

Thermodynamic and Kinetic Based Simulation Approach to CO₂ and CO Methane Hydrogenation

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Methane hydrogenation is an important process in the power to methane system which is a novel energy saving technology. The current study is based on the simulation of CO₂ and CO methanation, using Aspen Plus® V8.6. First, different kinetic models obtained from literature are used in order to investigate methane mole fraction profiles along the reactor length. It can be found that methanation of pure CO leads to a higher value of methane yield and a reactant conversion related to CO₂ at the same operating condition and stoichiometric feed ratio. Moreover, a comprehensive thermodynamic simulation will be carried out to express the effects of different operating conditions on the system efficiency. It can be seen that the performance of both cases are highly affected by temperature and pressure. Although, CO and CO₂ seem to have the similar behavior but these have still differences which will be expressed in detail below.

1. Introduction

Methane is the lightest hydrocarbon which is the main component of natural gas. CH₄ can be found under earth or sea abundantly. Methane can be stored in pressurized container and it has 55.5 MJ/kg as heat of combustion.

Since the oil crisis in the early 1970s, the interest of methane generation has been increased (Mills et al., 1974). Many experimental studies have been conducted in the past for methanation fixed bed reactor with different process conditions and they are available as background for this process. (Er-Rbib et al., 2013)

Carbon oxide hydrogenation is the reaction by which CO₂ or CO and hydrogen are converted to methane and water as the main product. Methanation can be performed both in biological and catalytic reactors. A typical catalytic methanation process operates at temperature and pressure ranges of 200 - 600 °C and 1 - 100 bar respectively. The methanation reaction is catalyzed mostly by a nickel catalyst because of acceptable CH₄ selectivity, high activity and reasonable price.

The purification of synthesis gas (by removing CO₂) and methane production are two main methanation processes proposed in industry. But in the recent years methane has become an interesting and trustful product for energy saving technology researchers. Therefore, the power to methane process is very attractive and a new application in order to meet challenges related to renewable energy resources and seasonal energy savings.

Methanation is a reaction between CO_x (CO/CO₂) and H₂ as a second reactant. Carbon oxide can be captured from fossil fuel power plants and is a very common method for CO_x production. Through this process chemical and physical absorption, adsorption, separation applications are used (Finkenrath, 2015). Moreover, there are some industrial processes such as cement and steel production in which CO_x can be found in downstream product flow which is unavoidable in many cases and hazardous to the environment. Thus, the processing of capturing CO_x is an opportunity for these industries to reduce their carbon footprint. The post processing technologies for the cleaning of flue gases are similar to fossil fueled power plants.

The biomass process can be categorized in gasification, fermentation and combustion applications. In the fermentation process of biomass to ethanol, CO_x can be found in the product. Capturing CO_x from gasification or combustion process is quite similar to the fossil fueled power plant application. The concentration of atmospheric CO₂ has increased since the beginning of the industrial revolution mostly because of the burning

of fossil fuels. To date, CO₂ is available in the air (up to 400 ppm). Some technologies such as separation are needed to capture CO₂ from the air (Joshua, 2015).

CO₂ contains a blend of CO₂ and CO in different composition. Converting CO₂ to CO consumes energy and heat in order to break double C-O bond. At atmospheric pressure and temperatures of 25 °C, CO₂ can be converted into CO and O₂ by +293 kJ/mol as heat of reaction. However, the higher Gibbs free energy reactant H₂ in the reversible and methanation reaction leads to the conversion of CO₂ with a standard enthalpy of formation of -167 kJ/mol (Jacquemin et al., 2009).



In the catalyzed hydrogenation of carbon oxides to methane, three independent reactions are important (see Eqs(1-3)). If the stoichiometric ratio of the reactants H₂/CO_x sets three or more, carbon monoxide reacts with hydrogen to form methane and water (see Eqs(1) and (3)), accompanied by a molar reduction up to 50 %. This reaction is called CO methanation reaction Eq(1). Meanwhile, in CO methanation the water gas shift reaction Eq(2) takes place where the H₂/CO ratio can be adjusted by converting CO with H₂O to CO₂ and additional hydrogen.

Methanation of CO₂ Eq(3) releases the enthalpy of reaction of -165 kJ/mol. It has to be noted that the CO₂ methanation does not occur in the presence of CO (Mills et al., 1974).

