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Simulation of Feed Modulation on Dynamic Fixed-Bed Reactor for CO Methanation over Ni-based Catalyst

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Abstract. The hydrogenation of CO to produce synthetic natural gas (SNG) is highly exothermic and usually catalyzed by nickel as an active site. These reactions are typically conducted under elevated pressures and low temperatures to shift the reversible reactions to the products. However, conducting reaction under such low temperature is kinetically limited. An alternative method that can be applied to ameliorate this limitation is by conducting a dynamic operation. This study focused on model development and reactor approach for dynamic fixed-bed operation intended for CO methanation. One dimensional pseudo-homogeneous reactor model was developed for a typical laboratory scale by neglecting internal and external diffusion based on Weisz-Prater, Anderson, and Mears criteria. The gas phase model was governed for compounds in the bulk phase. The model consisted of the dynamic term, convective term, diffusive term, and source term. The design criteria involving pressure drop, ratio of the height of catalyst bed to particle diameter (L_B/d_p), ratio of reactor diameter to particle diameter (d_r/d_p), ratio of bed length to reactor diameter (L_B/d_r) and axial dispersion were taken into consideration. A kinetic model to complement the simulation was taken from literature. The reactor model was simulated for steady-state and unsteady-state operation with optimum feed composition. The result of steady-state model simulation was considered as a base case and comparison to judge the reactor performance under unsteady-state operation. Modulating the value of the inlet CO fraction in step function was introduced to the unsteady-state model in order to enhance methane production. The simulation results showed that the highest methane production could be achieved by modulating CO inlet fraction between 0.45 and 0.4 with the overall switching time of 25 s.

Keywords: energy storage, CO methanation, Ni-based catalyst, feed modulation, reactor design

1. Introduction

The current effort to surmount the lack of alternative clean energy source is to generate synthetic natural gas (SNG) having characteristic closes to natural gas [1]. This can be achieved by reacting carbon monoxide (CO) with hydrogen (H_2), or so-called CO methanation reaction, in the presence of a heterogeneous catalyst. This process has been evaluated as a means of storing non-continuous electrical power from wind and solar devices, in which the energy is produced at locations where it is not directly consumed [2,3]. The accumulated electrical power is first converted to hydrogen (H_2) through electrolysis process. Then CO gas coming from coal or biomass gasification is injected into the



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methanator unit together with hydrogen input [4,5]. Carbon monoxide methanation is typically comprised of a series of parallel reactions [6]. There are two reactions involved as follows [5]:



Methanation of CO as in equation (1) is the key reaction and water-gas shift (WGS) reaction as in equation (2) is one of many side reactions that may occur during methanation. In industrial application, the WGS reaction is usually carried out before methanation to raise the H_2/CO ratio for high yield of methane (CH_4) [7]. According to thermodynamic analysis, methanation strongly depends on the chemical equilibrium. To obtain high yield and selectivity of methane (CH_4), low temperatures and high pressures operating conditions are recommended. However, it would be kinetically limited in regard to the deployed catalyst [6,8]. At temperatures higher than 350°C , the reverse reaction of CO methanation, steam reforming of methane, becomes thermodynamically favorable, thus resulting in limited amounts of methane and an increase in CO and CO_2 [2]. These conditions must be avoided as much as possible thermodynamically and kinetically.

A catalyst with high activity below 350°C is required to maximize the yield of methane [2]. Transition metal such as nickel has been widely examined as an active catalyst for CO methanation [9] despite being easily deactivated in low-temperature operation [10,11]. The deactivation is resulted from the interaction of the metal particles with CO and formation of mobile nickel carbonyl species [11]. In the catalysis, catalytic performance is influenced by the nature and properties of the applied support. A support acts as a stabilizer for the active phase as well as an enhancer for the adsorption of key reactants [9,12-14]. For the promotion of CO methanation, metal oxide supports are widely applied (Al_2O_3 , SiO_2 , zeolites, TiO_2 , CeO_2 , MgO , etc) and alumina supported catalysts are the commercial ones [9,14-16].

