Kinetic Modelling of In-situ Catalytic Adsorptive Gasification Unit Utilizing Oil Palm Empty Fruit Bunch (EFB) and Palm Kernel Shell (PKS) for Hydrogen Production

By
Muhammad Hafiz bin Suleiman (12735)

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Supervisor: Dr. Periyasamy Balasubramanian
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CERTIFICATION OF APPROVAL

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Approved by:

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Dr. Periyasamy Balasubramanian

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD HAFIZ BIN SULEIMAN

ABSTRACT

The energy crisis and environmental issues caused by fossil fuels usage have brought new light on hydrogen as a potentially significant form of energy in the future. The idea of producing hydrogen from oil palm biomass in Malaysia seems attractive due to the resource abundance. Biomass steam gasification with *in-situ* carbon dioxide capture in the presence of catalyst has good prospects for the enhanced production of hydrogen rich gas. Despite these potentials, its application at industrial scale is limited due to the energy intensiveness, costs, and hazards of gasification process at high temperature (>823K). Modelling and optimization become an increasingly attractive design approach to investigate the gasification performance within extensive range of operating parameters.

In the current study, a kinetic model for oil palm empty fruit bunch (EFB) and palm kernel shell (PKS) have been developed to determine the dynamics of hydrogen gas and other gases components with the different value of operating parameters; gasifier temperature, steam/biomass ratio and sorbent/biomass ratio. The results gained from the simulation were validated with the experimental data and other comparable studies.

To determine the dynamic gas components (H_2, CO, CO_2, and CH_4), the kinetic constants were gained using optimization approach and also from other relevant literatures.

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CHAPTER 1
INTRODUCTION

1.1 Background study

The world's accessible oil reservoirs are gradually depleted thus it is essential to figure a new sustainable energy to counteract the declining fossil fuel production [28]. In this respect, biomass energy seems the best replacement with the abundance of biomass worldwide. In fact, the hydrogen gas produced from the steam gasification process attracts many interests for a new source of clean energy. In Malaysia's perspective, it is a great potential in hydrogen production from biomass due to the high availability in agricultural land and agricultural wastes [6].

1.1.1 Uses of Hydrogen

The extraction of hydrogen gas from the product gas shows interesting demands as the hydrogen gas able to give potential benefits in the energy economy. These include (i) reductions in greenhouse gas emissions; ii) reduction in urban air pollutants; and (iii) increases energy efficiency in the hydrogen fuel cell technologies [15]. Hydrogen also commercially used in the chemical industry especially in the production of hydrochloric acid. Hydrogen gas chemically reacted with chlorine gas in the burner process [35]. Hydrogen also becomes an essential reactant in the production of ammonia gas where the nitrogen gas reacted with hydrogen gas in order to form ammonia gas. This process is famously known as Haber process.

A part of that, hydrogen also becomes an attractive sustainable source of electrical energy where the energy is generated from hydrogen cell. A fuel cell combines hydrogen and oxygen to produce electricity, heat, and water. Fuel cells are often compared to batteries. Both convert the energy produced by a chemical reaction into usable electric power. However, the fuel cell will produce electricity as long as hydrogen is supplied, never losing its charge.

Fuel cells are a promising technology for use as a source of heat and electricity for buildings, and as an electrical power source for electric motors propelling vehicles. Many companies are working to develop technologies that might efficiently exploit the potential of hydrogen energy for mobile uses. Conceptually, hydrogen gas is ignited and burned in a combustible engine to produce mechanical power to a vehicle. German's giant automotive company, BMW, use this technology in their production limited hydrogen-based car.

Figure 1.1 : BMW's Hydrogen Car

Literally, hydrogen gas is really important as it gives many benefits to mankind. Therefore, the extraction of hydrogen gas from biomass in gasification process seems the best new alternative to increase the hydrogen production worldwide.

1.1.2 Gasification Process

Gasification is the conversion of solid or liquid feedstock into useful and convenient gaseous fuel or chemical feedstock that can be burned to release energy or used for production of value added-chemical [30]. Gasification and combustion are two closely related thermochemical processes, but there is important difference between them.

Gasification packs energy into chemical bonds in the product gas; combustion breaks those bonds to release energy.

Gasification of biomass char involves several reactions between the char and the gasifying mediums. The reaction between the char and the gasifying medium needs to be conducted at high temperature to produce several gases products comprising of CO,CH_4, H_2, H_2O, and CO_2.

