

Mathematical Models for Packed Bed Reactor for Methanation of Carbondioxide

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Abstract: Models for carbondioxide methanation in a packed bed reactor was developed from first principles by the application of the law of conservation of mass and energy. The kinetic expressions of the process were obtained from relevant literatures and incorporated and solved simultaneously with the developed models using Matlab ODE45 solver. Sensitivity analysis was performed to ascertain the optimal conditions gave reasonable results, which were validated with plant data and was found to be accurate with deviations within allowable range. The research study focuses on carbondioxide methanation reaction for production of synthetic natural gas (SNG) and the performance of the process is characterized by carbondioxide conversion under various operating conditions. One dimensional pseudo-homogeneous packed-bed reactor model neglecting all possible mass and heat constraints was used as a reference and the resulting model equations are solved numerically. The reaction rates and exothermicity ($\Delta H^\circ = -165 \text{ KJ/Mol}$) prevent a packed bed reactor to be operated at high conversions and the reactant inlet temperature is used as a primary parameter, while an optimum inlet temperature is determined at which the carbondioxide conversion has maximum value. With inlet temperature higher than the optimum temperature, CO_2 conversion decreases due to the reverse Sabatier reaction.

Keywords: Carbondioxide Methanation, Synthetic Natural Gas, Packed Bed Reactor, Sensitivity Analysis, MatLab ODE45 Solver

1. Introduction

There is rapid or geometrical increase in energy demand in the chemical, power and transportation industries as a result of population and economic growth, while energy production depends mainly on non-renewable energy sources such as fossil fuel. One of the main environmental threats today is considered to be the rapidly increasing climate changes which is as a result of emission harmful gases in the environment [1]. The atmospheric concentration of greenhouse gases can roughly be grouped as carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), fluorocarbons (CFs) and chlorofluorocarbons (CFCs). Among these gases, the concentration of CO_2 in the atmosphere has been found to be the highest with $3.86 \times 10^{-4} \text{ ppm}$ which is far from the pre-

industrial levels of $2.80 \times 10^{-4} \text{ ppm}$. This has been the major factor of the earth's temperature rise. There is worldwide awareness of carbondioxide emission reduction and development of efficient way of carbon capture by industries [2]. Carbon sequestration and storage (CSS), has been applied to capture and store CO_2 underground or in deep oceans, but this process has been challenging as a result of several reasons such as cost, the distance from safe sequestration sites, small or medium sized sources, a diluted concentration of CO_2 in the emitting gas with non-information about the long-term impact on environment. Recently, the Sabatier reaction also called methanation has been of interest as result of the reaction importance in carbondioxide conversion that it is the most occurrence GHGs, a chemical storage for excess hydrogen as well as a source of production of synthetic natural gas [3]. Thus, the catalytic hydrogenation of carbondioxide to methane

at temperatures of 250-500°C with pressures of 1-80bar is called the Sabatier reaction. It is an exothermic reaction and methane formation is favored at low temperatures. CO₂ has also been found useful as a building block in organic synthesis for chemist as it is highly functional, its abundance and the utilization complimentary to its storage is very interesting especially when its conversion to useful bulk products is economical. Carbondioxide utilization as chemical feedstock is limited to a few processes presently such as urea synthesis (for nitrogen fertilizers and plastics), acid salicylic (a pharmaceutical ingredient) and polycarbonates (for plastics). However the actual application of carbondioxide only corresponds to small percentage of carbondioxide potential. Carbondioxide utilization for fuel synthesis may therefore be considered an alternative to methanol or syngas production from the conventional process with low efficiency [4].

