Simulation of CO_X Methanation Reactor
for the Production of Natural Gas

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Because of the increasing demand for natural gas and the reduction of greenhouse gases interests have focused on the production of natural gas, which is suggested as an undeniable role in future energy. Many thermodynamic and kinetic reactions details involved in the methanation process are not completely understood yet. In this study, a full analysis of the main possible reactions occurring in the reactor of carbon oxides methanation is considered using the Aspen Plus® V8.6. The effects of temperature, pressure, and CO_X/H_2 ratio in the feed, on the methane yield and CO_X conversion were investigated. Equilibrium constants of possible reactions occurring in the methanation reactor process are presented as a function of temperature. The comparison between the simulation results and the experimental data shows that the proposed model can predict the methanation reactor performance with high accuracy. The results can be beneficial in the design and performance analysis of a methanation reactor prior to experimental realisation.

1. Introduction

The increase in global emissions of carbon oxide from fossil-fuel combustion and other different kinds of industrial sources – the main cause of global warming (Van-Dal and Bouallou, 2012) – slowed in 2012, while the global average annual growth rate of 2.4 ppm in atmospheric (CO_X) concentrations in 2012 was rather high. The actual global emissions increased by 1.4 % over 2011, reaching a total of 34.5 Gt in 2012. After a correction for the leap year 2012, this increase was reduced to only 1.1 %, compared with an average annual increase of 2.9 % since 2000. The carbon oxide emission trend mainly reflects energy-related human activities which, over the past decade, were determined by economic growth, particularly in emerging countries. In 2012, a 'decoupling' of the increase in carbon oxide emissions from global economic growth (in GDP) took place, which points to a shift towards reducing fossil-fuel intensive activities, higher use of renewable energy sources and increased energy saving systems (Emissions Database for Global Atmospheric Research EDGAR).

There are three main strategies for reducing CO_X emissions: reduce the production, storage of CO_X and the use of it. Hydrogenation of carbon oxide is an attractive C1 building block for making organic chemicals, materials, and carbohydrates (i.e. foods) if considering reducing emissions by usage of CO_X. The hydrogenation into more useful fuels or chemicals uses hydrogen as the required high energy material for transformation. The products of the CO_X hydrogenation are currently being investigated including methane, methanol, ethanol and higher alcohol, hydrocarbons, dimethyl ether, formic acid, formates and formamides. Some of these products can be fuels for internal combustion engines, raw materials, and intermediates in many chemical industries, easily liquefied allowing for easy storage and transportation, and are in general more desirable than carbon oxide. Methane is the main component of natural gas (Brooks et al., 2007). If a natural gas plant with carbon capture and storage technology were utilised for producing electricity using methane/natural gas produced from all carbon oxides, three strategies for reducing its emissions would be implemented. Table 1 lists possible reactions involved in the methanation of carbon oxides.

The simulation of a process allows the engineer to evaluate the effect of the variables in the process, to find out new configurations, and to conduct the optimisation. The following manipulation can be performed with Aspen Plus® V8.6:

- Simulation of the methanation process by using different reactor models
- Using different kinetic models at the same operation condition
- Carrying out sensitivity analysis for operation parameters

Table 1: Possible reactions involved in the methanation of carbon oxides (Xu and Froment, 1989)

Equation No	Reaction	ΔH_{298}, kJ/mol
1	$CO + 3H_2 \rightarrow CH_4 + H_2O$	-206.1
2	$CO + H_2O \rightarrow CO_2 + H_2$	-41.15
3	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-165
4	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247
5	$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O$	-330
6	$CH_4 \rightarrow C + 2H_2$	74.8
7	$2CO \rightarrow C + CO_2$	-173
8	$CO + H_2 \rightarrow C + H_2O$	-131.3
9	$CO_2 + 2H_2 \rightarrow C + 2H_2O$	-90.1
10	$CH_4 + 2CO \rightarrow 3C + 2H_2O$	188

