

Simulation of Methanol Synthesis from CO₂ Hydrogenation in a Packed Bed Reactor using COMSOL Multiphysics

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Abstract

Global warming has been a worldwide issue leading to climate changes, therefore the growing need for sustainable solutions. The technology of CO₂ hydrogenation to form methanol with copper as a catalyst in a reactor as the key process equipment is envisaged as the most appropriate solution. This study aims to design a reactor and perform simulations of the CO₂ conversion to produce methanol using the COMSOL Multiphysics, and validation by comparing results. Methanol synthesis from the hydrogenation of CO₂ was experimented by several researchers in a packed bed reactor at 50 bar and various temperatures of 210 °C, 230 °C, 250 °C, and 270 °C. The experimental and simulation results obtained were in agreement, and the highest conversion at 230 °C. However, the simulation shows that methanol synthesis was less efficient at increased temperature due to the exothermic nature of the reaction.

Keywords: COMSOL, CO₂ hydrogenation, methanol synthesis, packed bed reactor.

INTRODUCTION

The global consumption of fossil fuel in the industrial and transportation sector has released a significant amount of greenhouse gases (GHG) that affect the global climate and increase the temperature of the atmosphere. In the oil and gas industry, most well fluids have a high CO₂ content that must be separated and released into the atmosphere at the end of the processes. It is the same case in the power generation industry that utilizes coal and natural gas as its fuels. The emission of CO₂ could be reduced if additional process technology is considered for conversion to useful chemicals, such as methanol (MeOH), through catalytic hydrogenation[1].

Methanol, the simplest form of alcohols, is found in small amounts in interstellar space and naturally on earth, where it is produced by anaerobic metabolism [2, 3]. It is essential due to its industrial use as a solvent and an intermediate in the production of many products such as formaldehyde as well as fuel additives such as dimethyl ether (DME) and methyl-tert-butyl ether (MTBE) [4-12]. It has been identified as a potential

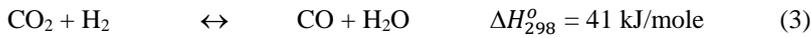
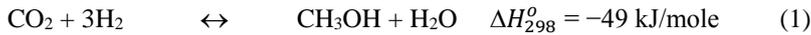
multipurpose molecule for storage and transportation of energy and CO₂ [7]. It stores both carbon and hydrogen in liquid form and serves as a base chemical for direct conversion into light olefins, gasoline, and hydrocarbons over acidic zeolites [14], thereby providing an alternative to today's fossil energy sources and petrochemical feedstock [7, 14, 15].

Gas-to-Methanol (GTM) processes based on methanol synthesis have attracted significant attention over the past decade due to its increased demand and the abundant natural gas supply at relatively low prices [16-19]. Methanol is mainly produced from natural gas and coal due to its abundant reserves than oil, therefore, serving as a substitute to decrease the dependence on petroleum [20, 21]. Additionally, the use of anthropogenic CO₂ as a carbon source for methanol production is an appropriate process [13, 22]. It is produced industrially from CO, CO₂, and H₂, typically using copper-based catalysts incorporating zinc and aluminium at pressures of 50–100 atm and temperatures of 230–300 °C [1, 23-26]. In biodiesel production, it plays an important role as a feedstock component. Not only is it consumed directly in transesterification [27-29] but also indirectly used to produce sodium methoxide, that act as a catalyst in biodiesel production [13, 20, 21, 23, 30]. The catalytic dehydration process converts methanol into DME used as a chemical intermediate and alternative energy carrier in the automotive and power industry [31].

On the commercial scale, methanol is mainly made from syngas, which is a mixture of CO and H₂ which flows to a packed bed reactor with a copper catalyst bed. The feed gas mixture contains CO₂ in addition to syngas obtained from the natural gas conversion process. Hydrogenation reaction occurs, converting CO₂ to methanol in the presence of CO, although researchers have attempted the process without CO [32].

