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Design and Simulation of Methanol and Dimethyl Ether (DME) Production from Biomass-Derived Syngas

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The synthesis of methanol and dimethyl ether (DME) through the hydrogenation of CO_2-enriched syngas derived from biomass gasification represents a promising approach to mitigate global warming and to reduce dependence on non-renewable crude oil sources.
This study aims to comprehensive assess one-step DME synthesis, focusing on key performance indicators such as molar feed ratios, carbon oxides (CO_x) conversions, and product yield. Using Aspen Plus simulation software, this research delves into the diverse compositional spectrum of CO_2-enriched syngas feedstocks generated from biomass gasification. The evaluation process spans a broad parameter space, considering factors like reaction temperature (ranging from 200°C to 300°C), reaction pressure (varying between 30 and 80 bar), and molar feed ratios of H_2/CO, H_2/CO_2, CO/CO_2. An H_2/CO_x=3 ratio strikes a delicate balance between large H_2 partial pressure, boosting the reaction (thermodynamically and kinetically), and reduced H_2 excess. The thermodynamic and kinetic analysis reveal a negative CO_2 conversion. Within the investigated range of operating conditions, 50 bar pressure and 220 °C temperature provided the highest yields and CO conversion.

1. Introduction

The combustion of carbon-based fossil fuels results in significant CO_2 emissions, disrupting the earth's natural carbon cycle and leading to global warming, ocean acidification, sea-level rise and climate change. The utilization of CO_2 as a feedstock for the production of chemical building blocks and synthetic fuels has become a prominent technological challenge. Particularly, synthetizing methanol and dimethyl ether (DME) through the hydrogenation of CO_2-enriched syngas derived from biomass gasification offers a promising route to mitigate global warming and reduce dependence on renewable crude oil sources as it contains a substantial fraction of CO_2 along with CO and H_2 (Tripathi et al., 2023). According to Azizi, the DME is considered an alternative and clean fuel since the ether will not form explosive peroxide, allowing it to have safe storage (Azizi et al., 2014). Furthermore, it has the advantage of decreased emissions of NO_x, SO_x and particulates over conventional diesel and it does not produce soot (Makos et al., 2019). DME, due to its autoignition property and clean burning, serves as an excellent alternative to diesel fuel in the transportation sector and small-scale power generation. It is also applicable as a liquid petroleum gas (LPG) blend, due to its vapor pressure similar to LPG, aerosol propellant, and a chemical precursor for various compounds, including formaldehyde, ethanol, and light olefins (Han et al., 2009). The most challenging aspects of DME as a fuel are related to its physical properties, such as its viscosity lower than that of diesel, causing an increased amount of leakage in pumps, and some lubrification issues resulting in premature wear and eventual failure of pumps and fuel injectors (Semelsberger et al., 2006). Thermodynamic analysis plays a crucial role in modelling any reactor system, serving as a preliminary step to understand the reaction mechanism of involved chemical reactions (Stangeland et al., 2018). However, there is a lack of knowledge about the development of novel processes regarding the simultaneous production of methanol and DME in poly-generation systems. This work is part of a more comprehensive work aiming at the development of a novel biomass-to-liquid (BTL) process (Ciccone et al., 2024). In particular, in this work, to provide comprehensive thermodynamic insight into the conversion capability of CO_2-rich syngas derived from biomass, the performance of DME and methanol synthesis has been studied. Furthermore, one-step process

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has been preferred to the two-step process. The ensuing evaluation process encompassed a broad parameter space, involving variables such as reaction temperature (ranging from 200°C to 300°C), reaction pressure (varying between 30 and 80 bar), and molar feed ratios of H_2/CO, H_2/CO_2, and CO/CO_2. After thermodynamic analysis, we directed the focus towards process simulation in Aspen Plus for a better understanding of the overall process for DME synthesis.

