Energy and exergy analyses of dimethyl ether production using CO and CO₂ hydrogenation

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Abstract

The purpose of this work was to study the dimethyl ether production from CO and CO₂ in the single-step process using thermodynamic analysis. The simulation study was divided into two parts: First, the effects of the H_2/CO_2 , H_2/CO_2 , and $H_2/CO+CO_2$ molar ratios and operating conditions on yields of dimethyl ether were investigated. Then, the energy and exergy analyses of all routes were compared to determine the performance of the overall DME production system. The results showed that the highest DME yields were $H_2/CO=4$, $H_2/CO_2=5$, and $H_2/(CO+CO_2)=4$ (CO₂/CO=2.0), respectively. It was found that adding CO₂ to the syngas significantly decreased the yield and that increasing pressure while reducing temperature significantly increased the yield. All routes compared, using H_2/CO and co-feeding CO₂ resulted in the highest energy and exergy efficiency of the overall DME production system.

Keywords: Energetic, Exergetic, CO2 utilization, Dimethyl ether synthesis

1. Introduction

Nowadays, the demand of energy has been increasing due to the population growth and industrial development. In the combustion of fossil fuels, including petroleum, coal, and natural gas; is the majority source of CO_2 emission resulting in global warming and negative human health effects. Alternative energy is a very interesting energy source in order to replace the fossil fuels as energy. However, in the face of climate change, the energy source should be clean, environmentally friendly, and sustainable. Among alternative fuels, the dimethyl ether is an attractive energy in the near future that can replace the petroleum-based fuels. This is because it has many advantages such as high cetane number, expediently liquefied under low pressure, and no emission of particulates and toxic gases [1]. The DME can also be employed in many the industries. For instance, it is used as a feedstock for chemical production, domestic cooking fuel, power generation fuel, and transportation fuel.

Generally, there are two processing manufacturing of the dimethyl ether: single step process and twostep process. Two-step process is the conventional technology which uses the methanol as a feedstock. The methanol synthesis and methanol dehydration reactions require different reactors. The single step process, the methanol synthesis and methanol dehydration reactions are combined in one reactor [2]. The advantages of the single step process are its operating and maintenance cost effectiveness, higher yield of DME, and lower energy consumption when compared with the two-step process. DME can be produced from various sources such as natural gas, coal, biomass, biogas and waste materials. The syngas production via the reforming of methane is not optimum for DME production due to the richness of hydrogen. However, in the DME production, biomass gasification is utilized to adjust the syngas ratio because of its rich CO in the syngas. The performance of DME process depends on many parameters such as operating temperature, pressure, space velocity, water removal, and H2/CO ratios. In the present study, the effect of the H2/CO molar ratios on the performance of the DME yield was investigated. To help ease

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global warming, the study proposed CO₂ as route and co-feeding of syngas.

In the energy points of view, the energy and exergy analyses are useful methods to analyze the conversion energy system [3]. In the energy and exergy analysis calculation is based on the first and second laws of thermodynamics. In order to study the efficiency of the two different routes (CO and CO_2), the DME production based on the single step process in the thermodynamic equilibrium model was used. Also, the parametric study included the effects of operational temperature and pressure used in the present study.

2. Methodology

In the synthesis of dimethyl ether, the reaction pathway comprises methanol synthesis, methanol dehydration, and water gas shift reactions as shown in Table 1. As can be seen, all of the reactions which take place in the DME reactor as exothermic reactions. The DME production process has three steps, syngas preparation, DME synthesis, and DME separation, as shown in Fig.1. In the syngas preparation step, the syngas is compressed (COM-1) to increase the pressure between 30-70 bar, and then preheated (HX-1) at 200-3000C before feeding into the DME reactor. In the DME synthesis, the RGibbs model was used as a DME reactor. It is determined based on the chemical and phase equilibrium by minimizing the Gibbs free energy. In addition, the RGibbs models are does not require the reaction data and reaction stoichiometry. The DME product from the synthesis feed stream into the DME separation. The RadFrac model is used for the separation simulations. The assumptions of the thermodynamic analysis of DME production via the single step process in different routes are:

- (1) The dimethyl ether system is operated in a steady state;
- (2) The dimethyl ether reactor is isothermal;
- (3) The environmental state is at 25 °C and 1 atm, respectively; and
- (4) The feedstock and gaseous components behave idea gas.

Table 1. Reaction path ways of the DME synthesis [2].

