



Optimal conditions in converting methanol to dimethyl ether, methyl formate, and hydrogen utilizing a double membrane heat exchanger reactor



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ABSTRACT

Following importance of investigating new sources of energy with highly efficient processes, a new configuration for simultaneous production of high purity dimethyl ether (DME), hydrogen and methyl formate (MF) is numerically studied in this work. In this regard, a catalytic heat-exchanger reactor assisted with two different membranes for methanol conversion and in-situ separation of products is simulated. The interesting feature of this system is utilizing only one feedstock (i.e. methanol) to produce different valuable products. Methanol is dehydrated through an exothermic reaction and supplies required energy for the methanol dehydrogenation reaction. Produced water in the exothermic side and produced hydrogen in the endothermic side are separated by permeation to particular membranes. A steady state one-dimensional plug flow model is developed to evaluate molar and thermal behavior of the system. Optimum operating conditions are determined applying genetic algorithm as a powerful optimization method. The proposed configuration working under optimum conditions promotes methanol conversion to DME to % 95.1 and methanol conversion to MF to % 99.6 providing high purity products in the output streams.

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1. Introduction

Diverse fuels and chemical intermediates such as dimethyl ether (DME), formaldehyde, formalin, methyl formate (MF), and acetic acid are produced directly or indirectly from methanol. Besides, methanol is a potential medium for hydrogen reserve (Semelsberger et al., 2006; Ball and Wietschel, 2009). Accordingly, any enhancement in methanol associated processes leading to higher efficiency and lower energy consumption is promising for petrochemical and chemical industries. Heat integrated processes with energy efficient separation techniques for converting methanol to downstream products are currently of a great interest.

1.1. Process intensification: an advanced methodology in reducing energy consumption

Given increasing worldwide energy demand, environmental problems and limited sources of fossil fuels, seeking for clean and non-hydrocarbon energy resources and more energy efficient processes is crucial. Hydrocarbons e.g. natural gas, liquefied petroleum gas (LPG), and natural gas liquid (NGL) are main energy sources of chemical industries as a major energy consumer (Ross, 1981). Reconfiguration and reformation of equipment may result in heat integration and then reducing energy consumption (Axelsson et al., 1999; Ebrahim and Kawari, 2000; Jegla et al., 2000). Hence, proposing processes with lower energy consumption without decline in efficiency and productivity is still challenging.

An elegant approach in chemical process technology called process intensification (PI) has been running the art of increasing production rate and products quality since 1970s. These are achieved by compacting the equipment and reducing energy and raw material consumption (Friedler, 2010; Smith, 2000; Rossiter, 2003). Based on this approach, the generated heat in a part of system could

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be recovered and reused for heating or driving the endothermic processes in the other part. Such a point of view led to design of heat exchanger reactors (Rahimpour et al., 2012).

1.2. Heat exchanger reactors: thermally coupling and reusing heat of reactions

Chemical reactors with exothermic and endothermic reactions, have a key role in PI. The generated heat in the exothermic reactions may be recovered and reused as a heat source in endothermic reactions. Such a capability is obtained using a heat exchanger reactor. Two reactors are integrated in a shell and tube and heat of exothermic reaction is transferred through the reactor wall. The transferred heat makes the endothermic reaction proceed. As a result, equipment size is reduced, thermal efficiency of the reactor is enhanced, and energy consumption is noticeably lowered. Hence, heat exchanger reactors are vast field of study and they have attracted attentions of researchers and industries (Rahimpour et al., 2012).

Heat exchanger reactors with coupling and double coupling of different exothermic and endothermic reactions were studied by Rahimpour and coworkers. Both fluidized and fixed beds were examined for different reactions in diverse processes in chemical, petrochemical, and refining industries. GTL technology and Fischer–Tropsch synthesis (Rahimpour and Bahmanpour, 2011; Rahimpour et al., 2010), naphtha reforming (M, 2009; Iranshahi et al., 2010), various methane reforming and syngas production (Rahnama et al., 2014), methanol synthesis, DME synthesis, and dehydrogenation reactions are various processes tried to enhance with heat exchanger reactors (Rahimpour et al., 2013; Rahimpour and Pourazadi, 2011; Farniaei et al., 2013; Bayat and Rahimpour, 2011; Farsi et al., 2010; Khademi et al., 2011; Goosheneshin et al., 2012). Benefits and drawbacks of heat exchanger reactors are summarized in a review published by Rahimpour et al. (Rahimpour et al., 2012).