Carbondioxide emissions, which is as a result of over dependence on fossil fuel have over the years done more harm than good to the environment and human lives. Global warming which have led to shrinking sea ice, increased sea level and high atmospheric temperatures are some of the many detrimental effects of CO₂ emissions in the environment. This and the recent depletion of known fossil fuel reserves have forced the world in searching for alternative and sustainable sources of energy to replace fossil fuels. Innovative solutions are therefore needed to mitigate carbondioxide emissions to the atmosphere and hydrogen storage due to the intermittency of renewable energy sources. Besides, this research study focuses on the above concerns by utilizing carbon IV oxide to yield methane, which is a synthetic fuel that could be stored in an existing infrastructure or as a chemical compound with huge industrial benefits. thereby preventing or reducing CO₂ emission [5] Thus, the research study aim at developing mathematical models for CO₂ methanation in a packed bed reactor. This is achieved by developing the models for the methanation of CO₂ in a packed bed reactor from first principle through the application of the principles of conservation of mass and energy, deduction of kinetic parameters of the methanation reaction mechanisms from relevant literatures and incorporate the kinetic expressions into the developed mathematical models, these models were solved using MatLab ODE45 solver and models' results are compared with plant data.

2. Process Description

The Sabatier reaction was first reported by Paul Sabatier, a French chemist whose work on the catalytic hydrogenation of organic species was published in 1913 [6] The Sabatier reaction is an highly exothermic process between hydrogen and carbondioxide. The forward Sabatier reaction is frequently described in literature as CO₂ methanation, whilst the reverse reaction is referred to as steam-methane reforming, implemented industrially to produce hydrogen [7]. In the past, Sabatier reaction was regularly investigated in the temperature range of 200-400°C using group VIII metal

supported catalysts such as Ni, Ru, Rh or Pd [8].



Nickel has generally been used for CO₂ methanation catalyst due to its low cost and widespread use [9] Nickel has the ability to convert about 40-70% CO₂, but with rather varying selectivities towards CH₄. Several problems were encountered with the use of a Ni-based catalyst. To ensure Ni is in its most active form, hydrogen reduction at reactor start-up is compulsory [10] Carbon deposition may occur at high temperatures and slow catalyst deactivations can be expected as a result of sulphur poisoning due to presence of feed-gas impurities such as hydrogen sulphide. The use of Rh and Pd as active supported catalysts for CO₂ methanation was also investigated, but showed undesirable CO₂ conversions in fixed bed reactors [11, 12].

Also, there was difficulty to establish the exact Sabatier reaction mechanism being followed. Uncertainties about the intermediate compound present during the rate-determining step have led to two main reaction mechanisms being proposed [13] The first proposed mechanism for methanation of carbondioxide involves the conversion of absorbed CO₂ into adsorbed CO. Consequently, CO undergoes dissociation to form surface carbon. The successive elementary steps are based on the same reaction mechanism as CO methanation originally proposed [14]. With the formation of adsorbed CO, there is still no definite proof for the mechanism of CO methanation either. The second proposed mechanism is based on the formation of CO and carbon formats as reaction intermediates [15]. Catalytic methanation process has been researched and realized for process concepts that include various reactor types and operating conditions. Some commercially available methanation processes mostly involved carbonmonoxide methanation but these technologies can also be applied to the hydrogenation of CO₂ as a result of similar steps in the thermochemistry of CO and CO₂ methanation processes. In addition, studies by other authors in the past have shown some operational limitations such as catalyst calcination and low percentage conversion of CO₂ and other studies have also been based on just the Sabatier reaction [16]. Thus, this research study entails the application of three reactions namely, CO₂ methanation, CO methanation and the reverse water gas shift reaction to develop its mathematical models in contrast to focusing on the global Sabatier reaction. This research study consists of a pseudo-homogeneous reactor models of the three reactions as proposed [1, 17].

3. Material and Method

3.1. Model Development

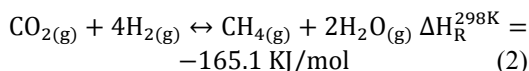
A packed bed reactor is mainly used for gas-phase catalytic reactions and consists of a cylindrical tube packed with immobilized solid catalyst pellets. The pseudo-homogeneous models for a packed bed reactor for

carbondioxide methanation is developed in this study.

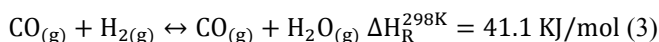
3.2. Kinetic Model

Kinetics study proposed by Xu & Froment showed that three major reaction processes have to be implemented in understanding the operational process. They defined the kinetics based on a Langmuir-Hinshelwood mechanism and the carbondioxide methanation process consists of the following reaction steps [18].

