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The optimal operating conditions of a thermally double coupled, dual membrane reactor for simultaneous methanol synthesis, methanol dehydration and methyl cyclohexane dehydrogenation

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ABSTRACT

In this study, the concept of thermally double coupled reactor is proposed as an alternative configuration to mix the energy efficient concept of coupling two exothermic with one endothermic reaction. In this multi-tubular fixed bed reactor, methanol synthesis and methanol dehydration, as two exothermic reactions occur in the inner and outer tubes while the methyl cyclohexane dehydrogenation, as an endothermic reaction takes place in the middle tube. Two water permselective membranes are also applied in the inner and outer tubes to remove water from both exothermic sides. Extraction of water as one of the main byproducts in the DME (dimethyl ether) and methanol synthesis processes increases the production rate and the catalyst life time. In this configuration, the operating conditions are optimized using a differential evolution method in order to maximize the outlet methanol and DME mole fractions of the inner and outer exothermic sides respectively. Then the optimized results of the thermally double couple dual membrane reactor are compared with the optimized thermally double couple reactor and the ones in conventional methanol and DME synthesis reactors. This comparison shows the superiority of this configuration to the conventional ones owing to the enhancement of methanol and DME mole fractions (10.9% and 19.5% increase compared with conventional ones respectively). Hydrogen and toluene, as two valuable products, are also produced in a favorable mode.

1. Introduction

Nowadays, effective monetization of natural gas has become an imperative action as a result of two main reasons; firstly, the growing demand in the fuels and chemicals market and secondly, increasing environmental concerns and toughening regulations. Chemical conversion which is economical and environmentally sustainable, is of great interest, increasing the value of the raw material 3–10 times. Future energy carriers like hydrogen, methanol and dimethyl ether (DME) can be produced by natural gas conversion (Løvik, 2011). Simultaneous production of these three energy sources might be economically feasible in a thermally double coupled reactor in which the endothermic reaction of methyl cyclohexane dehydrogenation is coupled with two exothermic reactions of methanol dehydration and methanol synthesis and which are assumed to occur in a single multi tubular reactor. The topic is complex hence this paper seeks to introduce the concept for future consideration and development. Certain simplifying assumptions are made to make the theoretical work manageable and are noted in the paper.

1.1. Methanol synthesis

Given large natural gas reserves and advances in CH_4 chemistry and technology, the accepted usages of natural gas can vary widely such as fuel gas, conversion to liquid fuels or in the manufacturing of petrochemicals (Taniewski, 2008). Methanol is one of the largest volume commodity chemicals produced from natural gas. This feasible and sustainable route to natural gas monetization can be considered as a strategy for solving certain environmental problems. The methanol synthesis process has four main steps including: feed purification, synthesis gas production, methanol production and product treatment/storage.

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1.2. Methanol

Methanol synthesis technology is a smart environmental protection process in which useful conversion of CO_2 takes place to a clean burning fuel (Jean-Paul, 2001; Hironori, 1998). Methanol is used in the production of chemicals such as methyl tertiary butyl ether (MTBE) which has been used as a gasoline additive. Utilizing methanol instead of gasoline can result in reducing "knock" in the conventional combustion engines due to its higher octane rating. A synthetic fuel may also be produced from methanol by the methanol to gasoline (MTG) process. Currently, the second main usage of hydrogen after ammonia synthesis is methanol production (Zhang et al., 2003; Wang et al., 2005; Zhang and Zhao, 2006; Ji et al., 2007; Cheng and Kung, 1994). One of the main problems related to hydrogen is its long-term storage and long-distance transportation. Conversion to methanol is advantageous since it is a liquid under standard conditions. Moreover, methanol has an extensive usage in the synthesis of biodiesel, formaldehyde and acetic acid and DME (Semelsberger et al., 2006). Widespread application of methanol in novel processes such as direct methanol fuel cell (DMFC) and micro channel methanol steam reforming may lead to more interest in the future (Hao et al., 2011; Park et al., 2012). Sometimes, only a few percent improvements in the production efficiency of important globally traded chemicals like methanol can result in significant profit increases, energy conservation and environmental impact reduction (Schack et al., 1989). Recently, considerable attention has been given to coupling reactors which makes the process more economic and efficient.

1.3. Hydrogen by dehydrogenation reaction

Hydrogen has been regarded as an attractive energy carrier to support energy consumption. Hydrogen, the most common element in the earth, can be used as an environmentally friendly, efficient, safe and sustainable energy source (Lokurlu et al., 2003; Heinzel et al., 2002). The product of hydrogen combustion is only water and tiny amount of NO_x which can be reduced by means that it is free from any greenhouse gases when used as a fuel. Hydrogen production however does have severe environmental issues (Muler-Langer et al., 2007).