2. Methodology

2.1 Thermodynamic analysis approach

Gibbs free energy is commonly employed to determine the equilibrium state of a reaction system. Equation (1) is utilized to calculate the total Gibbs free energy under specified reaction conditions. The minimization of Gibbs free energy serves as a precise method for identifying the composition of a reaction system at thermodynamic equilibrium. In this study, the RGibbs reactor module and the Soave-Redlich-Kwong (SRK) property package in Aspen Plus software were employed to apply this concept.

$$G_T = \sum_{i=1}^{m} n_i \left[G_i^0 + RT\ln\left(\frac{P}{P_0}\right) + RT\ln\left(\frac{n_i}{\sum n_i}\right) \right] \quad (1)$$

where, for component *i*, n_i is molar flowrate, G_i^0 is Gibbs free energy at standard temperature and pressure, *R* is molar ideal gas constant, *T* is reaction temperature, *P* is reaction pressure, and P_0 is atmospheric pressure. The product composition at the reactor outlet was evaluated by calculating the CO_x conversion, product selectivity, and product yield defined as follows:

$$CO_x \text{ conversion } (\%) = \frac{N_{CO_x,in} - N_{CO_x,out}}{\sum N_{CO_x,in}} \times 100 \quad (2)$$

$$\text{Selectivity of species i } (\%) = \frac{j_i N_{i,out} - j_i N_{i,in}}{\sum N_{CO_x,in} - \sum N_{CO_x,out}} \times 100 \quad (3)$$

$$\text{Yield of species i } (\%) = \frac{N_{i,out}}{\sum N_{CO_x,in}} \times 100 \quad (4)$$

Where $N_{i,in}$ and $N_{i,out}$ is the molar flow rate of species i at the inlet and outlet of the reactor, respectively, while j_i is the number of carbon atoms in species i.

The components integrated into the DME synthesis simulation encompass the primary species: CO_2, CO, H_2, CH_3OH, CH_3OCH_3. The analysis excludes the formation of hydrocarbons due to the potential for minimization through the reduction of residence time in the reactor and catalyst optimization.

The primary objective of this investigation is to optimize the inlet stream composition defined by H_2/CO_x, with a specific focus on its influence on product yield and CO_x conversion; CO/CO_2 was fixed at 1. Four different H_2/CO_x ratios (1; 2; 3; 4) were systematically examined to evaluate variations in CO and CO_2 conversion, DME and methanol yield, elucidating their interdependence with the feed ratio.

2.2 Kinetics

The synthesis of dimethyl ether (DME) from syngas is an exothermic reaction. This study employs a bifunctional catalyst of commercial methanol synthesis catalyst ($CuO/ZnO/Al_2O_3$) and the methanol dehydration catalyst ($\gamma - Al_2O_3$). The syngas derived from biomass gasification mainly contents carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2). The overall DME synthesis involves a three-step reactions: CO and CO_2 hydrogenation (methanol synthesis) and methanol dehydration. The methanol synthesis is delineated by two mechanisms, as expressed in reactions (5) and (6), with the assumption that both reactions can concurrently produce methanol. Subsequently, methanol undergoes dehydration in reaction (7) with DME synthesis catalysts. The respective enthalpies of these reactions are indicated as follows:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.55 \text{ kJ/mol} \quad (5)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -49.43 \text{ kJ/mol} \quad (6)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -21.003 \text{ kJ/mol} \quad (7)$$

The rate expressions have been selected from Vakili et al. (Vakili, Setoodeh, et al., 2011) and are represented as follow:

$$r_{CO}=\frac{k_1 f_{CO} f_{H_2}^2 (1-\beta_1)}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}+K_{H_2}f_{H_2}\right)^3} \quad (8)$$

$$r_{CO_2}=\frac{k_2 f_{CO_2} f_{H_2}^3 (1-\beta_2)}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}+K_{H_2}f_{H_2}\right)^4} \quad (9)$$

$$r_{DME}=\frac{k_3 f_{CH_3OH} (1-\beta_3)}{\left(1+\sqrt{K_{CH_3OH}f_{CH_3OH}}\right)^2} \quad (10)$$

$$\beta_1=\frac{f_{CH_3OH}}{K_{f1} f_{CO} f_{H_2}^2} \quad (11)$$

$$\beta_2=\frac{f_{CH_3OH} f_{H_2O}}{K_{f2} f_{CO_2} f_{H_2}^3} \quad (12)$$

$$\beta_3=\frac{f_{DME} f_{H_2O}}{k_{f3} f_{CH_3OH}^2} \quad (13)$$

Where f_i and K_{fj} are the fugacity of component *i* and equilibrium constant of reaction *i*, respectively (Aguayo et al., 2007). The reaction rate constants are tabulated in *Table 1* and equilibrium constants are described in equations (14)-(16).