No.	Reaction	Reaction name	Heat of reaction (kJmol ⁻¹)
R1	$2CO + 4H_2 \longleftrightarrow 2CH_3OH$	Methanol synthesis	-205
R2	$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$	Methanol synthesis	-49
R3	$2CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O$	Methanol dehydration	n -23
R4	$CO + H_2O \longleftrightarrow CO_2 + H_2$	Water-gas shift	-41



Fig. 1. Aspen plus flowsheet used for dimethyl ether production

The conversion of CO and CO₂ can be calculated as following equations:

$$CO \text{ conversion}(\%) = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100$$
(1)

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$$CO_{2} \text{ conversion(\%)} = \frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}} \times 100$$
⁽²⁾

where CO_{in} and CO_{out} are the molar flowrates of the carbon dioxide at the inlet and outlet streams. Also, the $CO_{2,in}$ and $CO_{2,out}$ are the molar flowrates of carbon monoxide at the inlet and outlet streams, respectively. To indicate the performance of the DME synthesis, The DME yield (Y_{DME}) for CO and CO_2 routes are defined as

$$Y_{DME,CO} = \frac{DME_{out}}{(CO_{in} + CO_{2,in})} \times 100$$
(3)

3. Energy and Exergy Analysis

In this section, the energy and exergy analyses are discussed. The energy analysis is based on the first thermodynamics law which is the conservation of energy, while the exergy analysis is determined based on the second thermodynamic law. Energy analysis consists of the chemical and physical energies as shown in Table 2 [3]. The physical energy (E^{ph}) in material stream is investigated from the sum of the specific enthalpy at the operating temperature. The chemical energy (E^{ch}) can be calculated by higher heating value (HHV) of the component *i*. In the exergy analysis, the total exergy is calculated from the physical and chemical exergies, which are similar to the energy analysis. The exergy chemical (Ex^{ch}) relies on the molar fraction of the component of stream in the system as well as standard chemical exergy (ex_i^{ch}) of gaseous component [4]. The standard chemical exergy values used in the present study have been adopted from [4]. Besides, the physical exergy (Ex_i^{ph}) depends on the difference in the enthalpy and entropy resulted from the temperature and pressure deviation from the environmental state. To perform the energetic (η_E) and exergetic efficiencies (η_{Ex}) of the DME production, the energy and exergy efficiency are obtained from the ratio of the energy or exergy of the product to the energy and exergy at the input as feedstock or fuel.

Table 2. Energy and exergy analysis equations.								
	Parameter	Energy	Exergy					
	Physical	$E^{\mathrm{ph}} = \sum_{i=1} n_i h_i$	$Ex^{\mathrm{ph}} = \sum_{i=1} n_i Ex^{\mathrm{ph}}_i$					
	Chemical	$E^{\rm ch} = \sum_{i=1} n_i {\rm HHV}_i$	$Ex^{\rm ch} = \sum_{i=1}^{n} n_i (ex_i^{\rm ch} + RT_0 \ln y_i)$					
	Efficiency	$\eta_{\scriptscriptstyle E} = \frac{E_{\scriptscriptstyle \rm Product}}{E_{\scriptscriptstyle \rm Fuel} + Q} \times 100\%$	$\eta_{Ex} = \frac{Ex_{\text{Product}}}{Ex_{\text{Fuel}} + Ex_q} \times 100\%$					

4. Results and Discussion

4.1. Influence of temperature and pressure on yield of DME

The influences of the operating temperature and pressure on the CO and CO₂ conversion and yield of DME are shown in Fig. 2. In this study, the molar ratio of H_2/CO at the inlet of the reactor is maintained of 4 for H_2/CO and 5 for H_2/CO_2 . The operating temperature is varied from 200 to 300 °C, while the pressure is ranged from 30 to 70 bar. The CO and CO₂ conversions and DME yield are calculated using Eqs. (1)-(3). As can be seen, it can be observed that DME yield and CO conversion increase when increased the pressure. This can be described using Le Chatelier's principle. An increase in pressure favours the equilibrium to shift in forward direction. In CO hydrogenation (R1), the reaction goes towards to produce methanol and then convert to DME. However, the elevation of the pressure can affect to individually CO hydrogenation reaction. On the other hand, the CO conversion decreases with increasing

the temperature, caused in decreasing of the DME yield. This is because the CO hydrogenation (R1) is exothermic reaction. The maximum yield of DME and CO conversion are 0.44 mol (mol CO)⁻¹ and 99.89%, respectively located at the temperature and pressure of 200 °C and 70 bar. For CO₂ route, the results are similar to those of CO route, increasing the pressure can enhance the DME yield and CO₂ conversion. The increase of the temperature results in dramatic decrease in DME yield. The maximum conversion of the CO₂ and yield of the DME are 0.36 mol(mol CO₂)⁻¹ and 99.89%, respectively at a reaction temperature and pressure of 200 °C and 80 bar.