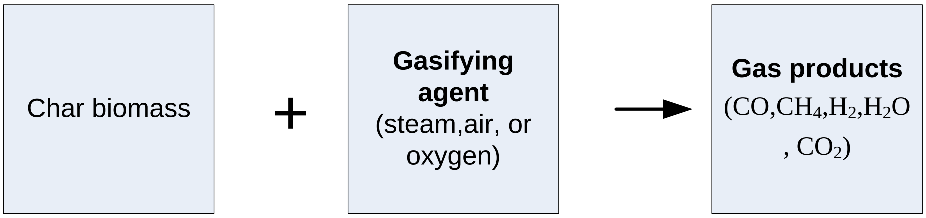


Figure 1.2 : Char Gasification Reaction

The hydrogen gas produced resulted from these reactions between the char and the gasifying agent is the main discussion topic in this research. To determine quantitatively the performance of the gasification process take place, a mathematical model is required for the gasification process.

The reactions which occur in the steam gasification of biomass coupled with CO_2 capture comprising of char gasification, methanation, Boudouard, methane reforming, water gas shift and carbonation. The steam gasification reactions of biomass are mainly endothermic, thus, external heat needs to be supplied to the gasifier. Biomass is gasified at high temperature with steam and converted into gaseous products. The product from from biomass steam gasification consists of a mixture of hydrogen, carbon monoxide, carbon dioxide, methane and char.

There are five main reaction involved in the biomass steam gasification [3].

Char gasification

$C + H_2O \rightarrow CO + H_2 \quad (\Delta H = +131.4 \text{ kJ/mol})$

Boudouard

$C + CO_2 \rightarrow 2CO \quad (\Delta H = +172.6 \text{ kJ/mol})$

Methanation

$C + 2H_2 \rightarrow CH_4$ (ΔH=-74.9 kJ/mol)

Methane Reforming

$CH_4 + H_2O \rightarrow CO + 3H_2$ (ΔH=+206.2 kJ/mol)

Water gas shift

$CO + H_2O \leftrightarrow CO_2 + H_2$ (ΔH=-41.2 kJ/mol)

Hydrogen production from catalytic steam gasification has also been shown to be more efficient and economically viable than conventional gasification. Hydrogen yield can be improved via a catalytic conversion of biomass, as catalysts surface are used to promote the reactions forward to produce more hydrogen specifically via methane reforming and water gas shift reactions [10]. Furthermore, catalyst also decreased tar from the system. The characteristics required for catalyst are that it must be thermally stable, inexpensive, and effective and also can be able to be regenerated. Zeolite is effective catalyst but for hydrogen production using biomass gasification has received only limited attention [21].

The purity of hydrogen in the product gas from the gasification process can be further increased by combining the gasification process with CO_2 adsorption step using calcium oxide (CaO) as a sorbent [6]. CaO reacts with the CO_2 present in the system and produced calcium carbonate ($CaCO_3$) [1,6,21].

Carbonation Reaction

$CaO + CO_2 \rightarrow CaCO_3$ (ΔH=-178.3 kJ/mol)

The CO_2 adsorption step strongly promotes the forward water gas shift reaction by reducing the partial pressure of CO_2 from the system. However, carbonation reaction is reversible at high reactor temperature (>1023K) [15].

1.1.3 Modelling and Simulation of Hydrogen Production from Biomass Gasification

Modelling and simulation becomes increasingly more attractive tool to study and investigate the extensive range of process parameters for biomass gasification process.

As a simulation and modelling approach is expected to be more cost saving, safe, and easy to scale up using model of biomass gasification process. There are several modelling approaches for biomass gasification process based on the kinetics, equilibrium and the fluid dynamics behaviours. A kinetic model provides important data regarding the conversion of biomass to hydrogen which is essential to improve the process. The predictions from the kinetics model is more accurate compared to the thermodynamic equilibrium models [26], so the process can be simulate better with experimental data. Kinetics models are used to determine kinetics parameters of the several simultaneous reactions involved in the process, using the minimization of the least square difference between the experimental work and the model predictions. The validated kinetic model with the actual experimental work and literature could provide all the data required to study the biomass gasification process.