Table 1: Reaction rate constants and equilibrium constants for DME synthesis (Vakili, Pourazadi, et al., 2011).

k = A exp (B/RT)	A	B
k_1	1.828×10^3	-43.723
k_2	0.4195×10^2	-30.253
k_3	1.939×10^2	-24.984
K_{CO}	8.252×10^{-4}	30.275
K_{CO_2}	2.1×10^{-3}	31.846
K_{H_2}	0.1035	-11.139
K_{CH_3OH}	1.726×10^{-4}	60.126

$$K_{f_1}=\exp(21.84+9.04 \times 10^3/T - 7.66 \times \ln T + 54.07 \times 10^{-4} \times T - 57.50 \times 10^{-8} \times T^2 - 6.75 \times 10^3/T^2) \quad (14)$$

$$K_{f_2}=\exp(-24.08 + 7012.4/T) \quad (15)$$

$$K_{f_3}=\exp(-9.76+3.20 \times 10^3/T + 1.07 \times \ln T - 6.57 \times 10^{-4} \times T + 4.9 \times 10^{-8} \times T^2 + 6.05 \times 10^3/T^2) \quad (16)$$

The simulation results of the single-step Dimethyl Ether (DME) synthesis model employing a catalyst in a plug flow reactor with a specified temperature were conducted using Aspen Plus. The outcomes portray the mole fraction (%) of DME and Methanol under varying catalyst weight (kg) at three distinct temperature (220 °C, 250 °C, 280 °C), while the pressure is set at 50 bar.

2.3 Flowsheet description

The inlet stream (IN) represents a CO_2-rich syngas feed supplied with a molar flow rate of 44.33 kmol/hr at 25°C and 1 bar (Ciccone et al., 2024). This syngas was passed in a compressor set at discharge pressure of 50 bar. The S1 stream was heated to 280°C in heat exchanger (HX1) before entering the DME reactor (isothermal reactor). The product stream (P) from the reactor was a mixture of DME, methanol, water and residual gases. The process stream passed through a cooler (HX2) to lower the temperature.

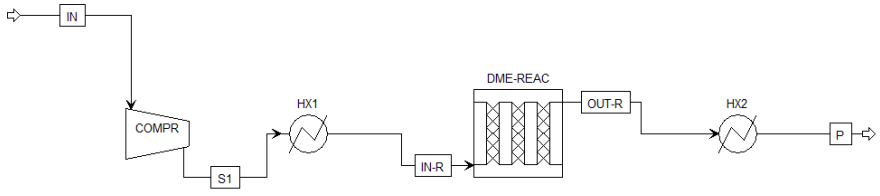

Figure 1. Dimethyl ether (DME) synthesis flow-sheet.

3. Results and discussion

3.1 Thermodynamic analysis

Thermodynamic investigations on concurrent methanol and dimethyl ether (DME) synthesis are presented in this study. Figure 2 depicts the CO_x conversion and products yields as a function of temperature and H_2/CO_x ratio at fixed pressure (50 bar), indicating that the H_2/CO_x=3 ratio yields the best overall performance. The judicious choice of the ratio ensures that there is sufficient H_2 available to drive the synthesis reactions efficiently without incurring the drawbacks associated with excessive H_2 utilization observed in the H_2/CO_x=4 ratio. A detailed optimization of this parameter by a complete techno-economic analysis is beyond the scope of this work and will be reported in a further paper. In Figure 2, a noteworthy descending trend in CO_2 was discerned. The observed negative CO_2 conversion signifies a departure from the anticipated consumptive nature of the process and, instead, indicates a net production of CO_2.
Additionally, the study explores the sensitivity of the process to changes in pressure and temperature. Figure 3 illustrates the effects of varying pressure and temperature on DME and methanol yield, along with DME selectivity, at H_2/CO_x ratio equal to 3. This investigation uncovers notable trends. Particularly, a discernible increase in product yield is observed under high-pressure conditions coupled with low temperatures, indicating favorable thermodynamic conditions promoting the formation of desired products. However, with an increase in temperature, a subsequent decline in product yield becomes evident, as expected for exothermic reactions. The slopes of iso-yield curves for DME are high, clearly suggesting that the effect of temperature on the actual thermodynamic value is more significant than that of pressure. On the contrary, the effect of pressure is more pronounced on methanol yield. Accordingly, low temperature and high pressure represent the best operative conditions from a thermodynamic point of view. This suggests a complex interplay of kinetics and thermodynamics, where the beneficial effects of high pressure on both thermodynamics and kinetics are mitigated by the adverse impact of elevated temperatures on thermodynamic constraints. Under the investigated reaction conditions, it is worth noting that DME yields are higher than methanol ones. Actually, the preferential product will mainly depends on the relative kinetics between methanol synthesis and its dehydration to DME, rather than on thermodynamic constraints.

