gadek et al., 2013; Hu et al., 2008). In the two-step DME production procedure (i.e. indirect synthesis of DME), methanol production, and its dehydration to DME are implemented in distinct reactors (Aziz et al., 2014; Raouf et al., 2008). Presence of bi-functional catalyst in the direct method and in-situ methanol dehydration may help to eliminate limitations thermodynamic restrictions of CO conversion to methanol. Also, extra charges of methanol separation (that is highly energy intensive) are eliminated in this manner (Hu et al., 2008; Lu et al., 2005). Although, the direct DME production comes across as an efficient route, unreacted syngas and CO₂ existence in the product streams are some drawbacks of this method (You et al., 2009; Wang et al., 2013). Accordingly, any improvement in the conversion of CO and CO₂ resulting in higher purity of the product is of a great interest.

In addition to DME, there are different compounds which are good candidates to overcome problems of fossil fuels. Many of these compounds are synthesized industrially. C₁ chemistry is associated with formation of valuable multi-carbon molecules from feedstocks with single carbon such as carbon dioxide, carbon monoxide, methanol and syngas. Syngas and methanol play crucial roles in the production of a vast variety of products. Hence, they could be considered as a building block in C₁ chemistry. Efficient production and easy handling and transportation are characteristics a certain building must have. Besides, there must have efficient methods to produce downstream products from the building block (Lee et al., 1990; Jenner, 1995). Methyl formate (MF, also known as methyl methanoate) is expected to become an important building block in C₁ chemistry in the near future due to the following advantages (Lee et al., 1990; Jenner, 1995; Keim, 1983; Wender, 1984; Calkins, 1984):

- Various routes to synthesis MF such as direct synthesis from syngas, dehydrogenation of methanol, dimerization of formaldehyde, oxidative dehydrogenation of methanol, carbonylation of methanol and hydrocondensation of carbon dioxide with methanol
- Similarity of storing, handling, and transporting with LPG
- One more CO in the molecule than that of methanol bringing it up as a promising source of CO/H₂ mixture
- Manufacturing formic acid, formamide and dimethylformamide

In-situ hydrogen production by dehydrogenation is a capability of liquid fuels such as MF (Lee et al., 1990; Jenner, 1995; Jiang et al., 2011). A commercial method to produce MF with 96% selectivity of methyl formate was proposed by BASF (Couteau and Ramiouille). Investigating new processes to produce MF with considerations of energy enhancement is commercially of a great interest.

Up to now, different authors have studied DME synthesis from syngas and methanol in thermally coupled reactors. Vakili et al. proposed a thermally coupled heat exchanger reactor for direct synthesis of DME and dehydrogenation of cyclohexane to benzene and developed a mathematical model for this reactor. Smaller reactor, increasing conversion, producing valuable products such as hydrogen and benzene and low temperature of the output streams were mentioned as improvements of their system. In their subsequent study, they tried to boost hydrogen and DME production rate by changing flow direction and utilizing a membrane and determining operating conditions by an optimization technique (Vakili et al., 2011a,b, 2012). Farniaei et al. and Rahimpour et al. proposed thermally double-coupled reactors for production of methanol, DME

and hydrogen simultaneously. Enhanced methanol, DME and hydrogen production rates were achievements of their system (Rahimpour et al., 2013; Farniaei et al., 2013). Farsi et al. and Samimi et al. have made efforts to study different thermally coupling reactors for production of DME from methanol coupled with different endothermic reactions such as dehydrogenation of cyclohexane (Farsi et al., 2010a,b; Khademi et al., 2011) and methyl cyclohexane (Samimi et al., 2013). Goosheneshin et al. investigated simultaneous production and recycling of methanol for methyl formate synthesis in a looped thermally coupled heat exchanger reactor. Produced methanol in the exothermic side was aimed to recycle and used as the feedstock for MF production side (Goosheneshin et al., 2010). In recent studies, Bakhtyari et al. presented new recuperative reactors for production of DME by methanol dehydration beside MF and hydrogen production from methanol. Higher methanol conversion in both exothermic and endothermic sides and hydrogen production were obtained utilizing water and hydrogen perm-selective membranes (Bakhtyari et al., 2015, 2016).

Energy consumptions in the chemical industries may be reduced with process integrations and some reformations in equipment configurations (Axelsson et al., 1999; Ebrahim and Kawari, 2000; Jegla et al., 2000). Process intensification (PI), as an innovative methodology in chemical process technology, actually is used to increase production rate and products quality with lower energy and feedstocks consumption (Friedler, 2010; Smith, 2000; Rossiter, 2003). Chemical reactors working as the heart of chemical processes, have a significant role in PI. A wide range of chemical products is produced through exothermic reactions with high heat generation rate. One of the applications of PI is designing of heat-integrated equipment to use generated heat in one section to drive processes in other sections. Hence, the produced heat in the exothermic side could be transferred to the endothermic side within a heat exchanger reactor. Consequently, with integrating two reactions in a shell and tube, the generated heat in the exothermic side is captured and used to make the endothermic reaction start and proceed (Rahimpour et al., 2012). Various multifunctional systems with different reactions in fixed bed and fluidized bed reactors were studied by Rahimpour and coworkers. Capability of these types of reactors were examined in Fischer–Tropsch synthesis (Rahimpour and Bahmanpour, 2011; Rahimpour et al., 2010a,b,c), reforming of naphtha (Rahimpour, 2009; Rahimpour et al., 2011a; Iranshahi et al., 2011; Iranshahi et al., 2010), different methane reforming, syngas production routes, methanol synthesis, DME synthesis with different dehydrogenation reactions (Vakili et al., 2011a; Rahimpour and Bahmanpour, 2011; Rahimpour et al., 2010a, 2011a; Rahimpour, 2009; Iranshahi et al., 2011; Bayat and Rahimpour, 2011a; Khademi et al., 2010; Khademi et al., 2009; Arab Aboosadi et al., 2011; Vakili et al., 2011c; Rahimpour et al., 2011b; Rahimpour and Pourazadi, 2010; Rahimpour et al., 2010d,e; Bayat and Rahimpour, 2011b). Rahimpour et al. reviewed different concepts, advantages, and disadvantages of thermally coupling reactors (Rahimpour et al., 2012).

By considering very fast improvement and progressing rate of new technologies and applying of them in different industries, new technologies such as membranes can be used as an auxiliary tools in different industries in order to save energy. For example, Membranes because of especial characteristics, such as high surface area per unit volume, high selectivity and permeability and possibility of controlling permeation rate, can be used as an alternative for simultaneous reaction and separation (Rahimpour, ; Rahimpour1,). Besides, phase separations with high-energy efficiency could be managed utilizing perm-selective membranes. Unlike the conventional separation methods such as distillation (with 3% share in the worldwide energy consumption (Jana, 2010)), phase change is not essentially observed in a separation using membranes. Therefore,

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