It can be seen that the exothermic CO₂ methanation is suppressed as the temperature increases and because of its high equilibrium constant in the range of 200 - 550 °C. In addition, methane can also be decomposed by reverse reaction of carbon oxide hydrogenation Eq(4).

2. Methanation Simulation using Aspen Plus®

There are some important issues like mass transfer, equilibrium, occurrence of secondary reactions such as water gas shift reaction and exothermicity, which make methanation reactor process more complicated especially in industrial scale. Therefore, simulation and modeling of the process before the industrial plant operation is necessary.

Numerous studies for various assumptions of the rate-determining steps and for many types of nickel catalysts were have been undertaken. The kinetics of CO and CO₂ methanation including water gas shift reaction has been widely investigated.

In this part, some kinetic models were taken from literature and were used to model a plug flow reactor by Aspen Plus® V8.6. Considering the Xu and Froment (1989) kinetic model reaction rate Eqs (5-8) are as follows:

$$r_1 = \frac{k_1}{P_{\text{H}_2}^{2.5}} (P_{\text{H}_2} P_{\text{CO}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_1}) / \text{DEN}^2 \quad (5)$$

$$r_2 = \frac{k_2}{P_{\text{H}_2}} (P_{\text{H}_2} P_{\text{CO}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_2}) / \text{DEN}^2 \quad (6)$$

$$r_3 = \frac{k_3}{P_{\text{H}_2}^{3.5}} (P_{\text{H}_2}^2 P_{\text{CO}_2} - \frac{P_{\text{H}_2}^4 P_{\text{CO}_2}}{K_1 K_2}) / \text{DEN}^2 \quad (7)$$

$$\text{DEN} = 1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2} \quad (8)$$

Where k is rate coefficient of reaction, K is equilibrium constant of reaction, P_i is partial pressure of component i and r_i is rate of reaction i.

The Xu and Froment (1989) kinetics model (model 1) was compared with other kinetic model which was presented by Vanherwijnen et al. (1973) (model 2) at the same operating condition.

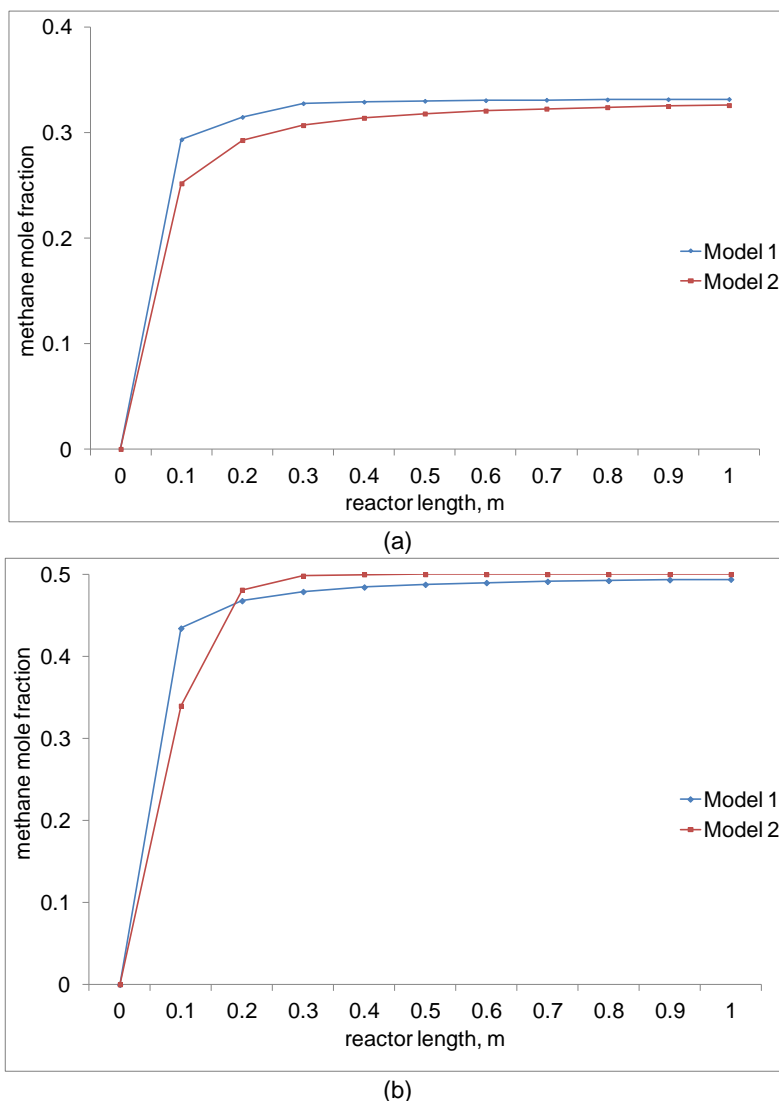


Figure 1: Comparison of kinetic models, methane molar composition VS reactor length, at 250 °C and 1 bar for (a) CO₂ methanation, H/C=4, and (b) CO methanation, H/C=3