1.2 Problem Statement

The determination of the maximum hydrogen production with the use of different value of operational conditions in the fluidized bed reactor for the steam gasification process requires a lot of work, cost and time. These experimental work need to be repeated using the different value of the parameters in order to determine the highest concentration of hydrogen from the product gas. Therefore, the development of kinetic model for in-situ catalytic adsorptive gasification unit for hydrogen production is essential to predict the behavior of biomass-derived components in the reactor. This model will help us to estimate quantitatively the gas concentration in the steam gasification process using empty fruit bunch (EFB) and palm kernel shell (PKS) as the sources of biomass. The inclusion of CaO in the model also needed to maximize the production of hydrogen gas in the system. This absorbent captures the carbon dioxide in the gas phase thus increases the hydrogen purity from the gas products.

Limited data in the literatures which provided the dynamic of gas products resulted from steam gasification coupled with CO_2 across experimental time is the one of the reason the research was conducted. Most of the results are presented by equilibrium value. Therefore, this model is really essential to predict the behavior of gas components across simulation time.

1.3 Objective of the project

The objectives of this study are as the following:

- To develop a kinetic modeling of in-situ catalytic adsorptive gasification unit for hydrogen production

- To determine the hydrogen yield from the simulation with the different operating conditions in the reactor such as reaction temperature, steam/biomass ratio and sorbent/biomass ratio

1.4 Scope of Study

In this study, the main subjects under investigation are:

i. *The working mechanism of fluidized bed reactor*

   Determines the behavior of the fluidized bed reactor with the presence of steam stream and biomass stream into the reactor.

ii. *The steam gasification process with the used of CaO as the absorbent agent*

   CaO is the CO_2 absorbent, thus will boost the purity of hydrogen in the synthesis gas.

And the aspects being studied are:

i. *The MATLAB software (computational method)*

   This software will be used for the simulation of mass and energy balance equation.

ii. *The reaction kinetics which are essential for the development of mass and energy balance equations*

   The stoichiometric reactions occur in the gasifier are been taken into consideration to represent the gasification process. These include char gasification, methanation, Boudouard, methane reforming, water gas shift and carbonation reaction.

1.5 Relevancy to The Objectives

This project is relevant to be conducted as it provide a simpler way to predict the composition of gas components in the biomass steam gasification coupled with CO_2 capture. The experimental works is really hazardous to be conducted due to high temperature operation. Therefore, this modelling approach is the best alternative to predict quantitatively the dynamic of gas products using different value of operational parameters. This model also able to predict the best operating conditions for PKS and EFB steam gasification coupled with CO_2 capture which later could be implemented in the real-scale industry where it able to yield maximum amount of H_2 from the gas products. Based on the statements, this project is relevant to be conducted.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

To create a steam gasification model, it requires an understanding of the gasification process on how its design, feedstock, and operating parameters influence the performance of the gasifier. This chapter comprises the review on the experimental and modelling published approaches to study the hydrogen production from biomass gasification. To investigate on gasification process, there are several modelling approaches available. Experimental studies on pure steam gasification and steam gasification coupled with CO_2 capture are been reported this part. For the modelling approach, kinetic and equilibrium model for hydrogen production are been reviewed. Since EFB and PKS are used as the biomass source in this research, the modelling of PKS and EFB works also been investigated.

2.2 Modeling and Simulation of Biomass Gasification for Hydrogen Production

There are several approaches available presented by researchers for biomass gasification based on the reaction kinetics and thermodynamic equilibrium modelling.

2.2.1 Kinetic Modeling and Equilibrium Modeling for Biomass Gasification

Reported by Schuster et al [12], kinetic models are always contain parameters which make them hardly applicable to different plants. Thus, the thermodynamic equilibrium calculations which independent to the gasifier design is more convenient for process studies. However, it is known that the thermodynamic equilibrium may be not achieved mainly because of the relatively low operation temperatures.

2.2.1.1 Catalytic Steam Catalytic Gasification

Reported by Basu [30], the uses of catalysts in the thermochemical conversion of biomass may not be essential, but it is can help under certain circumstances. Two main motivations for catalyst are:

- Removal of tar from the product gas, especially if the downstream application or the installed equipment cannot tolerate it.
- Reduction in methane content of the product gas, particularly when it is to be used as syngas.