1.3. Membrane reactors: low energy consuming separations

Membrane characteristics, e.g. high surface area per unit volume of membrane, high selectivity/permeability, and controllable permeation rate, make it promising for integrating reaction and separation in a single system (Rahimpour, 2016a; Rahimpour, 2016b). Unlike the traditional separation methods e.g. distillation (consuming about 3% of whole energy in the world (Jana, 2010)), there is no phase change in membrane based separations. Hence, thermal equipment such as reboiler is eliminated. On the one hand, highly efficient phase separations are achieved applying perm-selective membranes. Decline in high temperature and pressure systems, limited pH range, and problems with membrane clean up are some disadvantages of membrane reactors (Shu et al., 1991; Uemiyama et al., 1991). Yield/selectivity enhancement of products by shifting the equilibrium reactions toward products using membranes are widely studied in systems containing hydrogen and water vapor (Rohde et al., 2008; Fernandes and Soares, 2006; Khajavi et al., 2010). Hydrogen recovery from tail gas emissions, in-situ hydrogen production and separations in dehydrogenation reactions, water recovery from dehydration reactions, and simultaneous hydrogen and oxygen production from water are currently state of the art (M, 2009; Bayat and Rahimpour, 2011; Rohde et al., 2008; Omorjan et al., 1999). As a whole, recuperative reactors with simultaneous heat and mass exchange are a vast field of study and research.

1.4. Dimethyl ether (DME): a clean fuel with emissions standards

Hydrocarbons supply more than 80% of the energy required in household and industrial sections. Global warming, climate change, and defects in biodiversity caused by hydrocarbons emissions make the researchers and industries seek for clean sources of energy.

DME (IUPAC name: methoxymethane) is an isomer of ethanol, the simplest ether, volatile, non-toxic and colorless gas. It is liquefied when subjected to the pressures higher than 0.5 Mpa. Hence, its storage and transport is possible without high-pressure containers (Azizi et al., 2014; Zhang et al., 2010). Low maintenance costs due to simple engines and no need to spark plugs are advantages of DME as an engine fuel (Azizi et al., 2014). Followings are some benefits of DME that make it a promising energy resource with strict standards of emissions:

- Ease and safety of transport and storage due to lack of the explosive peroxides
- Low CO emission in comparison with natural gas (due to lack of carbon–carbon bonds)
- High cetane number with no NO_x emission

It's potential to become a hydrogen carrier in the fuel cells and intermediate in producing dimethyl sulfate, methyl acetate, and lower olefins are some applications of DME that have attracted researchers and industries attention (Raoof et al., 2008; Chen et al., 2012; Ladera et al., 2012; Tokay et al., 2012; Hayer et al., 2013; Faungnawakij et al., 2007; Ren et al., 2006).

Conventionally, DME is produced from syngas in single-step or two-step methods. In the single-step method, both methanol synthesis and dehydration occur in a single reactor filled with hybrid catalyst (Gadek et al., 2013; Hu et al., 2008; Lu et al., 2004). In the two-step method, DME is produced by dehydration of methanol primarily obtained from syngas (Semelsberger et al., 2006; Rahimpour et al., 2013; Farniaei et al., 2013). Presence of hybrid catalyst in the single-step method and in-situ methanol consumption can overcome thermodynamic restrictions of CO and CO_2 conversion to methanol. Besides, methanol separation step is eliminated in this way (Nie et al., 2005; You et al., 2009; Wang et al., 2013). Although, the single-step production of DME seems to be more efficient, presence of unreacted syngas and CO_2 in the product streams make the next purification steps difficult (Nie et al., 2005; You et al., 2009). Accordingly enhancing the two-step DME synthesis method resulting in higher purity of the product and higher methanol conversion makes some profits for the associated industries.

1.5. Methyl formate (MF): next candidate of C_1 chemistry

C_1 chemistry concerns with producing valuable multi-carbon molecules from single-carbon molecules (e.g. syngas, methanol, carbon dioxide, and carbon monoxide). A certain building block in C_1 chemistry must be produced in different routes and handled, stored and transported easily. Additionally, downstream products must be efficiently produced from a certain building block (Lee et al., 1990; Jenner, 1995). MF (IUPAC name: methyl methanoate) is coming up as a building block in C_1 chemistry in the near future due to the following potentials (Keim, 1983; Wender, 1984; Calkins, 1984; Couteau and Ramiouille, 2163; Jiang et al., 2011):

- various methods to synthesis e.g. direct synthesis from syngas, dehydrogenation of methanol, oxidative dehydrogenation of methanol, dimerization of formaldehyde, hydrocondensation of

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