Figure 1a presents the CO₂ and figure 1b shows the CO hydrogenation process. It can be found that the methanation of pure CO leads to a higher value of the methane yield and a reactant conversion related to CO₂ at the same operating condition and stoichiometric feed ratio.

The Plug reactor as a built-in reactor model in Aspen plus® V8.6 is chosen for this simulation. An ideal system is assumed for thermodynamics property section. An isothermal RPLUG with 0.25 m diameter as a rigorous model for plug flow is used. Figure 1a shows methanation of CO₂ performance in stoichiometric feed ratio (H₂/CO₂=4) and figure 1b presents the methanation of the CO performance at the same condition but different feed ratio (H₂/CO=3). The total feed flow rate in both cases is 10 kmol/h.

3. Sensitivity analysis

The Gibbs model provides reactor calculations without the need for a detailed reaction stoichiometry or kinetics model. This method is very useful when many unknown reactions take place in reactor and the system has enough time to reach equilibrium.

This reactor model is based on a thermodynamic model calculation method. The number of phases, which components are present in each phase and also how to distribute the phase on the outlet streams can be specified. It was shown before (Sharifian et al., 2015) that if the reactor operates at steady state conditions the Gibbs reactor model's performance is similar compared to the Plug model.

3.1 CO methanation

The hydrogenation of carbon monoxide is the simplest example of synthesis of hydrocarbon from synthesis gas. For a primary investigation of methanation catalysts in the laboratory scale, CO methanation is performed at atmospheric pressure.

It was found that the product stream mostly contains CH₄ and water with trace amount of other components by-product at a low temperature (200 - 300 °C). It also can be seen that with an increase in temperature, the mole fraction of water and CH₄ decreases as well, whereas reactant (CO, H₂), and deposited CO₂ increase simultaneously. The reaction temperature for CO methanation should be set at a low temperature to lead the best mole composition of the product, although for catalysts of methanation it is not recommended for industry to adopt such operation parameters.

Figure 2 illustrates the effects of pressure and temperature on CO methanation performance at stoichiometric feed ratio (H₂/CO=3). Methanation of carbon monoxide is a volume decreasing reaction Eq(1) thus a high pressure leads to a higher CO conversion at the same reaction temperature (Figure 2a). Another important issue about pressure changes of CO methanation is that a higher pressure (30 bar) does not change in a higher CO conversion below 600 °C by comparison to result at 20 bar. Carbon monoxide methanation is an exothermic reaction Eq(1) therefore, as can be seen at Figure 2a, at the constant pressure lower temperature leads the higher conversion.

Figure 2b presents the changes in the methane yield as a function of temperature at different pressures. A high value of methane yield (100 %) was achieved at low temperature (lower than 275 °C) at 1 up to 30 bar pressure.