The development of catalytic gasification is driven by the need for tar reforming. When the product gas passes over the catalyst particles, the tar or condensable hydrocarbon can be reformed on the catalyst surface with either steam or carbon dioxide, thus producing additional hydrogen and carbon monoxide .The reaction can be written in simple form as,

$$C_mH_m + nH_2O \rightarrow \left(n + \frac{m}{2}\right) H_2 + nCO \qquad [1]$$

The other option for tar removal is thermal cracking, but it requires a high temperature and produce soot; thus it cannot harness the lost energy in tar hydrocarbon.

The second motivation for catalytic gasification is removal of methane from the gas product. For this, the use of catalytic steam reforming is preferable. Reforming is very important for the production of syngas, which cannot tolerate methane and requires a precise ratio of CO and H_2 in the product gas. In steam reforming, methane reacts with steam in the temperature range of 700 to 1100 ^{0}C in the presence of metal based catalyst, and thus it is reformed into CO and H_2 as presented by equation below:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad [2]$$

This reaction is widely used in hydrogen production from methane, for which nickel based catalysts are very effective.

The catalysts for reforming reactions are to be chosen keeping in view their objective and practical use. Some important catalyst selection criteria for the removal of tar are as follows [30] :

- Effective
- Resistant to deactivation by carbon fouling and sintering
- Easily regenerated
- Strong and resistant to attrition
- Inexpensive

For the methane removal the following criteria are to be met in addition to those in the previous list :

- Capable of reforming methane
- Must provide the required CO/H_2 ratio for the syngas process

Catalysts can work in-situ and post-gasification reactions. It can be added directly in the reactor, as in a fluidized bed. Such application is effective in reducing the tar, as well reducing the methane. Meanwhile, nickel is highly effective as a reforming catalyst for reduction of tar as well as for adjustment of the CO/H_2 ratio through methane conversion. It performs best when used downstream of the gasifier in the secondary bed, typically at 780 ^{o}C. Deactivation of catalyst with carbon deposits is an issue. Nickel is relatively inexpensive and commercially available though not as cheap as dolomite. The presence of nickel is essential in the steam reforming reaction to increase the hydrogen concentration in the synthesis gas. This can be done by converting the methane into carbon monoxide and hydrogen by reacting with the gasifying agent, steam.

2.2.1.2 Biomass Steam Gasification for Hydrogen Production

Up to date, the thermochemical processes that have been studied are combustion, pyrolysis and gasification. Among them, the gasification of biomass is economically better than the rest and has efficient present technologies for biomass conversion to energy [21]. Gasification technology, primarily the biomass steam gasification has been proven experimentally to produce higher hydrogen content in the synthesis gas [6,28].

In general, the uses of different gasifying agents, i.e air, oxygen steam and pure steam affect the end compositions of product gas and the quality of hydrogen. From the records, the hydrogen concentration in the product gas is higher in the steam gasification process compared to the conventional steam-air gasification [1].
Hussain et al [29] reported only 5.9 vol.% of hydrogen produced in from the air gasification of empty fruit bunch (EFB). Since steam gasification yields higher hydrogen concentration, therefore the focus on this current study is actually on steam gasification.

Using thermodynamic equilibrium calculations, a model for steam gasification was developed by Schuster et al [12]. The steam gasification process is take place in fluidized-bed gasifier which provide excellent mixing gas and solid contact thus leads to high reaction rate and conversion efficiencies. The product gas compositions was calculated considering thermodynamic equilibrium of the main components CH_4, CO, CO_2, and CH_4 and the presence of solid carbon. The reaction scheme is similar to the one reported by Inayat et al [6] excluding the carbonation reaction. The model is simulated by varying biomass moisture, amount of fluidizing agent, gasification temperature and biomass composition. Among these parameters, gasification temperature had the strongest influence on chemical efficiency.

2.2.1.3 Equilibrium Model for Steam Gasification of Palm Kernel Shell (PKS) for Hydrogen Production

Reported Ahmed et al [4], a mathematical model is developed to predict the gas components composition in the palm kernel shell gasification. To imitate the gasification process in the reactor, series of reactions are included. These are water gas shift, methanation, Boudouard, water gas and steam reforming reaction. Therefore, the complete reaction is presented by chemical equation below.

$$C_{4.4}H_{5.9}O_{2.6} + \ kH_2O = aCO_2 + bCO + cH_2 + dCH_4 + fH_2O \qquad [3]$$

From the equation above, the value of a, b, c, d and f are determined from the species balance equation as presented by the following equations:

$$1 = a + b + d \qquad \text{(Carbon balance)} \qquad [4]$$

$$1.34 + 2k = 2c + 4d + 2f \qquad \text{(Hydrogen balance)} \qquad [5]$$

$$0.59 + k = 2a + b + f \qquad \text{(Oxygen balance)} \qquad [6]$$

The *fminunc* is used to solve the unknown value of stoichiometric coefficient in MALTAB. The study showed that the increase in the gasification temperature and steam/biomass ratio enhance the hydrogen production, similar to the trend reported by Inayat et al [6].