Beside catalyst support, high amount of nickel content is also giving positive effect on CO conversion and CH_4 selectivity [17]. Catalyst with a higher Ni-content provides a higher activity at low-temperature [12,16,18]. Increasing reaction temperature from 200 to 350°C [14,18] as well as conducting dynamic operation could improve the catalytic performance significantly [19]. Substituting one or more operating variables such as feed composition periodically could increase conversion and selectivity to the desired product [20-23]. In this study, we aimed to investigate a way to enhance the yield of methane in synthetic natural gas production by modulating one of the feed components in a step function form. The simulation results were then compared to the value obtained in steady-state operation.

2. Methods

2.1. Mathematic modeling of fixed-bed reactor

To simulate the dynamic behavior of the methane synthesis a reactor description is needed. An unsteady-state adiabatic fixed-bed reactor (FBR) was then constructed. A one-dimensional pseudo-homogeneous FBR with axial mixing was applied to model the reactor [24]. The effect of catalyst bed inside a reactor results in axial mixing. For design purposes, a Bodenstein number, Bo , of 150 was applied to calculate the value of effective diffusivity of mixture, D_{ax} , as used in mass balance equation. The chosen Bo number still ensures plug flow behavior [25]. The effective conductivity of catalyst bed in axial direction used in energy balance equation was adapted from literature [26]. The unsteady-state mass and energy balance equations as well as the steady-state pressure drop correlation are presented in table 1.

The effective conductivity of catalyst bed in axial direction used in energy balance equation was adapted from literature [26]. The unsteady-state mass and energy balance equations along with pressure drop criteria [27] are presented in the table 1. Ergun's equation [24] was applied to calculate the pressure drop along the catalyst bed. In this present work, the obtained pressure drop calculation was in agreement with the specified criteria. Thus it has been assumed to be negligible. The physical properties of gases were extracted from literature [28].

2.2. Design criteria

In designing the pseudo-homogeneous PFR model, one must ascertain that mass and heat transports do not limit the overall reaction rate. This is crucial because transfer phenomena between two phases in heterogeneous creates a film layer resistance. Consequently, causing concentration and heat gradients between the gas phase and the film covering the catalyst surface [29]. To investigate any significant temperature and concentration gradients either inside the catalyst bed or within the catalyst particles, criteria [30] listed in table 2 are employed. The external mass and heat transfer coefficients needed in table 2 are presented in table 3. The gas phase properties and transfer parameters required for all criteria were taken from literature. The following assumptions are considered during modeling the FBR:

- Temperature gradients both in axial and radial directions within the reactor are neglected according to criterion listed in table 4.
- Reactor is operated adiabatically, hence heat loss is neglected.
- Plug flow pattern inside FBR is also considered according to criteria listed in table 4.
- Pressure drop were calculated based on Ergun's equation for fixed-bed reactor.

Table 1. Mass and energy balances.

Definition	Expression	Equation
Mass balance	$\frac{\partial P_i}{\partial t} + u_z \frac{\partial P_i}{\partial z} = D_{ax} \frac{\partial^2 P_i}{\partial z^2} \pm \rho_B RT \sum v_{ij} r_i$ i = gas component; j = reaction number.	(3)
Energy balance	$(1 - \varepsilon_B) C_{p,s} \rho_b \frac{\partial T_G}{\partial t} + \varepsilon_B C_{p,g} \rho_g u_z \frac{\partial T_G}{\partial z} =$ $\rho_B \sum (-\Delta H_{R,i} r_i) + \lambda_{ea} \frac{\partial^2 T_G}{\partial z^2}$	(4)
Initial conditions	at t = 0 and $0 \leq z \leq L_B$ $P_i = y_i^* P_{in}$ $T_G = T_{G,in}$	(5)
Boundary conditions	at z = 0 $P_i = y_i^* P_{in}$ $T_G = T_{G,in}$ at z = L_B $\frac{dP_i}{dz} = 0$ $\frac{dT_G}{dz} = 0$	
Pressure drop criterion	$\frac{150(1 - \varepsilon_B)^2 \mu u_s L_b}{p_0 \varepsilon_B^3 d_p^2} + \frac{1.75(1 - \varepsilon_B) \rho_g u_s^2 L_b}{p_0 \varepsilon_B^3 d_p} \leq 0.03$	(6)

Table 2. Heat and mass transfer limitation criteria.