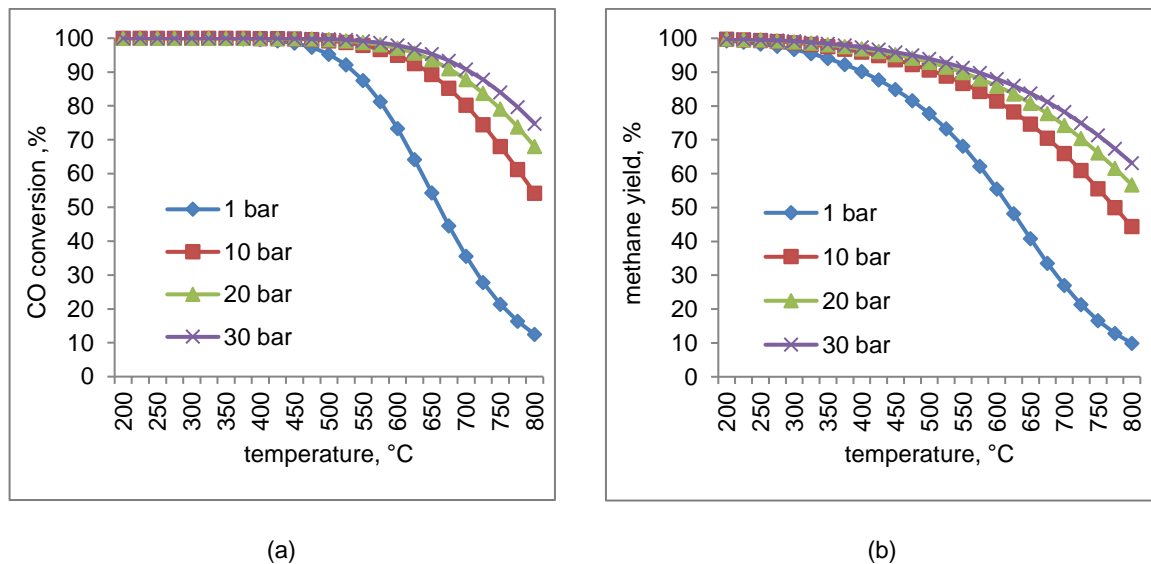


Figure 2: Effects of different operating conditions on methanation of carbon monoxide performance (a) CO

$$\text{conversion} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \quad (9) \text{ and (b) } CH_4 \text{ yield} = \frac{F_{CH_4, out}}{\sum F_{i, in}} \times 100 \quad (10)$$

Generally, high pressure and low temperature will boost the carbon monoxide hydrogenation. However, two main factors have a great influence on operation conditions. First of all, operating and fixed cost, as we know, high operation pressure and temperature in chemical industry are not economically recommended. Second, sufficiently active catalyst at lower temperature is another issue which is an important challenge for catalyst development.

3.2 CO₂ methanation

Methanation of carbon dioxide is a recommended process due to decreasing CO₂ in the atmosphere and also producing energy.

In the carbon dioxide methanator a set of reactions take place. In the beginning water gas shift reaction Eq(2) and then rapid methanation of carbon monoxide Eq(1) are the main side reactions after CO₂ methanation. Figure 3 illustrates the effect of pressure and temperature on carbon dioxide conversion. It is found that the CO₂ conversion decreases with raising temperature and increases with the increment of pressure, up to temperatures below 600 °C (at 1 bar) and up to 700 °C (at higher pressure values).

Like carbon monoxide, carbon dioxide methanation reaction is decreasing volume and exothermic. At 1 bar pressure, conversion of carbon dioxide increases after 550 °C. The main difference of CO and CO₂ system is the activation of the water gas shift reaction in the CO₂ methanator after 550 °C. Furthermore, it can be seen that in a higher pressure water gas shift reaction has a slight effect on the CO₂ conversion.

Another result which can be obtained by the comparison of Figures 2a and 3a is that CO₂ methanation is more difficult than CO methanation at the same operating condition.

Figure 3b presents CH₄ yield variation at the different temperature and pressure in the CO₂ hydrogenation application. It can be found that low temperature and high pressure enhance the CO₂ methanation performance. Moreover, by the comparison to the CO methanation it can be observed that both applications have similar reactions to temperature and pressure changes.

In order to reach a high CH₄ yield value at atmospheric pressure, the operating temperature should not exceed 300 °C. However, the reduction of carbon dioxide to methane which involves eight electrons changing is very complicated to perform. Therefore, at low temperature, for CO₂ hydrogenation to CH₄ a much more active catalyst is required.

