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Analysis, synthesis, and design of a one-step dimethyl ether production via a thermodynamic approach

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HIGHLIGHTS

- We analyze a one-step DME production via a thermodynamic approach.
- We synthesize a one-step DME process.
- We design a one-step DME process with pinch technology.

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ABSTRACT

In this work, we have developed a direct one-step process design on an oxygenate production, namely, dimethyl ether (DME). DME can be used as a cetane-number booster for diesel, in addition to being capable of a substitute for liquefied petroleum gas (LPG). In order to analyze the independent chemical reactions involved in the reactor, it is necessary to carry out a study of the chemical reaction stoichiometry. And with a specific syngas feed, the following reactions are found: (1) $CO_2 + H_2 = H_2O + CO$, (2) $CO + 2H_2 = CH_3OH$, and (3) $3CO + 3H_2 = (CH_3)_2O + CO_2$. To gain an insight into the reactor design, we have also utilized the concept of thermodynamics, including equilibrium-constant method and the minimization of Gibbs free energy. Additionally, we have also united the pinch technology with the base-case design for heat exchanger network synthesis in order to compare the energy consumption and capital costs of the process with/without heat integration. Two kinds of software were used in the research–Aspen Plus and SuperTarget. The former was used for the process synthesis, design, and simulation; the latter was used to carry out the pinch analysis and the synthesis of heat exchanger network.

1. Introduction

Dimethyl ether (DME) is a clean energy which can be produced from syngas. Due to its similar properties of LPG, DME can be used as a fuel for home heating and cooking. Additionally, it can be used as transportation fuel due to its high cetane number. Also it can be used as a starting reagent for making special chemicals such as methyl acetate and acetic anhydride. Previous related studies investigate a double integrated reactor for DME synthesis and hydrogen production [1], the optimization of reformer to produce syngas for methanol production [2], a large-scale combined production of methanol and electricity from natural gas from an economic point of view [3]. A comprehensive study from the perspective of thermodynamics has not been performed. This study aims to simulate a dimethyl ether process and its efficient use of energy. Chemical reactor's design is based on the concept of thermodynamics, including equilibrium constant method and the minimization of Gibbs free energy. The feed contains syngas, with a mole ratio of H_2:CO:CO_2 = 5:4:1. Plant capacity is on the order of 45,000 metric tons per year of 99.9 mol% purity DME. Pinch technology [4] is utilized to deal with energy savings of the dimethyl ether plant. Two process software tools, Aspen Plus [5] and SuperTarget [6] were used in this paper. The results of this study may be of interest to researchers interested in the development of clean energy.

2. Chemical reaction stoichiometry

Chemical reaction stoichiometry (CRS) is a branch of chemical stoichiometry dealing with the constraints, in the form of chemical reactions, placed on changes in the composition of a closed reacting system by the requirement for conservation of the amount of each atomic species. Using CRS for the reaction path analysis in the one-step dimethyl ether production, we find the independent equilibrium reactions involved are, given that chemical species H_2, CO, CO_2, H_2O, CH_3OH and $(CH_3)_2O$, as follows:

(1) $CO_2 + H_2 = H_2O + CO$

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(2) $CO + 2H_2 = CH_3OH$
(3) $3CO + 3H_2 = (CH_3)_2O + CO_2$

The reactions are the water–gas shift reaction, the methanol synthesis reaction, the DME synthesis reaction, respectively. It is noteworthy that the reaction formulas concerning DME synthesis [7] are:

(1) $3CO + 3H_2 \rightarrow (CH_3)_2O + CO_2$
(2) $2CO + 4H_2 \rightarrow (CH_3)_2O + H_2O$
(3) $2CO + 4H_2 \rightarrow 2CH_3OH$
(4) $2CH_3OH \rightarrow (CH_3)_2O + H_2O$
(5) $CO + H_2O \rightarrow CO_2 + H_2$

The afore-mentioned five reactions are not independent and can be reduced to three independent equilibrium reactions.

3. Sensitivity analysis of key thermodynamic parameters

The parametric analysis is achieved to evaluate the effects of key parameters, that is, reaction pressure and temperature, on the system performance. The yields of DME and methanol vs. the key parameters are as shown in Figs. 1–4. We will now use equilibrium constant method as well as free energy minimization method to analyze both temperature and pressure effects on the reaction yields in detail. According to the Gibbs free energy at standard state

$$\ln K_a = -\frac{\Delta G}{RT} \tag{1}$$

Eq. (1) states that the reaction temperature has effect on the equilibrium constant K_a. Therefore, we can calculate the equilibrium compositions under fixed reaction temperature. The following van't Hoff equation can be used to relate temperature to the equilibrium constant