Criteria	Expression	Transport process
Weisz-Prater	$\frac{r^{eff} \rho_b d_p^2}{4C_{CO} D_{CO}^{eff}} < 1$	Intraparticle mass transport.
Anderson	$\frac{r^{eff} \rho_b d_p^2 \Delta Hr }{4\lambda^{eff} T} < \frac{0.75RT}{E_A}$	Intraparticle heat transport.
Mears	$\frac{r^{eff} \rho_b d_p}{k_c C_{CO}} < 0.3$	External mass transport between bulk phase and catalyst surface.
Mears	$\frac{r^{eff} \rho_b d_p \Delta Hr }{hT} < \frac{0.3RT}{E_A}$	External heat transport between bulk phase and catalyst surface.

Table 3. Correlations used for estimating heat and mass transfer coefficients used in table 2.

Parameter	Correlation
External mass transfer coefficient	$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$ $Sc = u_z / D_{CO}^{eff}$ $Re = \rho_g u_z d_p / \mu_g$ $k_c = Sh D_{CO}^{eff} / d_p$
External heat transfer coefficient	$h = 500 \text{ W/m}^2 \cdot \text{K}$ [26]

Table 4. Aspect ratio criteria to maintain plug flow pattern in FBR.

Criteria	Limitation	Reference
$L_B/d_p \geq 50$	Radial mixing can be neglected against fluid velocity	[24, 27]
$d_r/d_p > 10$	Gas-solid wall effects can be neglected	[24]
$L_B/d_r > 0.04 (u_z d_r / \varepsilon_B D_{ar})$	Neglected intrareactor mass gradient in radial direction	[31]

2.3. Chemical reaction model

A set of detailed kinetic equations and constants is compulsory for complementing the simulation process. Since catalysts are reaction-specific, they own unique kinetic mechanism and lead to certain reaction rate equations. Choosing an applicable reaction rate equation for a wide range of operating conditions is of fundamental importance to model, simulate and optimize a conventional or novel reactor concept. The scarcity of published kinetic data for commercial nickel catalysts and the manifold differences of the applied catalysts are the other obstacles in finding the right equations. A guide to choose an appropriate kinetic approach especially for methanation might be based on catalyst's nickel content as reported from literature [5].

Rönsch *et al.* [5] had modified two methanation rate equations derived by Klose and Baerns [32] and Zhang *et al.* [33]. Both authors used different catalyst's nickel content, 18% wt and 50% wt, respectively. However, only Zhang *et al.* [33] who had considered involving water-gas shift reaction in

their CO methanation study. The modified reaction rate equations contain term of the reverse reactions, methane reforming and reverse water-gas shift. In this paper, the modified reaction rate equation which rooted from Zhang *et al.* [33] is adopted. The rate equations were valid for operating conditions with temperature window ranging from 250 to 360°C, while pressure between 1 and 5 bar. Moreover, the catalytic reaction kinetic was then incorporated into the reactor model developed earlier.

$$r_1 = \frac{k_1 K_C K_H^2 P_{CO}^{0.5} P_{H_2}}{(1 + K_C P_{CO}^{0.5} + K_H P_{H_2}^{0.5})^3} - \frac{k_1 K_C K_H^2 P_{CH_4} P_{H_2O} P_{CO}^{-0.5} P_{H_2}^{-2} \left(\frac{1}{K_M}\right)}{(1 + K_C P_{CO}^{0.5} + K_H P_{H_2}^{0.5})^3} \quad (7)$$

$$r_2 = \frac{\frac{k_2}{P_{H_2}} \left(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{WGS}} \right)}{\left(1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}} \right)^2} \quad (8)$$