Hydrogen has the highest calorific value, (61,493 BTU's) among fuels except the nuclear fuels. Thus, a fuel with a higher proportion of hydrogen has a greater energy intensity (Sun et al., 2012). There are many other applications of hydrogen. Hydrogen was first produced through the mixing of metals with strong acids in the early 16th century. Hydrogen is a secondary energy product from traditional processes including natural gas reforming, coal and biomass gasification and electrolysis of water (Sun et al., 2012). Another alternative method for hydrogen synthesis is the dehydrogenation of cyclic hydrocarbons. The dehydrogenation reaction is reversible being limited by thermodynamic equilibrium (Khang and Anderson, 1985).

1.4. Dehydrogenation of methyl cyclohexane

Cycloalkanes like cyclohexane, methyl cyclohexane (MCH), decalin, etc have a high hydrogen content, high boiling point and are a stable form for hydrogen storage. Among these cycloalkanes, methyl cyclohexane is proposed as a superior candidate as its' health impact is lower than other compounds. This choice of MCH has the following reasons:

- MCH has higher capacity for storage of hydrogen (6.2 wt% hydrogen content) than other possible candidates including liquid hydrogen, compressed hydrogen and so on (Yolcular and Olgun, 2008; Anshu et al., 2012).
- Toluene, a preferable product of the dehydrogenation of MCH has a lower environmental and safety impact compared to benzene which is a product of cyclohexane dehydrogenation.
- At the same condition, MCH has a higher conversion than cyclohexane.
- MCH has a lower freezing point than cyclohexane making it suited to cold regions.

The dehydrogenation reaction of MCH is reversible, so the products can be easily hydrogenated and recycled. Literature review reports that Pt-based catalysts are the most widely used catalyst for this reaction. Selectivity can be increased by using metal oxide as a support through strong interaction (Pereniguez et al., 2010). In this way, numerous studies are reported related to using various metal oxides as a Pt catalyst support including: La_2O_3, Al_2O_3, CeO_2, MnO_2, TiO_2, Fe_2O_3, ZrO_2 (Shukla et al., 2010). In this work, Pt/Al_2O_3 is used as a catalyst.

1.5. DME synthesis by dehydration of methanol

Significant commercial developments are driving large increases in dimethyl ether (DME) production capacity in the world. DME has a remarkable potential as an ultra clean, renewable, low-carbon fuel due to its special features. This simple ether has the characteristics of colorless, volatile, non-corrosive and non-toxic (Larson and Yang, 2004). Having high cetane number (55–60), zero-polluting combustion and low engine noise contribute to its' use in diesel engines, power generation, and other routes like a substitute for LNG (Adachi et al., 2000; Arcoumanis et al., 2008; Ji et al., 2011).

DME has been increasingly used in heating and home cooking with a visible blue flame similar to liquefied petroleum gas (LPG). Furthermore, it is a strategic raw material for chemical production of jet fuel, olefins, gasoline and as a hydrogen carrier in fuel cells (Simons et al., 1997; Naik et al., 2011). DME storage and transportation have limited problems due to its liquid form under low pressure (Khademi et al., 2011). It can be produced from a variety of feed-stocks including coal, natural gas, crude oil, biomass, agricultural residues, and waste products (Arcoumanis et al., 2008). The indirect (two steps) and direct (single step) methods are the two main processes for production of DME. The first process termed Synthesis gas To Dimethyl ether (STD) is developed for the direct synthesis of DME which combines synthesis and dehydration of methanol in a single reactor on a bifunctional catalyst (Lu et al., 2004; Bercic and Levec, 1993). In the indirect process that is the traditional and commercial technique for DME production, after methanol synthesis on a metallic catalyst in the one step, it is converted to DME in another step which has been considered in this study.

1.6. H-SOD membrane

Using a membrane reactor is a more compact design for simultaneous production and separation, reducing the operational and capital cost. Moreover, the production increases with driving equilibrium reactions toward greater conversion by removing some by-products (Farsi and Jahanmiri, 2011). One of the main byproducts in DME and methanol synthesis process is water, so extracting this material increases both products. Based on studies cited in the literature on hydrophilic membranes, microporous zeolite membranes surpass amorphous microporous membranes and polymer membranes. Hydroxy sodalite (H-SOD) is a zeolite-like material membrane prepared by direct hydrothermal synthesis on α-Al_2O_3