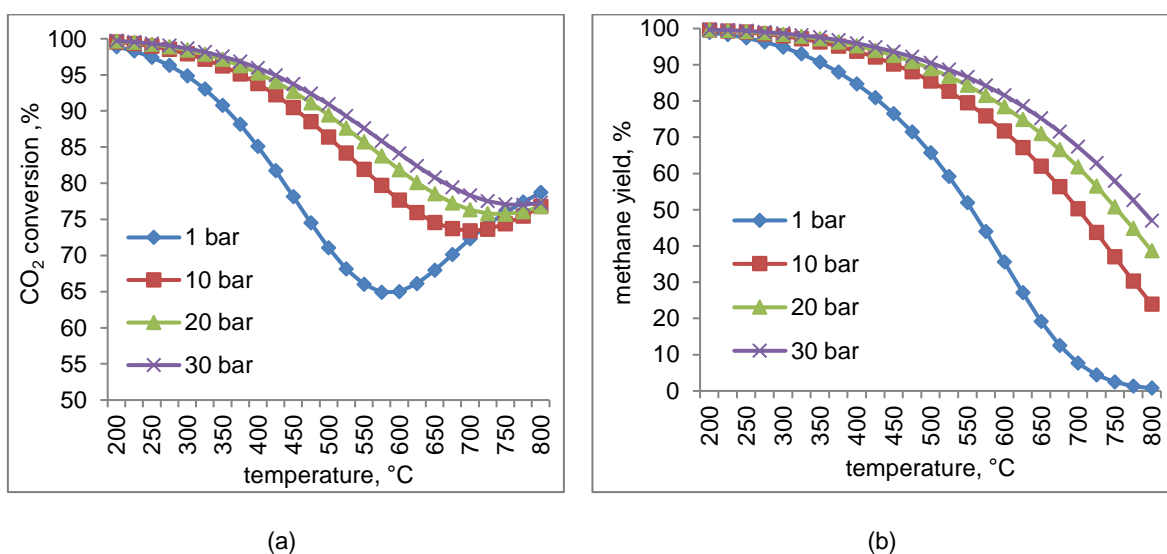


Figure 3: Effects of different operating conditions on methanation of carbon dioxide performance (a) CO₂

conversion = $\frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}} \times 100$ (11) and (b) CH₄ yield

Table 1: Comparison of methanator outlet stream of industrial data with simulation result

	Case 1			Case 2		
	IN	OUT (exp)	OUT (cal)	IN	OUT (exp)	OUT (cal)
T (°C)	300	604	604	398	729	729
P (atm)	27.2	27.1	27.1	30	30	30
Mole frac						
CO	0.0428	0.0117	0.0111	0.1861	0.084	0.0795
CO ₂	0.0613	0.0446	0.0437	0.1474	0.233	0.2369
H ₂	0.3688	0.2096	0.2031	0.2564	0.206	0.2033
H ₂ O	0.1919	0.2982	0.3029	0.4023	0.4196	0.4204
CH ₄	0.2812	0.3744	0.3785	0.0004	0.0494	0.0517
N ₂	0.054	0.0615	0.0607	0.0072	0.0079	0.0079

4. Validation

For the verification of the simulation results two different cases were chosen from the literature. Table 1 demonstrates the calculated results together with the empirical data reported. The feed gas in these cases contains H₂, CO, CO₂, CH₄, H₂O, and N₂ (or Ar) with a certain composition which can be found in the IN column. Case 1 (Harms et al., 1980) is chosen from reactor 1 of the ADAM I system, which was proposed by

the British Gas Corporation in March 1979, in which methanation reactions including water gas shift reaction are considered. It can be seen that in the outlet stream the calculated values of compositions have a good agreement with ADAM pilot data at certain operating conditions.

Case 2 comes from another methanation application which was performed in England (Woodward, 1980). The research aim was to take a typical gas composition, to subject it to the type of methanation process to produce SNG and evaluate the efficiency of different commercial catalysts. It is clearly found that the product mole fraction calculated surprisingly approach closely to reported, for example, the outlet CH₄ fraction as the main desirable product is 41.96 % for experiment and for 42.02 % calculated.

5. Summary

To conclude, a detailed CO₂ and CO methanation based on built-in reactor models in Aspen Plus[®] was investigated. These models are based on 1) thermodynamic equilibrium analysis of the methanation reactions (using minimization of the Gibbs free energy method) or 2) the kinetics base reactor models of carbon oxides (CO or CO₂).

The sensitivity analysis involved the influence of temperature (200 - 800 °C) and pressure (1 - 30 bar), on the methanator reactions were completely investigated in terms of their effects on the conversion of CO as well as CO₂ and CH₄ yield.

In general, CO methanation leads to more methane as a main product in the outlet stream than CO₂ methanation at the same operating conditions and stoichiometric feed ratio.

The results show that a high CH₄ yield can be obtained from CO methanation at low temperatures, high pressures, and high H₂/CO. Compared to the CO, CO₂ methanation is relatively difficult to be hydrogenated at the same reaction condition. However, the performance of CO₂ methanation is highly affected by temperature and pressure like the CO system.

At the end, for validation of the simulation a comparison of experimental data in the two case studies with the calculations illustrates that the calculated results are significantly effective for analysis of the methanation application.

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