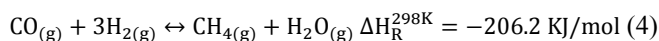
1) Carbondioxide Methanation



2) Reserve Water-Gas Shift Reaction



3) Carbonmonoxide Methanation:



3.3. Reactor Model

One-dimensional steady state pseudo-homogeneous plug flow reactor models was developed to describe mass and heat balances of the process with assumptions of negligible pressure drop, diffusional effects and wall resistances, uniform temperature, pressure and concentration profiles, constant cross sectional area with no momentum transport, kinetic and potential energy changes are neglected with no shaft workdone. Therefore, the general mass balance equation for carbondioxide methanation was derived by applying the principle of conservation of mass as.

$$\frac{dy_j}{dz} = \frac{\rho_B \cdot A_c}{F_T} \sum_{i,j} (v_{i,j} \eta_i r_i) \quad (5)$$

Similarly, the principle of conservation of energy was applied in evaluating the temperature effects of the methanation process based on the assumptions highlighted above as.

$$\rho_g u \cdot \bar{C}_p \frac{dT}{dz} = \rho_B \sum_{i,j} \{ (\Delta H_{R_i}) \cdot v_{i,j} \cdot \eta_i \cdot r_i \} + \frac{4U_A}{dt} (T_c - T) \quad (6)$$

Thus, the methanation process is defined by three main reactions namely, carbondioxide consumption, hydrogen consumption and production of methane.

3.4. Determination of Model Parameters

In solving the developed model equations, evaluation of certain constants and parameters are required. These constants and parameters are determined thus.

i. Specific Heat Capacity

The specific heat capacity is a function of temperature and

evaluated by using

$$\frac{C_{p,j}}{R} = A_j + B_j T + C_j T^2 + \frac{D_j}{T^2} \quad (7)$$

Table 1. Heat Capacity Coefficients Value.

Components	A	B (10 ⁻³)	C (10 ⁻⁶)	D (10 ⁵)
CO ₂	5.457	1.045	0	-1.157
CO	3.376	0.557	0	-0.031
H ₂	3.249	0.422	0	0.083
CH ₄	1.702	9.081	-2.164	0
H ₂ O	3.470	1.450	0	0.121

ii. Enthalpy of Reaction

The standard enthalpy of reaction is expressed thus

$$\Delta H_{R,i} = \Delta H_{R,i}^0 + \sum_{i,j} v_{i,j} \int_{298}^T C_{p,j}(T) dT \quad (8)$$

Table 2. Enthalpy of Reaction Value.

Reaction Path	$\Delta H_{R,1}$	$\Delta H_{R,2}$	$\Delta H_{R,3}$
Heat of Reaction at 298K (KJ/mol)	-165.1	41.1	-206.2

iii. Reactor Parameters

The reactor parameters consist of reactor dimensions and catalyst properties.

Table 3. Reactor and Catalyst Properties.

Reactor Configuration	Symbol	Values	Units
Internal radius	R		m
Wall thickness	Δ		m
Model length	L		m
Pellet diameter	d_p	3	mm
Pore diameter	d_{pore}	20	mm
Bed porosity	ϕ	0.4	
Catalyst density	ρ_{cat}	2350	Kg/m ³
Bulk density	ρ_B	$(1-\phi)\rho_{cat}$	Kg/m ³

iv. Process Condition

The process inlet conditions for carbondioxide methanation are shown thus.

Table 4. Inlet conditions for Carbondioxide Methanation Process.

Inlet Parameters	Values	Units
Temperature	553	K
Pressure	10	Bar
$y_{\text{CO}_2,0}$	0.35	—
$y_{\text{CO},0}$	0	—
$y_{\text{H}_2,0}$	0.50	—
$y_{\text{CH}_4,0}$	0.0	—
$y_{\text{H}_2\text{O},0}$	0.015	—

3.5. Kinetic Parameters

The kinetic parameters applied in carbondioxide methanation are highlighted in Tables 5 and 6 respectively.

Table 5. Carbondioxide Methanation Rate Constant.