In this study, a similar experiment for the synthesis of methanol in the absence of CO was conducted in a packed bed reactor. The result will be used in the validation of a COMSOL reactor model by comparing the conversion of the feed gas component. Cu.ZnO.Al₂O₃ catalyst was used to convert CO₂ to methanol through the hydrogenation reaction. According to Graaf et al. [33], chemical reactions (1), (2), and (3) occur in the production

of methanol. However, according to Bussche and Froment [34], reaction (2) may be omitted in reaction kinetics.



In the oil and gas industry, various operations have been exploited, leading to the production of stack gases as shown in the Table 1, which require conversion technology to reduce its emission. In this study, the conversion of CO₂ to methanol is the selected process as the product is an energy carrier and intermediate chemical in liquid form. Figure 1 outlines the plan and the position of the current study.

Table 1: Typical composition of stack gas from oil and gas processing plants

| Composition | Mole% |
|------------------|-------|
| CO ₂ | 86.59 |
| H ₂ O | 11.35 |
| CH ₄ | 2.05 |
| Inert | 0.01 |

This study aims to build a COMSOL reactor model and simulate methanol synthesis from CO₂ and H₂ in the absence of CO using Cu.ZnO.Al₂O₃ catalyst in a packed bed reactor at relatively moderate pressure and temperature. The study referred to the experimental results of Xin et al. in 2009 [35] on the synthesis of methanol. The published CO₂ conversion value and the yield of methanol will be compared with the packed bed COMSOL reactor simulation results. It is intended that the process will be implemented in the oil and gas industry. Therefore, it will represent the proposed technologies for the reduction of the GHG emissions.

A reactor model was built in COMSOL Multiphysics using the Finite Element Method (FEM) to perform simulations as a representation of the actual reactions conducted in the real packed bed reactor. The simulation study is expected to obtain corresponding results with the referred experimental data to prove that the actual reaction can be modelled in the accurate utilization of the computational COMSOL method. In the future, the reactor model could be used in the design and development of a large scale reactor for the synthesis of methanol since the development of rigorous simulations of reactor performance are beneficial in the analysis of the economic feasibility.

METHODS

According to Graaf et al. and Busche and Froment et al., kinetic correlations were previously developed utilizing the main catalyst, Cu.ZnO.Al₂O₃, which is popular for industrial use [33, 34].

Packed bed reactor

The packed bed reactor used in the study is based on the dimensions in Xin et al. experiment [35] as presented in Table 2. The inlet gas composition to the reactor was set with H₂/CO₂ ratio of 3:1, hence CO₂ of 22.5 mole% and H₂ of 67.5 mole% were used. Figure 2 shows a schematic of the packed bed reactor sizing.

Table 2: Operating condition and dimension of the packed bed reactor in the experiment by Xin et al. [35]

| Parameter | Value |
|-----------------------------------------------|--------------------|
| Inlet pressure (bar) | 50 |
| Temperature (°C) | 210, 230, 250, 270 |
| Weight hourly space velocity (ml/gr-cat.hour) | 6000 |
| Reactor diameter (mm) | 12 |
| Catalyst Weight (g) | 4 |
| Catalyst diameter (mm) | 0.05 |
| Reactor bed length (mm) | 100 |

Reaction kinetics

As mentioned in the previous section, methanol synthesis involves hydrogenation reactions (1), (2), and (3) for CO₂, CO, and the reverse water gas shift, respectively. Several researchers have developed kinetic models, e.g., Graaf et al. [33] and Bussche and Froment [34] used in this study to compare with the methanol synthesis simulation.

