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Exergy and exergoeconomic analyses of thermally coupled reactors for methanol synthesis

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ARTICLE INFO

Article history:

Received 25 July 2017

Received in revised form

23 August 2017

Accepted 5 September 2017

Available online xxx

Keywords:

Thermally coupled reactor

Thermally double coupled reactor

Membrane coupled reactor

Methanol synthesis

Exergy efficiency

Thermodynamic loss

ABSTRACT

Methanol synthesis is an exothermic reaction where heat is removed by using it for boiling water. This heat can be utilized for endothermic reactions in thermally coupled reactors. The dehydrogenation of cyclohexane or methyl cyclohexane are preferred reactions coupled with methanol synthesis. In the present study exergy and exergoeconomic analyses are carried out for various thermally coupled reactors used for methanol synthesis. Thermally coupled reactors, thermally double coupled reactors and membrane coupled reactors are compared on the basis of exergy efficiency, exergy destruction and hydrogen production. Such analyses can assist in the selection of suitable thermally coupled reactors. A new production facility for a methanol plant using a thermally coupled reactor is also suggested.

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Introduction

An alternative to petroleum fuels is needed due to their impact on the global environment and the long-term decline in this resource. Many crude oil and natural gas reserves are located in politically unstable regions, so supply risks pose a threat to the energy security of many nations. There are various alternate fuels, like ethanol, methanol, hydrogen, and coal gas. Due to its high octane number (108.7), methanol can be mixed in gasoline. Dimethyl ether is produced by

dehydration of methanol which, due to its high cetane number (55), can be used as a substitute for diesel fuel. Although today methanol is mainly produced from natural gas, renewable sources are also available which can be transformed into a synthesis gas, which can in turn be used in methanol production. Biomass, municipal waste, industrial waste and carbon dioxide are renewable sources for the production of methanol. Apart from a fuel, methanol can also be used as a hydrogen carrier in fuel cell applications, in the production of biodiesel, and as a feedstock for formaldehyde, acetic acid and olefins.

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<https://doi.org/10.1016/j.ijhydene.2017.09.055>

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Heat integration is of great importance in the chemical process industry. Heat generated during reactions is recovered within a process rather than using external heat to improve efficiency. Methanol synthesis is an exothermic reaction and the generated heat is used to produce steam. It is difficult to exchange that heat within the process but it is possible with other endothermic reactions. Coupling of exothermic and endothermic reactions is possible in a single reactor using a thermally coupled reactor. Various sets of exothermic and endothermic reactions have been investigated, including steam methane reforming coupled with catalytic methane combustion [1], Fischer–Tropsch synthesis with dehydrogenation of cyclohexane [2], methanol synthesis with cyclohexane dehydrogenation [3–9], naphtha reforming with hydrogenation of nitrobenzene to aniline [10,11], and dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline [12]. Thermally coupled reactors are often similar to shell and tube heat exchangers, where the heat sink and source are close together. This increases the heat transfer efficiency of the reactor and reduces equipment costs. In the present study, recuperative thermally coupled reactors for methanol production are analyzed from an exergy point of view. The dehydrogenation of cyclohexane or methyl cyclohexane is endothermic reaction which can be coupled with methanol synthesis. Organic chemical hydrides are a prominent source of hydrogen because they consist of 6–8% (wt) hydrogen. They can also act as a hydrogen storage medium, for subsequent hydrogen supply without emitting pollutants [13]. Heat from the methanol synthesis reaction can be used for the dehydrogenation reaction in a thermally coupled reactor to produce hydrogen. In the future, the role of hydrogen will likely become more important as a fuel. Traditionally methanol and hydrogen are produced in different processes and plants. But by integrating endothermic and exothermic reactions in a single thermally coupled reactor, both energy and financial resources can be saved. Khademi et al. optimized a thermally coupled reactor for methanol production using a differential evolution method, resulting in improvement to the methanol mole fraction [3]. By coupling two exothermic reactions with one endothermic reaction in a hydrogen production process, the hydrogen production rate can be increased [8,9,14,15]. In membrane assisted thermally coupled reactor (TCR), hydrogen can be removed by a membrane and used for methanol production. The membrane is useful for eliminating the equilibrium constraint by the removal of one of the products. Table 1 shows various schemes for thermally coupled reactors used for methanol synthesis.

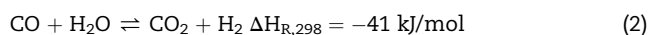
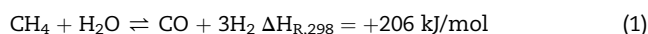
Although thermally coupled reactors for methanol synthesis and other purposes are used and relatively well understood, little is known about how they behave from the viewpoint of exergy and exergoeconomics. Such knowledge can help to enhance understanding of processes and improve them. In the present study, therefore, exergy and exergoeconomic analyses are carried out of various thermally coupled reactors for methanol synthesis. The objective is to improve understanding of thermally coupled reactors by examining thermodynamic performance. Exergy efficiency and thermodynamic loss rate to capital cost ratio calculations

are used to select suitable reactor for simultaneous production of methanol and hydrogen.

Production of Methanol

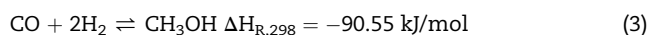
The feed for methanol is a synthesis gas, which contains carbon monoxide, carbon dioxide and hydrogen. Natural gas is used worldwide for methanol production. It is carried out via two main steps (Fig. 1): 1) production of synthesis gas, and 2) synthesis of methanol. Natural gas is desulfurized to avoid catalyst poisoning and then fed to the catalytic reformer with steam. Conventional steam reforming is a widely practiced method for synthesis gas production. The synthesis gas is cooled and compressed before entering the methanol synthesis reactor.

The following reactions occur in the reformer



Methanol synthesis is exothermic and involves the following reactions:

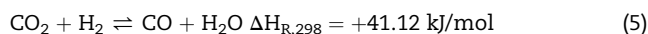
Hydrogenation of carbon monoxide



Hydrogenation of carbon dioxide



Reverse water gas shift reaction



According to Le Chatelier's principle, a higher methanol yield is obtained at higher pressure and lower temperature. A commercial CuO/ZnO/Al₂O₃ catalyst is used for the synthesis reaction. Chemical equilibrium limits the conversions. The methanol synthesis reactor is multi-tubular and is like a shell and tube heat exchanger. The catalyst is placed in the tubes and water is placed in the shell. Heat generated in the reaction boils water to produce steam. The temperature in the reactor is controlled by the steam pressure [16].

The temperature in methanol synthesis reactor must be controlled to obtain a good equilibrium value as well as to control catalyst activity. The maximum conversion of CO and CO₂ provides the maximum methanol yield. Product gases from the reactor exit at 523–543 K and exchange heat with the incoming synthesis gas. Further cooling is required before sending the product gas to the separator, where methanol is separated from the unreacted gas. This gas is compressed and recycled back to the reactor. A small amount of gas is purged to maintain the concentration of inert components in the

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