2. Methanation as catalytic reaction

The catalysts being investigated for carbon oxide methanation are generally made up of Group VIII, IX, X and XI transition metals. Nickel and Ruthenium based catalysts produce almost exclusively methane, while less reactive metal constituents like Pd, Pt, Rh, Mo, Re and Au catalyse simultaneously methane, methanol and carbon monoxide by reverse water-gas shift reaction. (Wambach et al., 1999) shows that Cu and Ag catalyse mainly methanol. Nickel based catalysts are the most common studied because of their high activity and low price, but sintering at reaction conditions diminishes their industrial viability (Er-Rbib et al., 2013). Ruthenium has been shown to be the most active metal for methanation, but its high cost makes it less attractive as an industrial application. (Hwang et al., 2011)

In this part, some kinetics models which were taken from literature are used to model a plug reactor by Aspen Plus® V8.6. In the feed stream hydrogen and carbon dioxide are the main components, then in the methanation process, the CO_2 hydrogenation - Eq(3) is a key reaction, accompanied by side reactions (e.g. water gas shift Eq(2) - and CO hydrogenation Eq(2)). Eqs(1) to (3) - Table 1 are three primary equations which play an essential role. Considering the Xu and Froment (1989) kinetics model reaction rate Eqs(11) to (14) are as follows:

$$r_1 = \frac{k_1}{P^{2.5}_{H_2}}(P_{H_2O}P_{CH_4} - \frac{P^3_{H_2}P_{CO}}{K_1})/DEN^2 \tag{11}$$

$$r_2 = \frac{k_2}{P_{H_2}}(P_{H_2O}P_{CO} - \frac{P_{H_2}P_{CO_2}}{K_2})/DEN^2 \tag{12}$$

$$r_3 = \frac{k_3}{P^{3.5}_{H_2}}(P^2_{H_2O}P_{CH_4} - \frac{P^4_{H_2}P_{CO_2}}{K_1 K_2})/DEN^2 \tag{13}$$

$$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O}P_{H_2O}/P_{H_2} \tag{14}$$

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 equilibrium constants of Eq(1) to (3) are presented as Eqs(15) – (17):

$$K_1 = 10,266.76 exp(-26,830/T + 30.11); kpa^2 \tag{15}$$

$$K_2 = exp(4,400/T - 4.063) \tag{16}$$

$$K_3 = K_1 K_2 ; kpa^2 \tag{17}$$

$$k_1 = 9.49 \times 10^{16} exp(-228,879/T); kpa^{0.5} kmol/kgh \tag{18}$$

$$k_2 = 4.39 \times 10^4 exp(-9,074.3/T); kpa^{-1} kmol/kgh \tag{19}$$

$$k_3 = 2.29 \times 10^{16} exp(-29,336/T); kpa^{0.5} kmol/kgh \tag{20}$$

The Xu and Froment (1989) kinetics model was compared with other kinetic models which are based on Ni/Al_2O_3 (Vanherwijnen et al., 1973) and $Ni/CaO/SiO_2$ (Ibraeva et al., 1991) catalyst at the same operation condition. The result is presented in Figure 1 which is based on the methane molar composition changing along the reactor length (diameter = 0.25 m). The simulation model was developed using Aspen Plus® V8.6. The used physical properties of the following compounds are provided in the Aspen Plus® component list: carbon dioxide, water, methane, hydrogen and carbon monoxide. For the thermodynamic model, the PRMHV2 is used. The PRMHV2 property method is based on the Peng-Robinson equation of state with modified Huron-Vidal mixing rules. This model is used for non-polar mixtures and polar compounds, in combination with light gases in different system pressure. An isothermal RPLUG which is a rigorous model for plug flow is used. (Feed = 10 kmol/h)
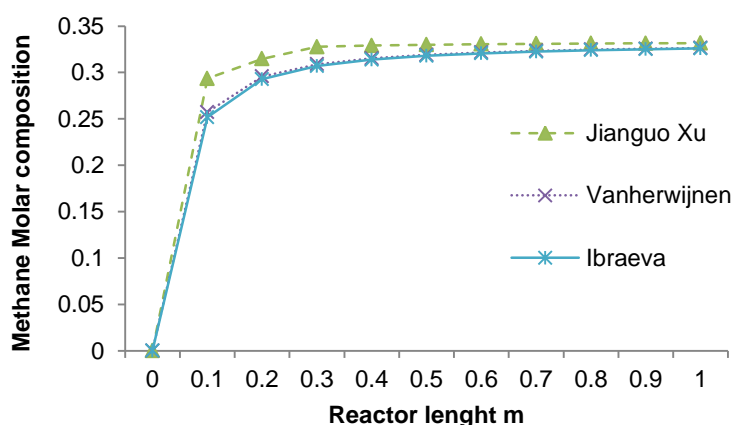