The rate coefficients k_1 and k_2 as in equation (7) and (8) denote the rate coefficient of CO methanation and water-gas shift reaction, respectively. The kinetic parameters of both reactions are showed in table 5. Meanwhile, the equilibrium constants for CO methanation (K_M) and water-gas shift reaction (K_{WGS}) as a function of temperature are adapted from different literature [8]. Properties of methanation reactor catalyst are listed in table 6.

Table 5. Kinetic parameters of equation (7) and (8) [5].

Symbol	Value	Unit
E_1	103,000	J/mol
E_2	62,000	J/mol
ΔH_C	-42,000	J/mol
ΔH_H	-16,000	J/mol
ΔH_{CO}	-70,650	J/mol
ΔH_{H_2}	-82,900	J/mol
ΔH_{CH_4}	-38,280	J/mol
ΔH_{H_2O}	88,680	J/mol
k_1	$(7.0/3.6) \times 10^{10} \exp(E_1/RT_G)$	mol/kg cat.s
k_2	$(7.83/3.6) \times 10^6 \exp(-E_2/RT_G)$	mol/kg cat.s.bar
K_C	$5.8 \times 10^{-4} \exp(-\Delta H_C/RT_G)$	bar ^{-0.5}
K_H	$1.6 \times 10^{-2} \exp(-\Delta H_H/RT_G)$	bar ^{-0.5}
K_{CO}	$8.23 \times 10^{-5} \exp(\Delta H_{CO}/RT_G)$	bar ⁻¹
K_{H_2}	$6.12 \times 10^{-9} \exp(\Delta H_{H_2}/RT_G)$	bar ⁻¹
K_{CH_4}	$6.65 \times 10^{-4} \exp(\Delta H_{CH_4}/RT_G)$	bar ⁻¹
K_{H_2O}	$1.77 \times 10^3 \exp(\Delta H_{H_2O}/RT_G)$	-
K_M	$\exp(25.8 + 24883/T_G)$	bar ²
K_{WGS}	$\exp(4.35 + 4593/T_G)$	-

Table 6. Properties of methanation reactor catalyst.

Property	Value	Reference
Catalyst material	Ni/Al ₂ O ₃ (50 wt% Ni)	[33]
Pellet shape	Sphere	Assumed
Void fraction, ε_B	0.4	[34]
CO effective diffusivity, D_{ax}	$1.36 \times 10^{-6} \text{ m}^2/\text{s}$	[26]
Effective thermal conductivity, λ^{eff}	$2.90 \times 10^{-4} \text{ kW/m.K}$	[26]

3. Results and discussion

3.1. Simulation frame conditions

The simulation was performed on a fixed-bed reactor designed earlier. The reactor physical dimensions and the appropriate catalyst loading for the typical laboratory scale were shown in table 7. The unsteady-state heat and material balances for five gas components were solved using a software package FlexPDE version 6.5.

Table 7. Reactor physical dimensions and catalyst loading used in the simulation model.

Parameter	Value	Unit
Catalyst bed height, L_B	0.07	m
Reactor diameter, d_R	0.008	m
Catalyst particle diameter, d_p	0.6	mm
Catalyst load, m_{cat}	0.2	mg
Bulk catalyst density, ρ_{cat}	56.87	kg/m ³

For the simulation of CO methanation process, the feed composition ratio of H₂/CO was set to be stoichiometric with referring to equation (1). The gas feed volume flowrate was fixed and derived from design criteria and assessment of transport limitations. Turning to temperature and pressure operating conditions, both were chosen based on the conditions used by [33] when investigating the kinetics of CO hydrogenation. Table 8 gives an overview of those operating variables.

Table 8. Operating conditions of CO methanation used in the simulation model.