$$r'_{\text{CH}_3\text{OH},\text{A3}} = \frac{k'_{\text{ps},\text{A3}} K_{\text{CO}} [f_{\text{CO}} f_{\text{H}_2}^2 - \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{H}_2}^{1/2} K_{\text{p1}}^0}]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{1/2}}\right) f_{\text{H}_2\text{O}}]} \quad (4)$$

$$r'_{\text{H}_2\text{O},\text{B2}} = \frac{k'_{\text{ps},\text{B2}} K_{\text{CO}_2} [f_{\text{CO}_2} f_{\text{H}_2} - \frac{f_{\text{H}_2\text{O}} f_{\text{CO}}}{K_{\text{p2}}^0}]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{1/2}}\right) f_{\text{H}_2\text{O}}]} \quad (5)$$

$$r'_{\text{CH}_3\text{OH},\text{C3}} = \frac{k'_{\text{ps},\text{C3}} K_{\text{CO}_2} [f_{\text{CO}_2} f_{\text{H}_2}^2 - \frac{f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}}}{f_{\text{H}_2}^{3/2} K_{\text{p3}}^0}]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{1/2}}\right) f_{\text{H}_2\text{O}}]} \quad (6)$$

Bussche and Froment [34] also proposed the following kinetic model without the CO in hydrogenation reaction (2).

$$r'_{\text{CH}_3\text{OH}} = \frac{k'_{5a} K'_2 K'_3 K_4 K_{\text{H}_2} p_{\text{CO}_2} p_{\text{H}_2} \left[1 - \frac{1}{K^*} \left(\frac{p_{\text{H}_2\text{O}} p_{\text{CH}_3\text{OH}}}{p_{\text{H}_2}^2 p_{\text{CO}_2}} \right) \right]}{\left(1 + \left(\frac{K_{\text{H}_2\text{O}}}{K_8 K_9 K_{\text{H}_2}} \right) \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) + K_{\text{H}_2}^{1/2} p_{\text{H}_2}^{1/2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} \right)^3} \quad (7)$$

$$r_{\text{RWGS}} = \frac{k'_1 p_{\text{CO}_2} \left[1 - K_3^* \left(\frac{p_{\text{H}_2\text{O}} p_{\text{CO}}}{p_{\text{H}_2} p_{\text{CO}_2}} \right) \right]}{\left(1 + \left(\frac{K_{\text{H}_2\text{O}}}{K_8 K_9 K_{\text{H}_2}} \right) \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) + K_{\text{H}_2}^{1/2} p_{\text{H}_2}^{1/2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} \right)} \quad (8)$$

Where

- $k'_{\text{ps,A3}}$ Pseudo reaction rate constant for reaction A (mole $\text{s}^{-1} \text{kg}^{-1} \text{Bar}^{-1}$)
- $k'_{\text{ps,B2}}$ Pseudo reaction rate constant for reaction B (mole $\text{s}^{-1} \text{kg}^{-1} \text{Bar}^{-1/2}$)
- $k'_{\text{ps,C3}}$ Pseudo reaction rate constant for reaction C (mole $\text{s}^{-1} \text{kg}^{-1} \text{Bar}^{-1}$)
- k''' Pseudo-first-order rate constant based on catalyst volume (s^{-1})
- K Adsorption equilibrium constant (Bar^{-1})
- K_{eq} Pseudo-first-order equilibrium constant
- K_p Chemical equilibrium constant based on partial pressures
- K_c Chemical equilibrium constant based on concentrations

Finite Element Method (FEM) Simulation

COMSOL is capable of modelling from zero dimension to 3D dimension depending on the cases needed for the investigation. In this study, we will use the 2D axisymmetric model to validate the Xin et al. experiment [35] as the diameter of the packed bed reactor is relatively shorter compared to the length. Therefore, the effect of the radial concentration gradient is not significantly considered to be different in the axial dimension. It is presented in Figure 1, where the Cartesian x-coordinate and y-coordinate is the radius and length or height of the reactor, respectively.