2.2.1.4 Modeling of Steam Gasification with *In-situ* CO_2 Capture for Hydrogen Production

Reported by Inayat et al [6], the research discussed on the mathematical model of hydrogen production via biomass steam gasification with calcium oxide as sorbent in a gasifier. A modelling framework consisting of kinetic models for char gasification, methanation, Boudouard, methane reforming, water gas shift and carbonation reactions is used to represent the gasification and CO_2 adsorption in the gasifier are implemented in MATLAB. The kinetic scheme used are as follows:

Table 2.1 : Reaction scheme for steam gasification with *in-situ* CO_2 capture [6]

Eq.No	Name	Reaction
1	Char gasification	$C + H_2O \rightarrow H_2 + CO$
2	Methanation	$C + 2H_2 \rightarrow CH_4$
3	Boudouard	$C + CO_2 \rightarrow CO + 3H_2$
4	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$
5	Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

For this model, first order with respect to reacting species concentrations is selected, yielding the rate of reaction as,

$$r_i = k_i C_A C_B \qquad [7]$$

where r_i is the rate of reaction i, C_A is the concentration of reactant A , C_B is the concentration of reactant B and k_i is the rate constant for the reaction i. From the model simulations, it is observed that hydrogen production and carbon conversion increase with increasing temperature and steam/biomass ratio. The model predicts a maximum hydrogen mol fraction in the product gas of 0.81 occurring at 950K, steam/biomass ratio of 3.0 and sorbent/biomass ratio of 1.0.

2.2.1.5 Thermodynamic Equilibrium Model for The Steam Gasification From Biomass Coupled With CO_2 Capture

In the research conducted by Florin and Harris [15], they demonstrate the applicability of thermodynamic equilibrium theory for the identification of optimal operating conditions for maximizing hydrogen output and CO_2 capture. CaO is a commonly used as a CO_2 sorbent because it capable in removing CO_2 to a very low concentration under conditions suitable for biomass gasification. For the gasification process to take place, Florin and Harris assume several chemical reactions occur in the gasifier as presented by table below.

Table 2.2 : Important chemical reactions in the steam gasification of biomass coupled with CO_2 capture

Eq.No	Name	Reaction
1	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$
2	Methanation	$C + 2H_2 \rightarrow CH_4$
3	Boudouard	$C + CO_2 \rightarrow CO + 3H_2$
4	Water gas (i)	$C + H_2O \rightarrow CO + H_2$
4	Water gas (ii)	$C + 2H_2O \rightarrow CO_2 + H_2$
4	Oxidation (i)	$C + O_2 \rightarrow CO_2$
4	Oxidation (ii)	$C + 0.5O_2 \rightarrow CO$
5	Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

In order to identify the optimal reaction conditions for the maximum H_2 output from the steam gasification of biomass coupled with CO_2 capture, the reaction parameters: (i) temperature; (ii) steam/biomass ratio/ sorbent/biomass ratio and (iv) pressure were investigated. The model predicted 83 % of hydrogen gas from the product gas when coupled with CO_2 sorbent. This maximum hydrogen is actually 20 percent higher than the one without the use of CO_2 sorbent. 1.5 steam/biomass ratio, moderate temperature around 800 to 900 K and 0.9 sorbent/biomass ratio are the operating conditions in the model for maximum hydrogen output.