Parameter	Value	Unit
H ₂ /CO	3	-
Volume flowrate	0.02	m ³ /h
Temperature	300	°C
Pressure	2	bar

3.2. Steady-state operation

Since the nature of methane production from syngas is highly exothermic, the purpose of this part of simulation was to investigate the appropriate feed gas composition which gave lower adiabatic temperature rise along the reactor length. A steady-state simulation with various feed gas composition was conducted and the results were presented in figure 1.

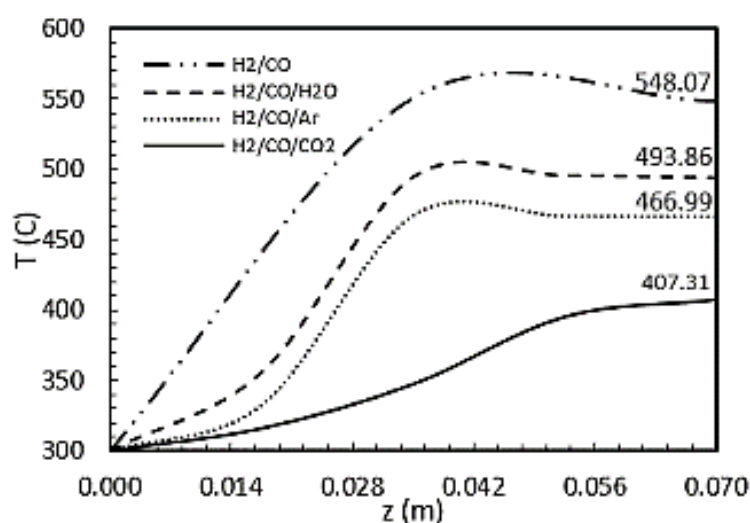


Figure 1. Adiabatic temperature rise distribution along axial direction of reactor length under steady-state simulation with $T_{in} = 300^{\circ}\text{C}$ and $P_{in} = 2$ bar. The ratio of H_2/CO for each variation was retained equal to 3 (67.5% H_2 , 22.5% CO , 10% Ar or CO_2 or H_2O).

As can be seen from figure 1, the presence of CO_2 in the feed gas results in lower adiabatic temperature rise. The CO_2 gas might act as a thermal flywheel. At temperature above 350°C the water-gas shift reaction occurred, hence limiting the methanation rate [15]. It is also worthy of notice that adding inert gas to the reactor benefited the exothermic reactions as the inert gas dilutes the reactant and absorbs the heat released during reaction [36]. Adding steam to the reactant gas mixture did not do much with lowering adiabatic temperature rise. Even higher adiabatic temperature rise might indicate higher methanation activity, the latter variation was not favorable. The product composition at reactor outlet was dominated by H_2 and H_2O (see figure 2). According to the results above, the option of adding CO_2 to the inlet feed gas mixture was chosen for the next simulations.

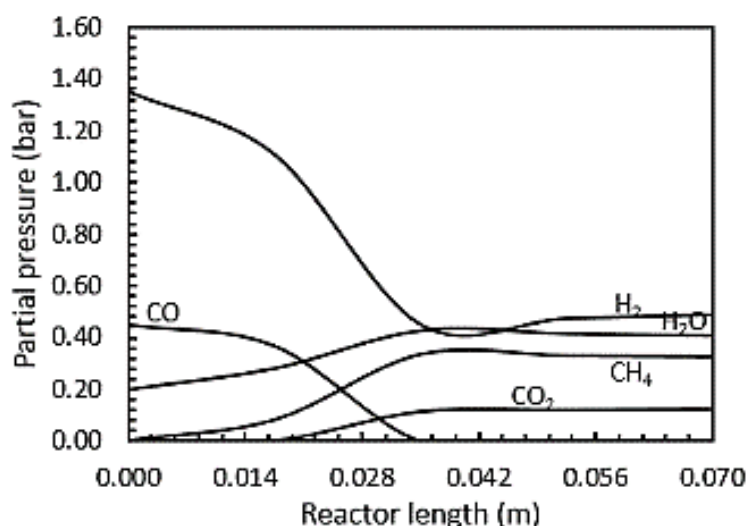


Figure 2. Gas partial pressure distribution along the reactor length under steady-state operation. Feed gas composition: 67.5% H_2 , 22.5% CO , 10% H_2O . Inlet temperature and total pressure: 300°C and 2 bar, respectively.