Reaction, i	Pre-exponential factor, $A(k_i)$	Units	Activation Energy	Units	Gibb's Free Energy at Standard State ΔG_{298K}^0	Unit
1	1.020×10^{15}	—	243.9	KJ/mol	113.60	KJ/mol
2	1.955×10^6	—	67.13	KJ/mol	33	KJ/mol
3	4.225×10^{15}	—	240.1	KJ/mol	142.23	KJ/mol

Table 6. Van't Hoff's Equation Adsorption Constants.

Component, j	Pre-exponential factor, $A(K_j)$	Units	Enthalpy of Adsorption, ΔH_j	Units
CO ₂	1.25×10^{-3}	—	-93.51	KJ/mol
CO	8.23×10^{-6}	—	-70.65	KJ/mol
H ₂	6.12×10^{-9}	—	-82.90	KJ/mol
CH ₄	6.65×10^{-4}	—	-38.28	KJ/mol
H ₂ O	1.77×10^5	—	88.68	KJ/mol

4. Discussion

The results obtained from the solution of the model equations are presented thus.

4.1. Model Validation

The results of the developed models were compared with results of literature data as shown thus.

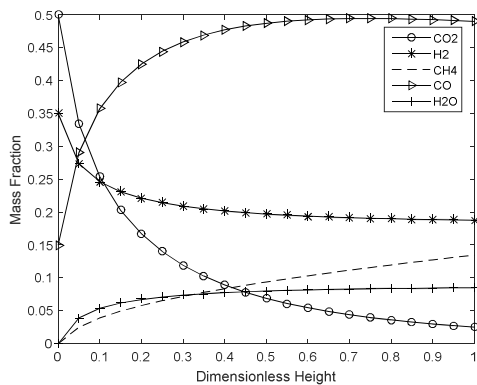
Table 7. Simulation Results Compared To Literature Data.

Component	Model predictions	Literature Data	Deviation (%)
Mass fraction of CO ₂	2.52	5.4	-1.14
Mass fraction of CO	49.01	46.90	0.04
Mass fraction of H ₂	18.77	1.4	0.93
Mass fraction of CH ₄	13.46	20.9	-0.55
Mass fraction of H ₂ O	8.50	25.4	-1.98

Table 7 showed the deviation or maximum percentage absolute error between the predicted models and literature data of methane production of 0.55%. There is depletion of H₂ and CO₂ but not completely and production of CH₄. H₂ has the highest rate of disappearance; due to its conversion into methane and water during chemical reactions. A similar trend is seen in CO₂ as it depletes during reaction, while CH₄ (desired product) and H₂O have a trend of formation as expected. Formation or depletion of CO depend on the prevailing reaction at the time (CO will react with H₂ to form CH₄ in reaction 1 but will also be formed in reaction 2 though at a lower rate). Thus, comparing the model predictions to literature data shows a percentage deviations within the acceptable limit, hence, the developed models predicts methanation reactor performance with high degree of accuracy.

4.2. Variation of Mass Fraction with Dimensionless Height

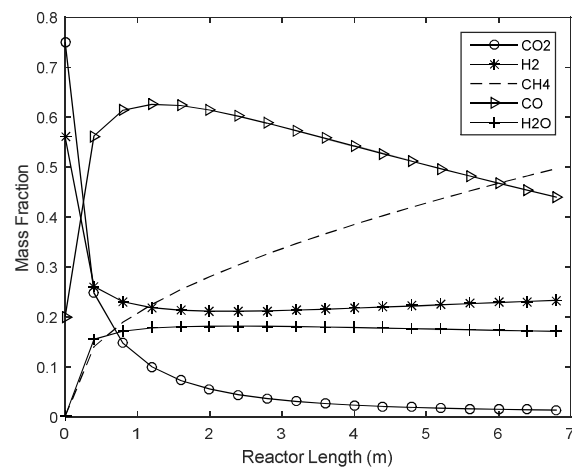
The variation of mass fraction with dimensionless height for the reactants and products of methanation process (CO₂, H₂, CH₄, CO, H₂O) are depicted in Figure 1.