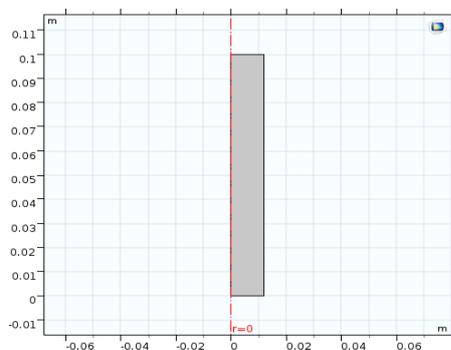


Figure 1: 2D axisymmetric of the fixed bed reactor in the COMSOL model

The aim for the development of the reactor model is to investigate the use of COMSOL finite element method which utilizes the kinetic correlations relationships mentioned above will obtain similar results as the experimental data. It is desired to obtain a valid simulation model for the representation of the experimental reaction, therefore, certify its use in future design purposes such as sizing of a large-scale reactor. COMSOL simulations are based on the numerical solution of partial differential equations to solve the mass transport, heat transport, and momentum transport correlations. Mass transport equation includes the diffusion convection equation for the steady-state of the species as follows.

$$\nabla \cdot (-D_i \nabla C_i) + u \cdot \nabla C_i = R_i \quad (9)$$

Where D_i , C_i and R_i are diffusion coefficient, the concentration of the species (mole/m^3) and the net reaction of species ($\text{mole}/\text{m}^3 \cdot \text{s}$), respectively. The equation in the direction of reactor length (x) can be written as follows.

$$\frac{\partial}{\partial x} \left(-D_i \frac{\partial C_i}{\partial x} \right) + u \frac{\partial C_i}{\partial x} = R_i \quad (10)$$

For momentum or flow transport, the following Darcy equation is used in COMSOL for flow across porous media.

$$\nabla \cdot (\rho u) = 0 \quad (11)$$

$$u = -\frac{\kappa}{\mu} \frac{\partial P}{\partial x} \quad (12)$$

Where ρ , μ , P , and κ are density, viscosity, pressure, and permeability, respectively. To calculate the heat exchanged and generated in the system, the following heat transport equation must be solved.

$$\rho C_p u \nabla T = \nabla \cdot k_{eq} \nabla T + Q \quad (13)$$

Where C_p , K_{eq} , Q and T are heat capacity of the gas, thermal conductivity, heat sources from a chemical reaction, and temperature respectively. In the direction of reactor length (x), the equation can be written as follows.

$$\rho C_p u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left(k_{eq} \frac{\partial T}{\partial x} \right) + Q \quad (14)$$

COMSOL finds the mass and heat transfer in the catalyst pellet boundary and carries out the more rigorous calculation of the packed bed catalyst rather than assuming a pseudo homogeneous reaction bed. In the pellet catalyst boundary, the mass balance equation used in COMSOL is given by the following equation.

$$4\pi N \nabla \cdot (-r^2 D_{pej} \nabla c_{pej}) = 4\pi N r^2 r_{pej}^2 R_{pej} \quad (15)$$

In the pellet fluid surface boundary, the concentration of the component adsorbed on the catalyst surface will be calculated based on the following equation.

$$N_{i,inward} = h_{Di} (c_i - c_{pej}) \quad (16)$$

$$h_D = Sh \cdot D / L \quad (17)$$

The coefficient of h_{Di} is calculated based on the Sherwood numbers. According to Frossling correlation [36], the

Sherwood number can be related to the Reynolds and Schmidt numbers.

$$Sh = 2 + 0.552 Re^{1/2} Sc^{1/3} \quad (18)$$

Where Sc , Re , D , and L are Schmidt number, Reynolds number, the diameter of the cylindrical bed, and length of the reactor, respectively.

RESULTS AND DISCUSSION

The experimental inlet feed gas conditions for methanol production are described in Table 3, where the 2D axisymmetric geometry was used for the cylindrical packed bed reactor. It was executed at the operating pressure of 50 bar and temperatures of 210 °C, 230 °C, 250 °C, and 270 °C.