Under steady-state operation within this simulation frame, the CO gas was almost completely consumed (98.14%) along the reactor length and the obtained CH₄ was 85.78% (see figure 3). The results are in agreement with Lazdans et al. [3] who reported that highest CO conversion rates can be achieved at temperature ranging from 300 to 400°C. Referring to the previous temperature profiles in figure 1, the obtained adiabatic temperature rise was also in agreement with the work done by Su et al. [37] that the rise in temperature did not exceed 550°C for reactant with H₂/CO ratio equals to 3. Hence, it was safe to say that our simulation was reliable enough to describe the methanation process.

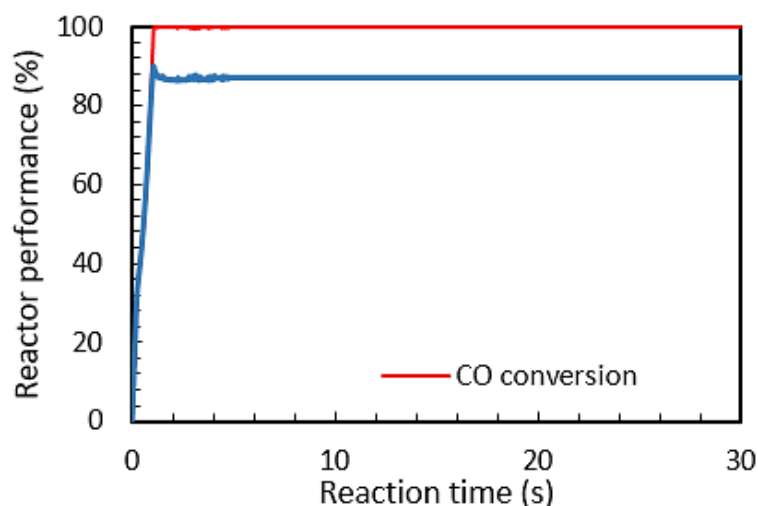


Figure 3. Ideal CO conversion (red line) and CH₄ yield (blue line) at reactor outlet within simulation time frame during start-up and steady-state operation. Feed gas composition: 67.5% H₂, 22.5% CO and 10% CO₂, inlet temperature and total pressure: 300°C and 2 bar, respectively.

3.3. Dynamic operations

From section 3.2, the optimum composition for methanation process was 67.5% H₂, 22.5% CO and 10% CO₂. This composition was then used as a starter to conduct dynamic operation. The aim of this section was to increase the yield of methane by examining appropriate contacting technique that will influence the reactor performance. Under this type of operation, the quantity of production becomes time-average quantity.