Similar investigation also reported by Acharya et al [14] who carried mathematical study based on Gibbs free energy minimization to find out the potential of hydrogen production from steam gasification in presence of CaO. The mathematical model is developed and the mass balance equation is similar to the one reported by Ahmed et al [4]. To identify the composition of gas product, equilibrium approach is used. At equilibrium, the total Gibbs free energy is given by

$$G^t = \sum_{i=1}^{N} n_i \, \mu_i \tag{8}$$

Where n_i is the number of moles species i, μ_i is the chemical potential of species i and it is defined as,

$$\mu_i = G_i^o + RTln\left(\frac{\emptyset P_i}{P^o}\right) \tag{9}$$

where G_i^o is the standard Gibbs free energy of species i, $\emptyset$ is fugacity coefficient and R is the ideal gas constant. Newton Raphson’s method is used to solve the non-linear simultaneous equations. 55.43 % of hydrogen gas is obtained at steam/biomass ratio of 0.83 and sorbent/biomass of 2.0. This model is validated with experimental work and the model over estimates the hydrogen concentration. So the correction equation is developed to match the experimental values.

For Lee at al [21], a mathematical model is developed to investigate the transient behaviour of catalytic steam reforming (MSR) coupled with simultaneous carbon dioxide removal by carbonation reaction. Methane reforming is a major route for the industrial production of hydrogen gas. The chemical equation is presented as,

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad [10]$$

Meanwhile, the carbonation reaction by CaO is defined as,

$$CO_2 + CaO \rightarrow CaCO_3 \qquad [11]$$

These two equations is included in the several research works for the steam gasification of biomass [6,14,15,17]. Based on the simulation, the reaction at lower temperatures than 650 ^{o}C failed to give a practical conversion of the CaO pellets. The model yields high hydrogen concentration a higher temperature of the fluidized bed gasifier. Operation at lower pressure, high ratio of steam/biomass and decreased feed rate at a given temperature is favourable for increasing the degree of carbonation reaction and for lowering the concentration of CO.

2.2.1.6 Modeling of EFB Steam Gasification Coupled With CO_2 Capture for Hydrogen Production

Inayat et al [1] did a research focusing on the process modeling for hydrogen production from oil palm empty fruit bunch (EFB) using MATLAB for parametric study. Applying the same series of reactions for the steam gasification process as reported by [6] for EFB steam gasification, the reactions scheme used are as follows:

Table 2.3 : Reaction scheme for EFB catalytic steam gasification with *in-situ* CO_2 capture [1]

Eq.No	Name	Reaction
1	Char gasification	$C_{3.4}H_{4.1}O_{3.3} + 0.1\,H_2O \rightarrow 2.15\,H_2 + 3.4\,CO$
2	Methanation	$C_{3.4}H_{4.1}O_{3.3} + 8.05\,H_2 \rightarrow 3.4\,CH_4 + 3.3\,H_2O$

3	Boudouard	$C_{3.4}H_{4.1}O_{3.3} + CO_2 \rightarrow 4.4\,CO + 0.9\,H_2O + 1.15\,H_2$
4	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3\,H_2$
5	Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

For this model, there are several assumptions considered in the process modeling :

- The gasifier operates under steady state conditions [1,6,7]
- The reactions occur at isothermal conditions and the volume of the reactor is kept constant [1,6,9,11]
- Tar formation is negligible in the process as the calculation of tar content leads to a higher rate of error in the final product gas composition [1,6,8,9,12]
- Perfect mixing and uniform temperature distribution in the gasifier [1,13]
- Instantaneous devolatilization of biomass due to high temperature of gasifier [13]
- The reactor is insensitive to the hydrodynamic properties
- The operating temperature range is within the range of 923 K to 1023 K

The performance of the gasifier is evaluated using hydrogen yield indicator. The definition of hydrogen yield is given as,

$$H_2\,yield = \frac{hydrogen\,produced\,in\,the\,gasifier\,(g)}{biomass\,fed\,into\,the\,gasifier\,(kg)} \qquad [12]$$

From the model simulation, 76.1 vol% hydrogen is predicted in the product gas at 1023 K and steam/biomass ratio of 3.0. A maximum 102.6 g/kg of hydrogen yield is retrieved at operating conditions of 1023 K, steam/biomass ratio of 3.0 and sorbent/biomass ratio of 1.0.

2.3 Experimental Work on Biomass Gasification for Hydrogen Production

2.3.1 Biomass Steam Gasification for Hydrogen Production

Weerachanchai et al [26] investigated the effect of steam gasification on the product gas composition using larch wood in fluidized bed gasifier. This study indicated that the gasification conditions had a strong influence on the gasification products derived from larch biomass. Steam utilization in the gasification process caused an increase in the amount of gas product and higher H_2/CO ratio. A maximum value of 55.68 vol.% of hydrogen gas is obtained from the experiments with a carbon conversion efficiency of 96%.