Table 3: CO₂ hydrogenation experimental conditions at the inlet pressure of 50 bar and various temperature

| Parameter | Value |
|-----------------------------------------------------|-------|
| Feed gas molar flow (mole/s) | 0.9 |
| Weight Hourly Space Velocity (ml/gcat.hr) | 6000 |
| Feed gas concentration CO ₂ (mol %) | 22.5% |
| Feed mixture ratio H ₂ / CO ₂ | 3 |

The simulation result shows the conversion of CO₂ and yield of methanol at the temperatures experiment of 220 °C, 230 °C, 250 °C, and 270 °C, as presented in Figure 3. The experimental of Xin et al. [35] and simulation results of Graaf et al. [33] and Busche and Froment et al. [34] were represented in Figure 2 and 3, respectively. Figure 2 shows that methanol production decreases with increased inlet temperature after 230 °C since the hydrogenation reaction is exothermic. Therefore, it is observed that there is a decline of methanol yield after a certain temperature since its kinetics activity favours a higher temperature at the initial period for catalyst activity after that curtailed by the exothermic reaction. This is noticeable in Figure 2 after 230 °C.

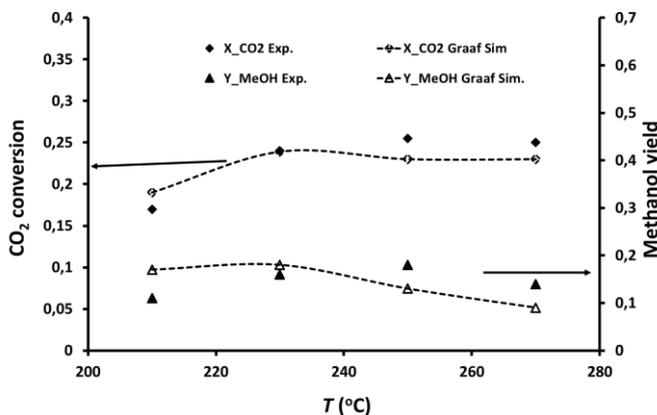


Figure 2: Experimental result for CO₂ conversion and methanol yield as compared with simulation result using Graaf et al. kinetic correlations [33]

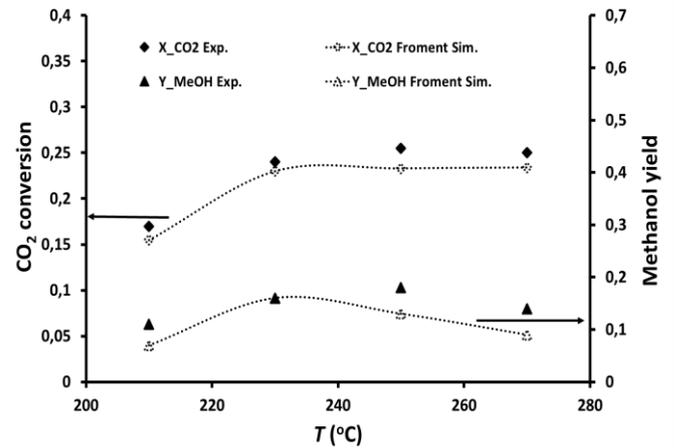


Figure 3: Experimental result for CO₂ conversion and methanol yield as compared with simulation result using Busche and Froment kinetic correlations [34]

From a Pearson Chi-square test, the Graaf et al. and Busche and Froment correlations is a good fit, although the later simulation has a better result. The chi-square value of 0.03 for the Graaf simulation result and 0.02 for the Busche and Froment simulation on CO₂ conversion to the referenced experiment value. The result of the Chi-square test is below the value of 7.8 as the critical value with an alpha of 0.05. On the yield of methanol, the chi-square test value is 0.59 and 0.78 for Graaf et al. and Busche and Froment correlations, respectively. Therefore, simulation using Busche and Froment kinetic model [34] was selected for use in large scale reactor design with a recommended inlet temperature of 225 °C based on the commercial plant reference data by Yusuf et al. [37].

The phenomenon beyond the temperature of 250 °C shows a significant reduction of methanol yield with no decrease of CO₂ conversion. As mentioned earlier in the hydrogenation, a reverse water gas shift reaction occurred and the CO₂ was converted to CO instead of to methanol. In their experiment, Busche and Froment [34] and Graaf et al. [33] also observed the equilibrium for the water gas shift reaction. Methanol produced decreases if the inlet temperature of the reactor is increased and as endothermic reaction favour at higher temperature with the rise in temperature. The effect of the exothermic and endothermic reaction agree with the results of the previous studies by Kiss et al. [38] and Adji and Kartohardjono [39].