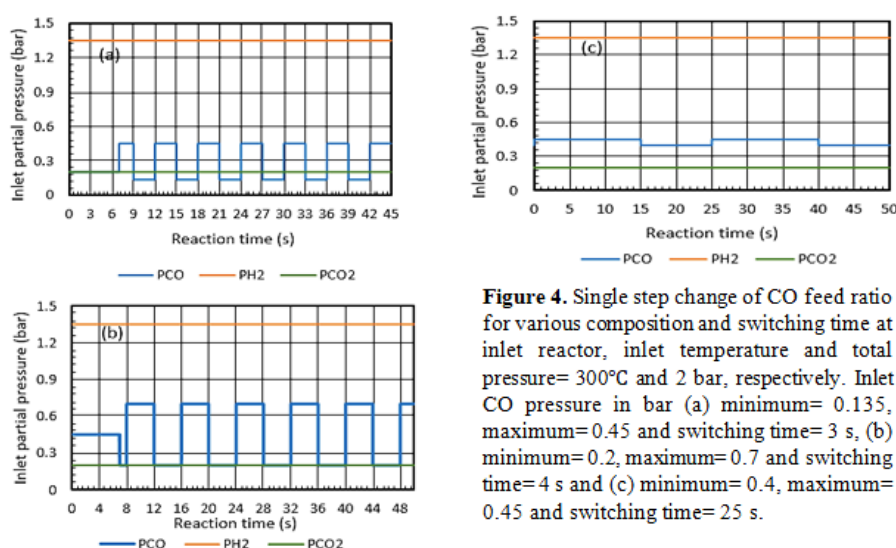


Figure 4. Single step change of CO feed ratio for various composition and switching time at inlet reactor, inlet temperature and total pressure= 300°C and 2 bar, respectively. Inlet CO pressure in bar (a) minimum= 0.135, maximum= 0.45 and switching time= 3 s, (b) minimum= 0.2, maximum= 0.7 and switching time= 4 s and (c) minimum= 0.4, maximum= 0.45 and switching time= 25 s.

The choices of manipulation for dynamic operation are so wide. In this simulation, the amplitude of CO composition in the feed gas as the input variable has been modulated periodically around its steady-state values at different switching time. The modulated variable is varied in the form of a square wave function. While the CO ratio in the feed was performed to be varied, the H₂ and CO₂ ratios were hold to be constant. The total inlet pressure in the reactor was kept at 2 bar. However, modeling a modulation with constant pressure in the reactor has a consequence that the mass flow rates into the reactor will vary during the cycle period as the changing composition causes changing consumption rates [21]. The visualization of the overall various processes were shown in figure 4.

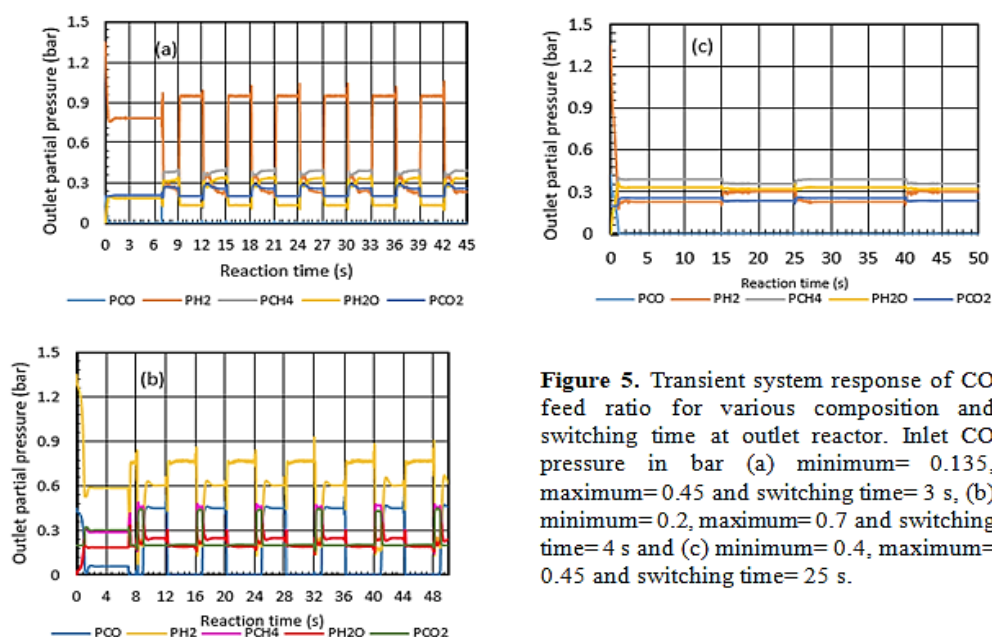


Figure 5. Transient system response of CO feed ratio for various composition and switching time at outlet reactor. Inlet CO pressure in bar (a) minimum= 0.135, maximum=0.45 and switching time= 3 s, (b) minimum=0.2, maximum=0.7 and switching time= 4 s and (c) minimum= 0.4, maximum= 0.45 and switching time= 25 s.