Figure 1: Kinetic models comparison, methane molar composition VS Reactor length, at 250 ºC and 1 atm, $H/C = 4$

3. Gibbs free energy minimising reactor model

The Gibbs model provides reaction calculations without the need for detailed stoichiometry or yield. The method is based on minimising the Gibbs free energy. The block takes one or more input and one or more output streams, and an optional heat input and/or output streams. If the restricted equilibrium is selected, reactions can be defined for the system. The block allows specifying the number of phases, which components are present in each phase, and also how to distribute the phase on the outlet streams (in case multiple output streams are used).

Figure 2 demonstrates a schematic of the process which compares the Gibbs reactor model and the plug reactor model performance at the isothermal condition. A kinetics model is used in the plug block, expressed by Xu and Forment (1989). A table is expressed below to show the differences between these two reactor models performances. This comparison can be found in stream 10 and stream 11 which are the reactor's output. Both models work at the same operation conditions. Splitter divides feed flow in two equal parts and each part after same increase in pressure (compressor) and temperature (heater) goes to reactor. The Plug model's diameter is 0.25 m and its length is 10 m.
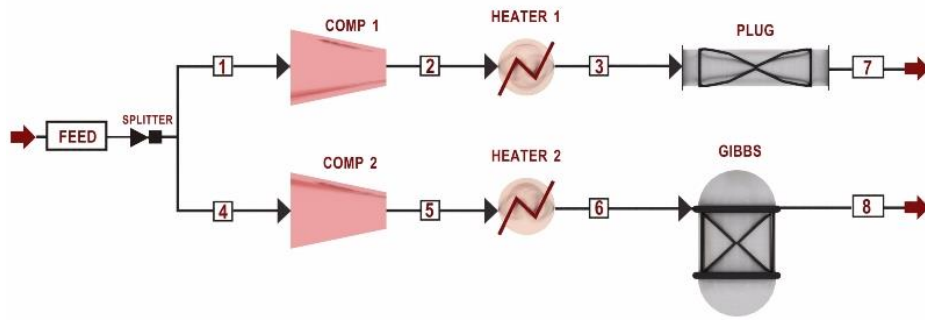
Figure 2: Schematic of Plug and Gibbs reactor models comparison

Table 2: Feed and outlet streams related to Figure 2

Stream	Feed	7	8
Temperature K	298.1	523.1	523.1
Pressure N/m²	101,325	506,625	506,625
Molar flow kmol/s	40	12.036	12
Mole Frac			
CO_2	0.16	0.02	18 ppm
CO	0.04	trace	22 ppb
H_2	0.8	0.072	0.068
H_2O	0	0.595	0.6
CH_4	0	0.331	0.333

4. Sensitivity analysis

One of the advantages of a simulation is that the sensitivity of process performance to changes in operating variables can be studied. By Aspen Plus®, you can allow inputs to vary, and can tabulate the effect on a set of results of your choice. The Gibbs reactor model is selected for sensitivity analysis. The same thermodynamic model (PRMHV2) is used in this part. Also the feed composition is the same with last part. ($H_2/CO_X = CO_2/CO = 4$)

4.1 Temperature and pressure effect

A sensitivity analysis based on different operation conditions was executed. Figures 3 and 4 illustrate the effects of pressure and temperature changing on the methanation performance. It can be seen that in Figure 3, a high pressure leads to a higher methane yield at the same reaction temperature.