Similar research also conducted by Umeki et al [27] but with different use of biomass source. They studied a high temperature steam gasification process to generate hydrogen rich fuels gas from woody biomass. Both temperature and steam/biomass ratio has been investigated on the product gas composition, carbon conversion efficiency, H_2/CO ratio, cold gas efficiency, higher heating value and total gas yield. Water gas shift reaction was the most important reaction among all the reactions that controlled the gas composition. It is recorded that the gasified gas contained over 40 vol.% H_2.

2.3.2 Biomass Steam Gasification With CO_2 Removal for Hydrogen Production

An experimental is conducted by Fujimoto et al [17] for a kinetic study of *in-situ* CO_2 removal gasification of woody biomass for hydrogen production. Commercial calcium hydroxide powder ($Ca(OH)_2$) is employed as a CO_2 sorbent. The experiment is incorporated with the reaction model proposed by Shafizadih and Chin [24]. Woody biomass was gasified in steam at high temperature (923K) and pressure of 6.5 MPa. From the experiment, the evolved CO_2 is completely absorbed by the sorbent in all experiments. At a temperature below 773 K, wood was decomposed to gas, tar and char and above this temperature, tar is decomposed to gas and methane. Reasonable kinetic constants were calculated from the product distribution.

Pengmei et al [25] investigated the characteristics of hydrogen yield from biomass in a catalytic steam gasification. In their experiments, they used dolomite as a catalyst in the fluidized bed reactor and nickel-based catalyst in the fixed bed reactor. From the findings, the addition of 120g/(kg h^{-1}) biomass and the use of nickel-based catalysts, the system shows good performance in hydrogen rich gas production. The content of

H_2 and CO_2 increased after the catalytic reactor while CH_4 and CO are decreased. Average of 50 vol.% of H_2 is recorded in the experiments.

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Introduction

The work is divided into two main parts; mathematical model development and validation of the model with experimental work and other models. The mathematical model which is developed using MATLAB is consist of two major chapters; mass and energy balance equations. Inside the model, the reaction kinetics also implemented in the model to simulate the rate of consumptions of reactants (char and steam) and the rate of accumulation of gas product (H_2, CH_4, CO and CO_2). MATLAB software is used because it has an ordinary differential equation solver that able to solve the mass and energy balance equations within specific period of time.

A separate kinetic model parameter has been developed to estimate the pre-exponential factor and activation energy of Arrhenius equation for six reactions occurring in catalytic steam gasification with in-situ CO_2 capture for palm kernel shell (PKS) and palm oil empty fruit bunch (EFB). For this model, hybrid particle swarm optimization method is used. The experimental data is gained from the experimental work carried out in gasification plant in Block P (Universiti Teknologi Petronas) and it being used to obtain the kinetic parameters and validate the model prediction profiles.

Since we have two different biomass for this research, two mathematical models are developed; each with different set of mass and energy balance equations. The EFB and PKS models are tested with several case studies to demonstrate the accuracy of the developed model with the experimental work and other comparable models. The models are simulated with different value of temperature, steam/biomass ratio and sorbent/biomass ratio.

The methodology for the current study is divided into four steps as shown by the flowchart in Figure 3.1.

1. A reaction kinetic model has been developed to predict the reaction kinetics for six different reactions occurred in the catalytic steam gasification with in-situ CO_2 capture using hybrid particle swarm optimization method.
2. The mass and energy balance equations for each biomass are developed and implemented in MATLAB.

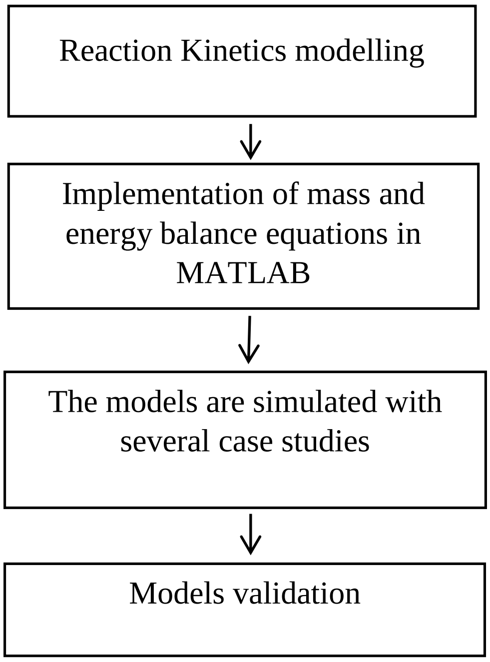


Figure 3.1 : Flowchart for The Research Methodology

3. Each model is tested with several case studies including temperature variation, different value of steam/biomass ratio and sorbent/biomass ratio.
4. The results gained from the simulation are validated with the experimental work and other comparable models.