In the study, both simulation using Graaf et al. [33] and Busche and Froment [34] kinetic correlations are presented in Figure 4, 5, and 6. However, at the moderate pressure of 50 Bar, the operating pressure of large scale reactor and the temperature range of 220-230 °C the simulation using Busche and Froment kinetic [34] shows a better fit to the referenced experiment value. Therefore, for the large scale simulation model, the Busche and Froment kinetic will be used as the correlation basis in the COMSOL simulation.

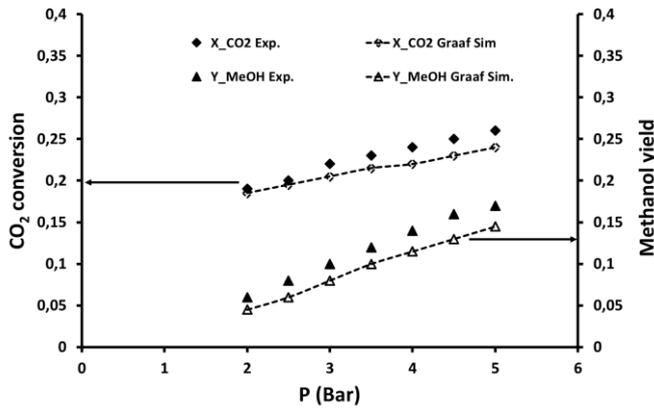


Figure 4: Experimental result for CO₂ conversion and methanol yield as compared with simulation result using Graaf et al. kinetic correlations [33] for variation of pressure at 250 °C

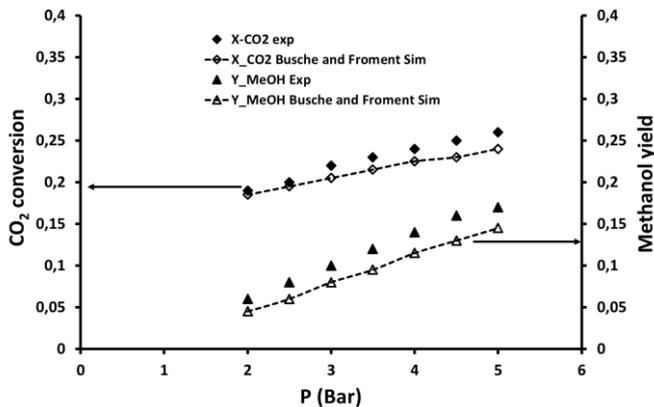


Figure 5: Experimental result for CO₂ conversion and methanol yield as compared with simulation result using Busche and Froment kinetic correlations [34] for variation of pressure at 250 °C

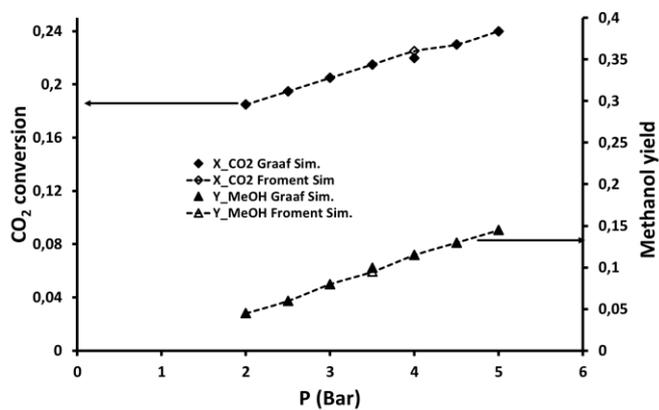


Figure 6: Simulation result for CO₂ conversion and methanol yield using Graaf was compared with simulation result using Froment et al. kinetic correlations

The model and the methanol reactor referenced in the industrial scale data is used in large scale simulation after it was validated in a laboratory experiment. The reference plant reactor was using data published by Yusup et al. [37], and it was a Lurgi shell, and tube type with catalyst packed inside the tube and the shell was heated media for steam flowing to maintain temperatures as shown in Fig. 7. The reactor dimension and operating conditions are stipulated in the Table 4.