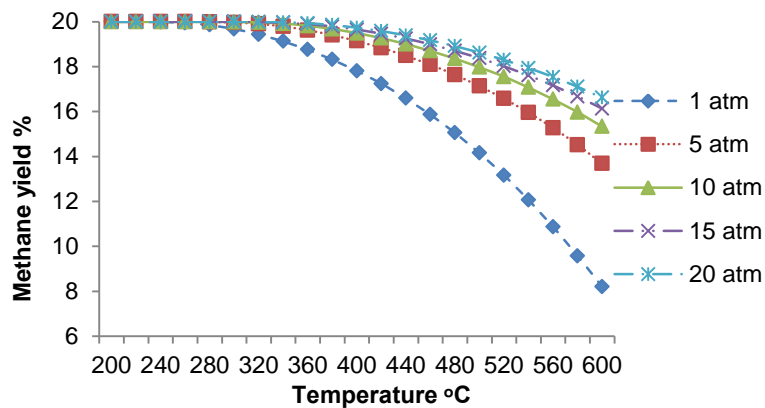$$yield = \frac{F_{CH_4,out}}{\sum F_{i,in}} \times 100 \qquad (21)$$

Figure 3: Methane yield changes in different temperatures and pressure

Carbon oxide methanation is a volume reducing reaction; on the other hand, a much higher pressure (20 atm) does not result in a much higher carbon oxide conversion. It is also known that high operation conditions (pressure and temperature) are economically not of high interest in industry. At the same reaction pressure, a lower temperature results in higher methane yields and also carbon oxide conversion because of the exothermic reaction of the CO_X methanation. Though, this requires sufficiently high active catalysts at the lower temperature, which is the challenge for producing catalysts.

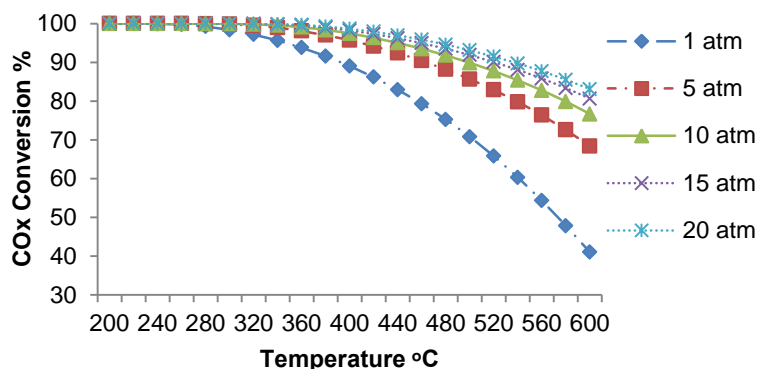$$conversion = \frac{CO_{x,in} - CO_{x,out}}{CO_{x,in}} \times 100 \tag{22}$$