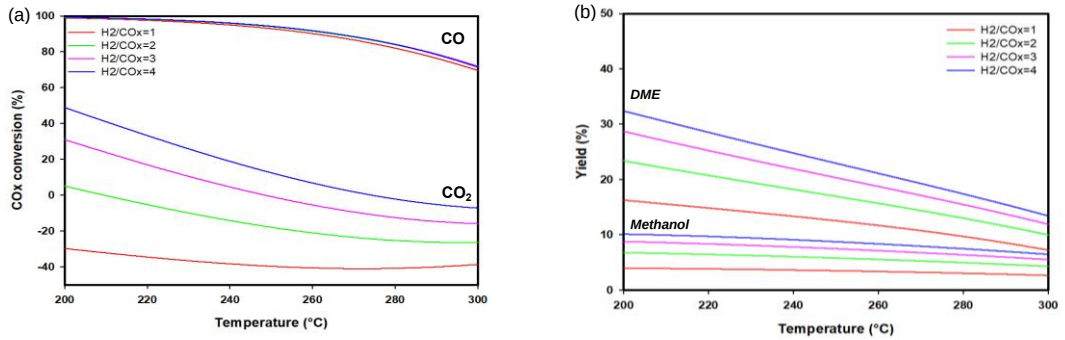

Figure 2. Comparison of (a) equilibrium CO_x conversion and (b) DME and methanol yield in DME synthesis reactions for different feed ratios and temperature values, with pressure set at 50 bar.

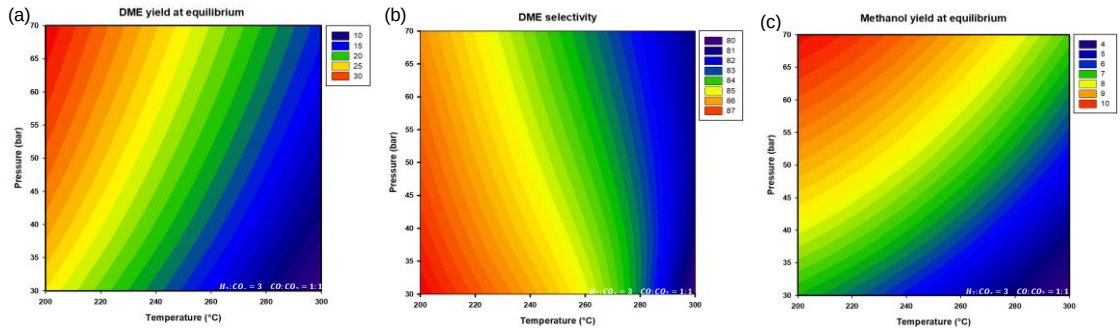

Figure 3. Comparison of (a) equilibrium DME yield, (b) DME selectivity and (c) methanol yield in DME synthesis reactions for different temperature and pressure values at fixed feed ratio (H_2:CO_x=3; CO:CO_2=1:1).