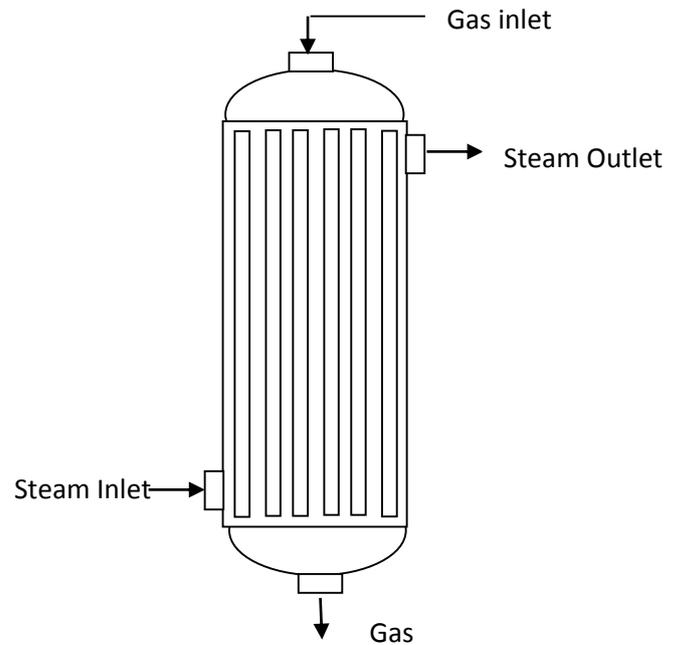


Figure 7: Schematic of shell and tube reactor

Table 4: Operating condition and dimension of the packed bed reactor in the referenced industrial plant

| Parameter | Value |
|-------------------------------|-------|
| Inlet pressure (bar) | 82 |
| Inlet Temperature (°C) | 225 |
| Steam Temperature (°C) | 250 |
| Total fluid flow (kmol/hr.) | 40789 |
| Tube quantity | 4801 |
| Tube diameter (mm) | 44.5 |
| Tube length (mm) | 7260 |
| Catalyst diameter (mm) | 0.06 |
| Inlet CO ₂ (mol %) | 8.42 |
| Inlet CO (mol %) | 7.95 |
| Inlet H ₂ (mol %) | 60.87 |

In the simulation of this reactor, the single tube was modelled and the assumption of the other tubes having homogeneous performance considered. The comparison of result with plant methanol production is presented in the Table 5.

Table 5: Methanol production

| Parameter | Plant | Simulation |
|---------------------------|-------|------------|
| Methanol Production (Tpd) | 2062 | 2129.9 |
| Outlet Temperature (°C) | 532 | 533 |
| Pressure drop (bar) | 1.08 | 1.00 |

Based on Table 5, the COMSOL simulation performance is sufficient to model the reactor on a large scale, were compared with the actual plant production; it has an error of about 3.2%. The simulation model has been satisfied with the large scale reactor. Therefore, it will be used in the design of the CO₂ hydrogenation of emitted gas in Table 1. The selected operating condition is 50 Bar, 225 °C, emission flow rate of 5 MMSCFD in packed bed reactor with H₂/CO₂ ratio of 3, and total molar flowrate becomes 996 kmol/hr. The inlet feed gas composition to the reactor is envisaged, as shown in Table 6. In this case, the emitted CO₂ flow is not similar to the commercial production from syngas since raw feed is collected from the stacks of oil and gas processing plant with a capacity of processing hydrocarbon from wells in the range of 50 to 100 MMSCFD.