Figure 4: CO_x conversion in different temperatures and pressures

4.2 H_2/CO_X ratio effect
Since syngas has a variable ratio of H_2/CO_X, according to the stoichiometric ratio (Eq(3)), it is required to be at around 4, which is normally controlled through a water-gas shift reaction (Eq(2)). However, according to the carbon monoxide methanation (Eq(1)) the stoichiometric ratio is around 3. It is very hard to define this value to be the exact number in the methanation industry. Therefore, it is necessary to know the effects of this ratio in the methanation process.
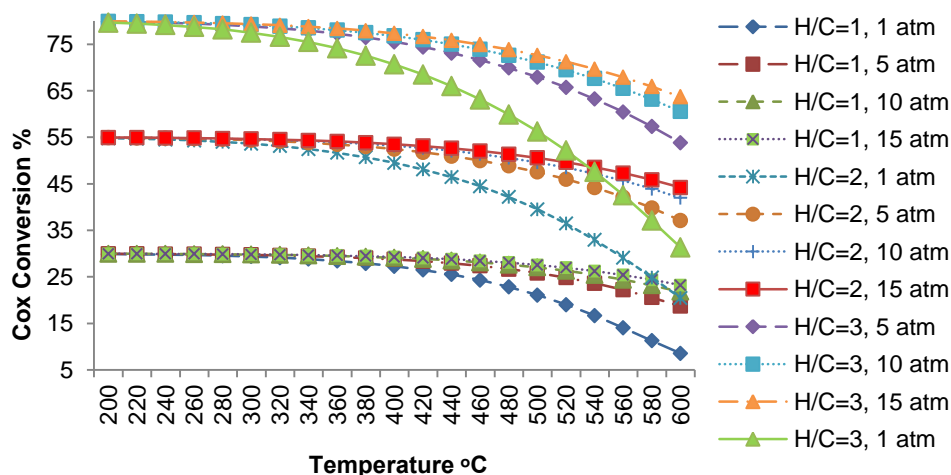

Figure 5: Sensitivity analysis in different feed composition

Figure 5 is presented to show effects of the feed composition in the methanation process. A higher H_2/CO_X ratio generally leads to more carbon oxide conversion. It is expressed that the carbon oxide conversion is remarkably affected by the H_2/CO_X ratio. Figure 6 shows the methane yield at different temperature and carbon oxide compositions as feed stream. The H_2/CO_X ratio and the pressure (10 atm) are constant.
For a comparison with the thermodynamic calculations, the carbon oxide methanation was carried out on commercial Ni-based catalysts ($Ni/MgAl_2O_4$) gotten from Khorasan petrochemical complex (Khorsand et

al., 2007). Table 3 shows the comparison of the thermodynamic calculations with the industrial results for methanation at 316 °C and 28.8 atm. It can be seen that the simulation results have a good agreement with the experiments.
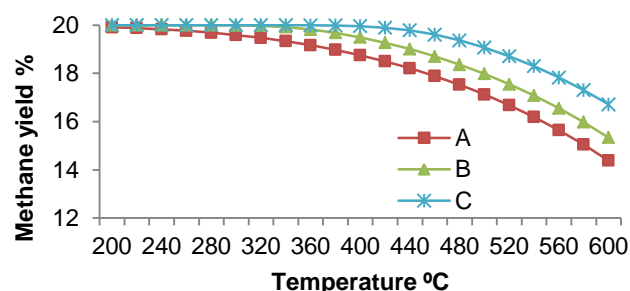

Figure 6: Effects of CO/CO$_2$ ratio at different temperatures at 10 atm (A=0, B=0.25, C=1)

Table 3: Comparison of calculated data industrial (Khorsand et al., 2007)

	Input	Output	
Component	Industrial (kmol/h)	Industrial (kmol/h)	Simulation (kmol/h)
CO$_2$	20.5	0	Trace
CO	3.4	0	Trace
H$_2$	4,186.7	4,111.5	4,111.6
CH$_4$	26.1	50.1	50.0
H$_2$O	58.0	85.3	85.30

5. Conclusion

In summary, the first three different kinetic models for methanation of carbon oxide were compared, then two reactor models which are based on different calculation methods were studied. Also a detailed thermodynamic equilibrium analysis of the methanation reactions of carbon oxides using the minimisation of the Gibbs free energy method was undertaken. The effects of temperature (200–600 ºC), pressure (1–20 atm), and feed ratio on the methanation reactions were comprehensively investigated in terms of their effects on the conversion of CO$_X$ and CH$_4$ yield.

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