Fig. 2. Yield of DME (a)
$$H_2/CO=4$$
 and (b) $H_2/CO_2=5$

4.2 Influence of H_2/CO , H_2/CO_2 and $H_2/(CO+CO_2)$ on yield of DME

The DME yield in various H_2/CO , H_2/CO_2 and $H_2/(CO+CO_2)$ ratios are shown in Table 3. In this study, the H_2/CO and H_2/CO_2 ratios are varied between 1 to 5, while the $H_2/(CO+CO_2)$ ratio is fixed at $H_2/CO=4$. The CO/CO₂ ratios are varied from 0.5 to 2.5. The operational pressure and temperature for H_2 /CO and $H_2/(CO+CO_2)$ routes are 200 °C and 60 bar, whereas the H_2/CO_2 are operated at 200 and 80 bar, respectively. The ranges of the DME yield based on H₂/CO are in the ranges of 0.32-0.44 mol mol CO⁻¹, while the yields of $H_2/(CO_2)$ ratios and $H_2/(CO_2+CO)$ are in the ranges of 0.10-0.35 mol mol $(CO_2)^{-1}$ and 0.36-0.42 mol mol (CO+CO₂)⁻¹, respectively. As seen in Table 3, at the $H_2/CO=5$ have a higher DME yield than those of $H_2/CO=4$ about 2.32%. In the CO₂ route, the DME yield at the $H_2/CO=5$ is lower than CO route, accounted 20.45%. This can be explained that the CO_2 hydrogenation (R2) is less exothermic than the CO hydrogenation reaction (R1), as seen in Table 2. It is meant that the CO_2 hydrogenation is limited by thermodynamic in the methanol synthesis. Thus, in the same operating temperature (200°C), the amount of methanol produced by CO hydrogenation is greater than CO₂ hydrogenation and can be converted to the DME as a product (R3). In the CO₂ utilization with syngas, the results were revealed that the maximum DME yield for CO route with co-feeding CO₂ (CO₂/CO=2.0) is 0.56 mol mol (CO+CO₂)⁻¹ which are higher than those of CO_2 and CO routes about 44 % and 60%, respectively. This can be indicated that using CO₂-cofeeding can provide the CO₂ hydrogenation to produce the methanol resulted in increase the DME yields. However, the use ratio of carbon dioxide and carbon monoxide (CO_2/CO) more than 2, the reverse water gas shift reaction are occurred leading to reduce the CO conversion as well as yields of DME.

Table 3. Influence of yield of DME various H_2/CO , H_2/CO_2 , and $H_2/(CO+CO_2)$ ratios.

CO route		CO ₂ route	CO ₂ route		CO route with co-feeding CO ₂		
H ₂ /CO	mol (mol CO) ⁻¹	H ₂ /CO ₂	$mol (mol CO_2)^{-1}$	H ₂ /CO	CO ₂ /CO	mol (mol CO+CO ₂) ⁻¹	
1	0.32	1	0.10	4	0.5	0.51	
2	0.38	2	0.19	4	1.0	0.54	
3	0.41	3	0.27	4	1.5	0.55	
4	0.43	4	0.32	4	2.0	0.56	
5	0.44	5	0.35	4	2.5	0.56	

4.3 Energetic and exergetic efficiencies

The energetic and exergetic efficiencies of the DME production system for H_2/CO , H_2/CO_2 and $H_2/(CO+CO_2)$ routes are shown in Fig.3, which are in the ranges of 34.35-45.60 % for energetic efficiency and 22-59-37.83% for exergetic efficiency. The CO route ($H_2/CO=4$) has the highest energetic efficiency, while the lowest energetic efficiency is a CO₂ route (H_2/CO_2). This is due to the use of CO route give a higher yield of DME that those of CO₂ route, even its using a lower energy input. The utilization of CO₂ with the syngas can enhance the energetic efficiency about 8% compared with CO₂ route. Similar to that of energy analysis, the highest exergy are H_2/CO and $H_2/(CO+CO_2)$ routes. The reasons of these results are the same as energetic efficiency, high yield of DME resulted in a higher energetic and exergetic efficiency. Furthermore, if considered the energy and exergy inputs. The energy and exergy input for all routes. Considering to the energy supply about 80% and 79% of the total energy and exergy input for all routes. Considering to the energy supply in the DME production system, the increase of pressure using compressors and DME separation (distillation) have a higher energy consumption than those of the equipment.



Fig. 3. Energetic and exergetic efficiency for H₂/CO=4, H₂/CO₂=5 and H₂/(CO+CO₂)=4.

5. Conclusion

The energy and exergy analyses to indicate the DME production based on three different routes, which are H_2/CO , H_2/CO_2 and co-feeding of CO_2 are investigated. The influence of the pressure and temperature of all routes was carried out to study the DME yields. The results revealed that high pressure and low temperature can enhance the yields of DME. The highest yield of DME are the $H_2/CO=4$ with co-feeding CO_2 ($CO_2/CO=2$), the values of 0.56 (mol $CO+CO_2$)⁻¹ located at the temperature and pressure of 200°C and 60 bar. In the energetic and exergetic efficiencies points of view, the DME yield is predominant affected on the performance of the DME production system. The utilization of CO_2 can improve both energetic and exergetic efficiency.

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