Table 6: Operating condition and dimension of packed bed reactor design

| Parameter | Value |
|-----------------------------|-------|
| Inlet pressure (bar) | 50 |
| Inlet Temperature (°C) | 225 |
| Total fluid flow (Kmol/hr.) | 996 |
| Reactor diameter (m) | 1 |
| Reactor length (m) | 3 |
| Catalyst diameter (mm) | 0.06 |
| CO ₂ (mol %) | 21.65 |
| H ₂ O (mol %) | 2.84 |
| CH ₄ (mol %) | 0.51 |
| H ₂ (mol %) | 74.99 |

The profile of methanol concentration generated in the packed bed reactor can be presented in a 3D profile, as shown in Figure 8, where it increases gradually along with the reactor axial dimension. Methanol is produced upon complete reaction in the catalyst bed at the outlet.

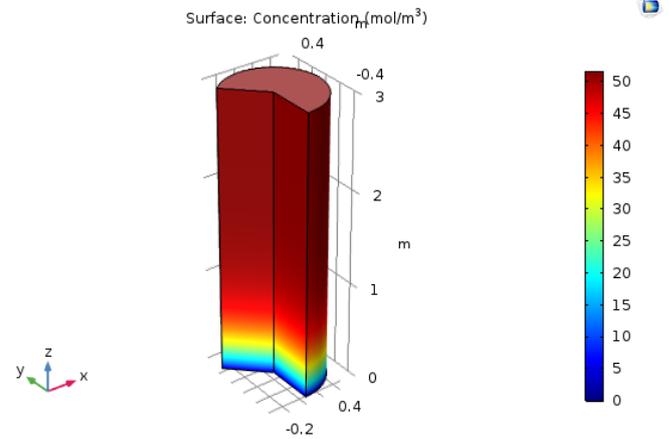


Figure 8: Methanol concentration in the reactor (mole/m³) at an inlet temperature of 225 °C

The profile of methanol production using COMSOL simulation is shown Figure 9. Methanol produced from processing the 5 MMSCFD emitted CO₂ gas is up to 32 ton per day, while CO₂ conversion and yield of methanol are around 26 and 20%, respectively.

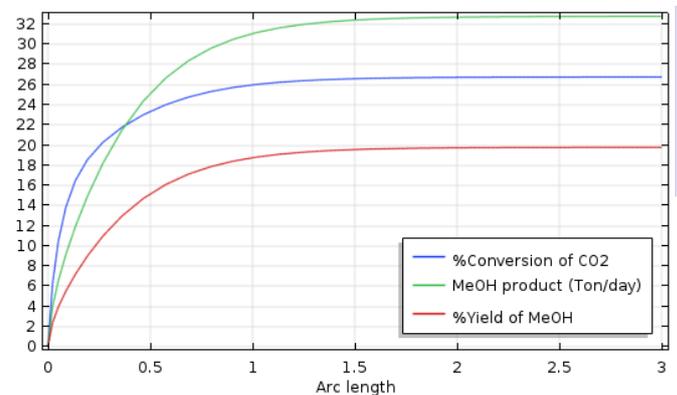


Figure 9: The profile of methanol production using COMSOL

CONCLUSION

The study have been conducted to build a COMSOL reactor model and simulate methanol synthesis from CO₂ and H₂ in the absence of CO using Cu.ZnO.Al₂O₃ catalyst in a packed bed reactor at relatively moderate pressure and temperature. The COMSOL FEM simulation is in agreement with the experimental CO₂ conversion as well as methanol yield from the hydrogenation reaction using the kinetic correlations of Bussche and Froment [34]. However, the increased temperature

of the reactor inlet above 230 °C produces less methanol and more CO. The simulation on large scale reactor shows satisfactory result compared to a large scale plant reference data. Therefore, COMSOL simulation is appropriate for calculating the methanol production from the hydrogenation process of emitted CO₂ stream at moderate operating pressure and temperature from a typical oil and gas plant stack. The simulation of 5 MMSCFD scales of emitted gas can produce 32 ton per day of methanol.

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