3.2 Kinetic analysis

In the conducted kinetic analysis, a discernible pattern unfolded, elucidating a sequential progression in the dynamics of product formation. Initially, a predominant formation of methanol was observed, a phenomenon ascribed to its thermodynamic and kinetic advantages over DME. With an increase in catalyst weight and the progression of the reaction, methanol production reached a peak, indicating an optimal point in its generation. Following the apex of methanol formation, a significant transition transpired, wherein DME production accelerated, surpassing the rate of methanol synthesis. This phase was marked by a simultaneous increase in DME production and a decrease in methanol, culminating ultimately in a plateau for both methanol and DME formation, corresponding to thermodynamic compositions. This observed phenomenon implies a kinetic shift favoring DME production over methanol at this juncture.
Further examination of Figure 4 in relation to temperature reveals a noteworthy correlation. Elevated temperatures correspond to an accelerated overall reaction rate, indicating enhanced kinetic activity. However, there was a simultaneous decrease in the mole fraction of both methanol and DME, as expected by the thermodynamic analysis. The observed shift in product selectivity with temperature variations underscores the intricate interplay between kinetics and thermodynamics, providing crucial insights into optimal operating conditions for maximizing desired product yield in DME synthesis.

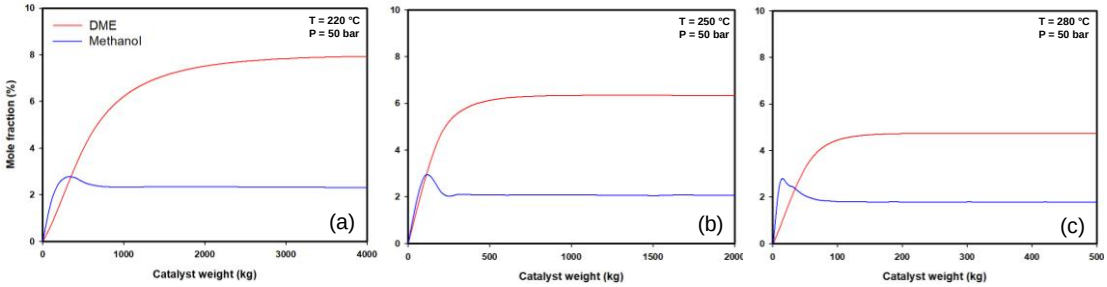

Figure 4. The mole fraction of DME and methanol varying the catalyst weight with fixed pressure at 50 bar and varying the temperature: (a) 220 °C, (b) 250 °C, (c) 280 °C.

Table 2 presents kinetic outcomes. The temperature-dependent trends are evident, with lower temperature favoring higher CO conversion and product yields. The negative CO_2 conversion values further indicate a production of CO_2 during the synthesis process.

Table 2: Kinetic outcomes.

	DME yield (%)	MeOH yield (%)	DME Selectivity (%)	CO conversion (%)	CO_2 conversion (%)
220	19.14	5.46	87.52	97.42	-13.14
250	15.81	5.13	86.05	92.82	-22.66
280	12.72	4.79	84.17	83.58	-26.30

4. Conclusions

This study delves into the intricate dynamics governing concurrent methanol and dimethyl ether (DME) synthesis from biomass syngas through comprehensive thermodynamic and kinetic analysis under the environment of ASPEN Plus. The examination of varying H_2/CO_x ratios elucidates a paramount finding – the H_2/CO_x=3 ratio strikes a delicate balance between providing ample H_2 for the reaction while mitigating excessive H_2 consumption and utilizing, demonstrating optimal performances. The thermodynamic and kinetic analysis reveal a negative CO_2 conversion, indicating a net production of CO_2 during the synthesis process. Further exploration of process sensitivity to pressure and temperature quantifies the trend observed. At fixed pressure of 50 bar, low temperature conditions (220 °C) are thermodynamically and kinetically advantageous, reaching higher yields and CO conversion (DME yield = 19.14 %, MeOH yield = 5.46, CO conversion = 97.42 %).
In essence, this study not only provides a qualitative understanding of the multifaceted dynamics governing DME synthesis but also quantifies the key parameters influencing process efficiency. Although the overall system is not optimized, it is the starting point for future techno-economic analysis.

Nomenclature

G – Gibbs free energy, kJ/mol
K_i – equilibrium constants of component *i*
N_i – Molar flow rate of component *i*, kmol/h
R – gas constant, 8.314472 J K^{-1} mol^{-1}
T – Temperature, °C
f_i – fugacity of component *i*, bar
k – reaction rate constant
r – reaction rate, mol kg^{-1} s^{-1}

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