The effect of switching time variation on reactor performance was also studied. The switching time is an importance parameter in periodic operation, which strongly influences the system dynamics. Short switching time results in the system having difficulty adjusting to the sudden change. As can be seen from figure 5, the reactor performance was constant for the following cycles, indicated by almost identical area formed during the cycle period. As for scenario (a), the CO conversion and CH₄ yield were indeed higher than the steady-state value. However, the obtained CH₄ product at the end of reactor was less than the other scenarios. This was due to the lower time-average of CO inlet value. Hence, this scenario was not suitable. The lower performance of scenario (b) compared to the steady-state value was caused by short switching time. Because of the short switching time, the process might not adjust to the sudden change. Within this ration and cycle of time, it cannot reach steady condition.

Modulating CO composition with scenario (c) as seen both in figure 4 and 5 did give slight improvement on reactor performance. Scenario (c) was performed with total switching time of 25 s. The selected CO maximum value was introduced to the reactor for 15 s and followed by adding the minimum value for the next 10 s. This was to ensure that every step change for each cycle approached steady-state condition. For the lower time-average CO pressure, the CH₄ product closed to the value of steady-state. The given CO conversion and methane yield was also satisfied. Our work results are also in agreement with [38] that modulating CO composition through step change function can give significant impact to the methanation performance. Table 9 summarized the resulted reactor performance for all variation.

Table 9. Summary of time-average reactor performance for all variation.

Steady-state		Scenario (a)	
P _{CO} in (bar)	4.5 x 10 ⁻¹	P _{CO} in (bar)	2.9 x 10 ⁻¹
P _{CO} out (bar)	8.4 x 10 ⁻³	P _{CO} out (bar)	1.9 x 10 ⁻⁴
P _{CH₄} out (bar)	3.8 x 10 ⁻¹	P _{CH₄} out (bar)	2.6 x 10 ⁻¹
CO conversion (%)	98.14	CO conversion (%)	99.93
CH ₄ yield (%)	86.13	CH ₄ yield (%)	88.73
Scenario (b)		Scenario (c)	
P _{CO} in (bar)	4.5 x 10 ⁻¹	P _{CO} in (bar)	4.3 x 10 ⁻¹
P _{CO} out (bar)	1.8 x 10 ⁻¹	P _{CO} out (bar)	4.7 x 10 ⁻³
P _{CH₄} out (bar)	2.5 x 10 ⁻¹	P _{CH₄} out (bar)	3.8 x 10 ⁻¹
CO conversion (%)	59.69	CO conversion (%)	98.90
CH ₄ yield (%)	54.61	CH ₄ yield (%)	87.51

4. Conclusion

The methanation of CO has been studied at temperatures ranging from 300°C to 400°C since it is limited by methane steam reforming at elevated temperature. The simulation showed that under steady-state process, methanation reaction can be enhanced slightly by adding CO₂ into the feed gas to retain low adiabatic temperature rise along the reactor. To increase the desired product, feed composition modulation was introduced. In this work, CO composition in the inlet reactor was chosen as a variable to be modulated. Modulating CO inlet fraction between the maximum and minimum amplitude value of 0.45 and 0.4, respectively, gives a minimum time-average value of CO fraction as 0.43 in order to reach the desired reaction performance. The overall switching time is also playing an important role in determining the dynamic operation regimes. The contacting time of different amplitude value within a total time of 25 s of each value benefited to keep the process being in the steady-state behavior whilst the system adjusts to the periodic change. By performing feed modulation with different contacting time, the obtained minimum time-average value of CO inlet fraction was able to produce CH₄ with amount closed to the steady-state value. Thus, this strategy is quietly applicable to CO methanation.

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