**Figure 1.** Variation of Mass Fraction with Dimensionless Height.

It can be deduced from the plot that there is decline in the concentration of CO₂, which is the limiting reactant with dimensionless height. Also, the concentration of H₂ decreases while the products (CH₄, CO and H₂O) are formed with increase concentration with dimensionless height.

4.3. Variation of Mass Fraction with Reactor Length

The mass fraction dependence on reactor length for the five species (CO₂, CO, CH₄, H₂, H₂O) of methanation process was investigated as shown in Figure 2.

**Figure 2.** Variation of Mass Fraction with Reactor Length.

The mass fraction of H₂ and CO₂ experiences a sharp decreases initially and then it continues to decrease gradually along the length of the reactor as the two species are being consumed in the methanation reaction process. There is also an increase in the mass fraction of CO, H₂O and CH₄ along reactor length as the process progresses due to their formation.

4.4. Variation of Mass Fraction with Cross Sectional Area of Reactor

The variation of reactants and products mass fraction with cross sectional area of reactor showed an increase in mass fraction of CO, H₂O and CH₄ due to increase in cross sectional area, while the mass fraction of CO₂ and H₂ decreases as cross sectional area increases.

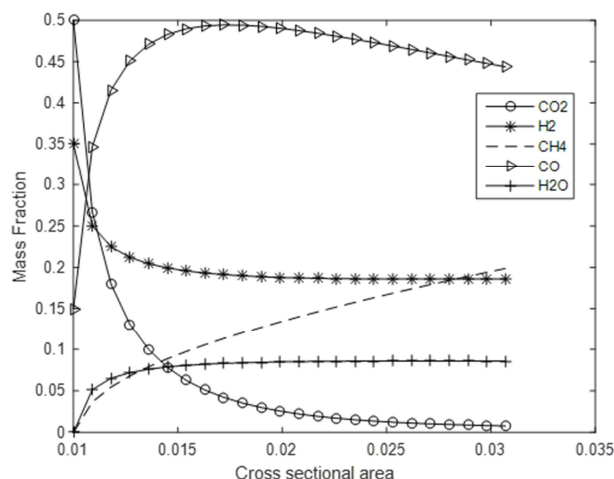


Figure 3. Variation of Mass Fraction with Cross Sectional Area of Reactor.

4.5. Variation of Mass Fraction with Molar Flow Rate

The dependency of mass fraction of process species were simulated with the molar flow rate of the five species. The yield of CH₄ and H₂O increases with an increase in the molar flow rate as the two species are being produced during the methanation reaction. In addition, the yield of CH₄ is higher than that H₂O as a result of CO₂ methanation process and methane being the main product.

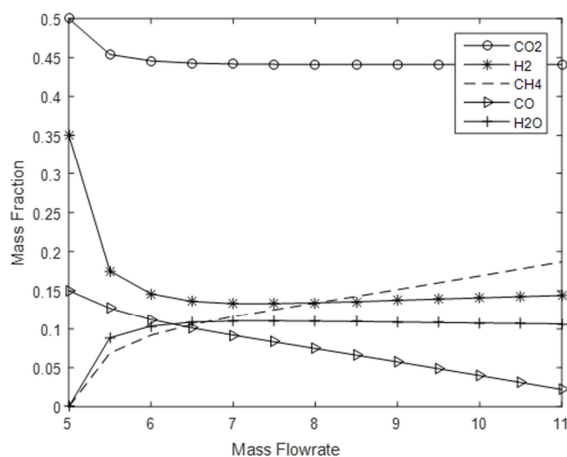


Figure 4. Variation of Mass Fraction with Molar Flow Rate.

4.6. Variation of Temperature with Dimensionless Height

The variation of temperature of the reactor with dimensionless height of the reactor showed there is a steady increase in temperature as dimensionless height increases due

to an exothermic state of the methanation reaction. In addition, the yield of main product (methane) decreases at higher temperature, hence temperature should be maintained between 300- 400°C.