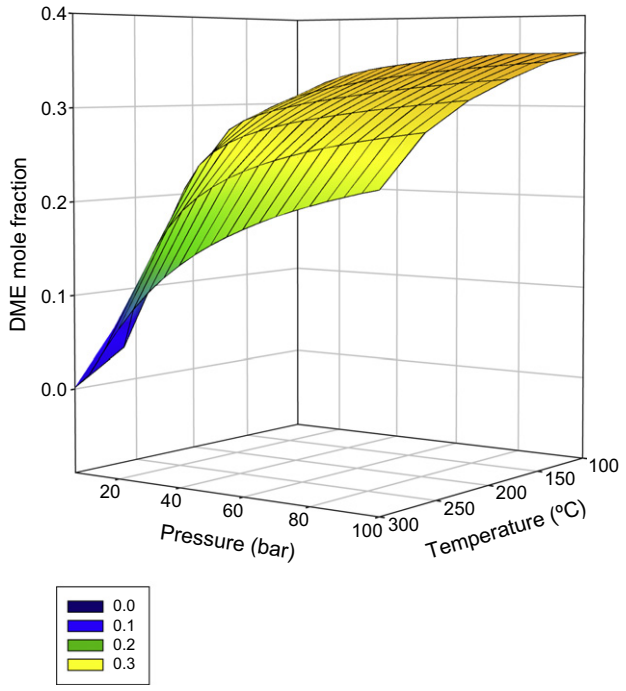

Fig. 1. Reaction yield of DME versus reaction pressure and temperature at a molar ratio of syngas H_2:CO:CO_2 = 5:4:1.

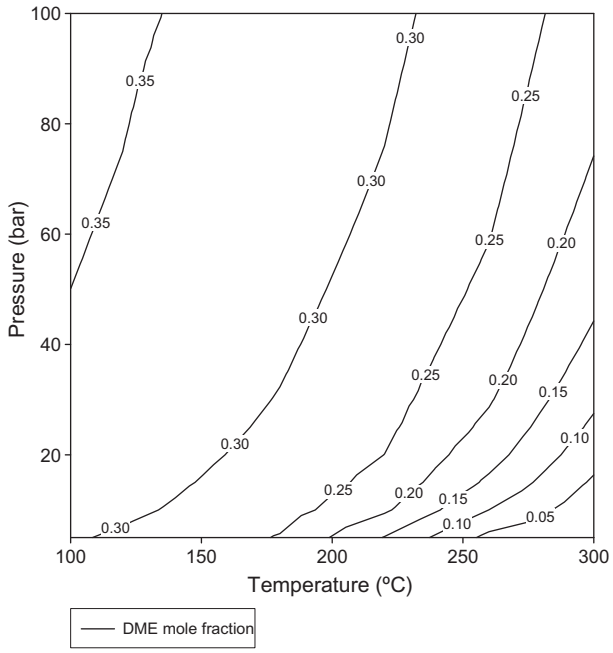

Fig. 2. Contours of DME yield versus reaction pressure and temperature at a molar ratio of syngas H_2:CO:CO_2 = 5:4:1.

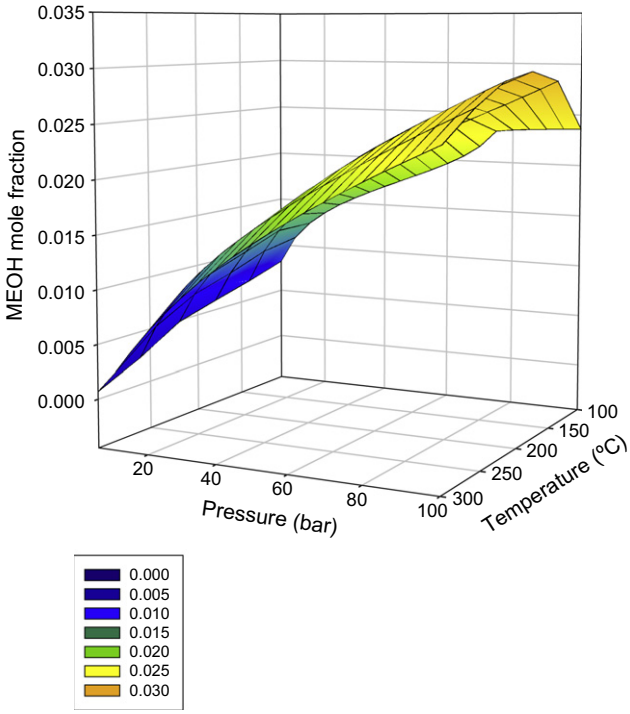

Fig. 3. Reaction yield of methanol versus reaction pressure and temperature at a molar ratio of syngas H_2:CO:CO_2 = 5:4:1.

$$\ln\left(\frac{K_a}{K_{aR}}\right) = \frac{\Delta G_R^0}{RT} - \frac{\Delta G_R^0}{RT_R} = -\frac{\Delta H_R^0}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \tag{2}$$

where ΔH_R^0 is the reaction at standard state, R the gas constant (8.314 kJ/kmol K), T the system temperature (K) and T_R is the reference temperature (K).

Eq. (2) states that if reaction is exothermic, $\Delta H_R^0 < 0$, the equilibrium constant will decrease as the temperature increases; if the reaction is endothermic, $\Delta H_R^0 > 0$, the equilibrium constant will