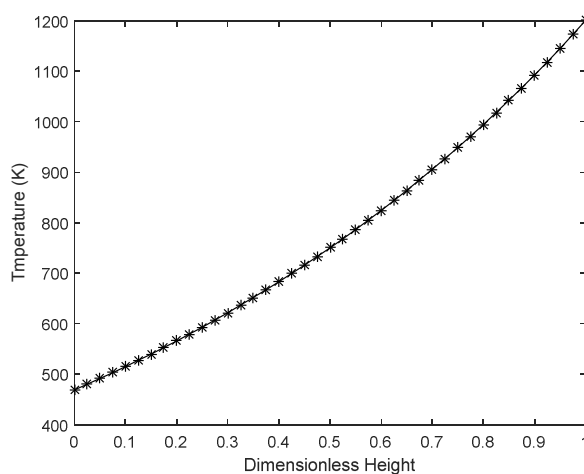


Figure 5. Variation of Temperature with Dimensionless Height.

4.7. Variation of Catalyst Activity with Time

The variation of the reaction or process catalyst activity with time is depicted in Figure 6 with a steady decline curve. As the reaction or methanation process progresses, catalyst is deactivated (reduction in catalyst efficiency) with reaction time. The activity of catalyst is one at the initial stage of the process and as time increases, there is a steady decrease in catalyst activity.

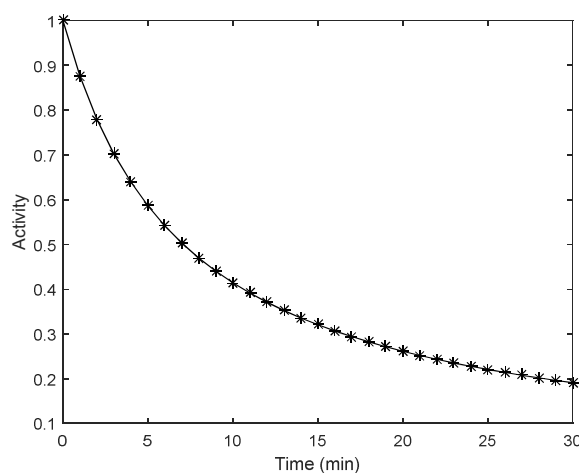


Figure 6. Variation of Catalyst Activity with Time.

5. Conclusion

There have been renewed interest in carbondioxide methanation due to methane production based on power to gas concepts. It is the main process by converting hydrogen produced by electrolysis and carbondioxide to synthetic natural gas (SNG) that can be stored, transported and reconverted to electric energy depending on the existing infrastructure of gas grids, storage and power plants. The

results obtained from developed models showed reasonable agreement when compared with literature data and sensitivity analysis showed that temperature, pressure and flow rate are major parameters which affects CO₂ methanation process. Furthermore, the research study pointed two major issues for the CO₂ methanation reaction namely, reaction rates and exothermicity of the first part of the reactor that requires an efficient heat removal if pure stoichiometric feed gas is converted without a product recycle or dilution by water or methane and catalyst activity under low temperature. Besides, models can be modified for further study by considering the effect of pressure drop or fluid dynamics, the effectiveness factor of catalyst as well as cooking rate on the reactor performance, with a more detailed consideration being made on cooling jacket and cooling medium used for the reaction process in a packed bed reactor.

Nomenclature

A _c	Cross sectional Area of Catalyst Bed
CO	Carbonmonoxide
CO ₂	Carbondioxide
CSS	Carbon Sequestration and Storage
CH ₄	Methane
F _j	Molar Flow Rate of Species
F _T	Flow Rate of Reaction
GHG	Green House Gas
ΔH	Enthalpy of adsorption kJ/mol
ΔG°	Gibbs free energy KJ/mol
H ₂	Hydrogen
H ₂ O	Water
ρ	Density of Reaction Mixtures
K _i	Rate Constant of Reaction
k _i	Equilibrium Constant of Reaction
K _j	Absorption Constant of Species
P _j	Partial Pressure of Species
ρ _B	Bulk Density
r ₁	Reaction Rate of Reaction 1
r ₂	Reaction Rate of Reaction 2
r ₃	Reaction Rate of Reaction 3
dT	Temperature Difference
T	Variable Operating Temperature
Q	Heat Loss through Wall of Reactor
U	Heat Transfer Coefficient
V _R	Reactor Volume
W	Weight of Catalyst

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