3.2 Reaction Kinetics Modelling

3.2.1 Biomass Feedstock

Researchers characterize various type of biomass by dividing them into four major categories which are energy crops, agricultural residue and waste, foresty waste and residues and lastly, industrial and manucipal wastes [28]. The EFB and PKS are the biomass which comes from the energy crops section.

3.2.1.1 Oil Palm Empty Fruit Bunch

The abundance of palm oil empty fruit bunch (EFB) as one of the main source of biomass in Malaysia yielded many studies in this field. The steam gasification of EFB had been studied comprehensively especially in the contact of the hydrogen production [1].

EFB char has a molecular formula of $C_{3.4}H_{4.1}O_{3.3}$ with a molecular weight of 97.7 kg/kmol [10]. The EFB is chosen as a source of biomass for the model due its high availability throughout the year especially in Malaysia [1]. The constituent elements of EFB are determined by the ultimate analysis as presented by Table 3.1 [2,3].

Table 3.1 : Elemental analysis of empty fruit bunch (EFB) [2,3]

Component	Proportion
Proximate analysis (wt.%)	
Cellulose	59.7
Hemicellulose	22.1
Lignin	18.1
Ultimate analysis (wt.%)	
C	48.79
H	7.33
N	0.00
O	36.30
S	0.68

3.2.1.2 Palm Kernel Shell

A moisture free palm kernel shell (PKS) has a molecular formula of $C_{4.4}H_{5.9}O_{2.6}$ with a molecular weight of 100.3 g/mol [4,10]. The ultimate analysis of palm kernel shell are given in Table 3.2 [5].

Table 3.2 : Ultimate analysis of palm kernel shell (PKS) [5]

Component	Proportion
Ultimate analysis (wt.%)	
C	48.79
H	7.33
N	0.00
O	36.30
S	0.68

3.2.2 Assumptions

Several studies use particular assumptions to simplify the complexity of the gasification process in their mathematical model [1,6]. The assumptions used for this kinetic model approach are as the following:

- The gasifier operates under steady state conditions [1,6,7]
- All chemical reactions in the gasification process occurs simultaneously in the gasifier which include char gasification, Boudouard, methanation, methane reforming, water gas shift and carbonation [1,6,8,12]
- Biomass is presented by char [6,9]
- Constant atmospheric pressure in the gasifier [9]
- The reactions occur at isothermal conditions and the volume of the reactor is kept constant [1,6,9,11]
- Tar formation is negligible in the process as the calculation of tar content leads to a higher rate of error in the final product gas composition [1,6,8,9,12]
- Perfect mixing and uniform temperature distribution in the gasifier [1,13]
- Product gas consist of H_2, CO, CO_2 and CH_4 [1,6,11,12]
- Instantaneous devolatilization of biomass due to high temperature of gasifier [13]

3.3 Reaction Kinetics Model Development

In the gasifier, there are six reactions occur simultaneously which made of char gasification, methanation, Boudouard, methane reforming, water gas shift and carbonation reaction [1,6,14,17]. Table 3.4 and Table 3.5 show the reaction scheme for EFB and PKS catalytic steam gasification with *in-situ* CO_2 capture respectively.

Table 3.3 : Reaction scheme for EFB catalytic steam gasification with *in-situ* CO_2 capture [1]

Eq.No	Name	Reaction
1	Char gasification	$C_{3.4}H_{4.1}O_{3.3} + 0.1\ H_2O \rightarrow 2.15\ H_2 + 3.4\ CO$
2	Methanation	$C_{3.4}H_{4.1}O_{3.3} + 8.05\ H_2 \rightarrow 3.4\ CH_4 + 3.3\ H_2O$
3	Boudouard	$C_{3.4}H_{4.1}O_{3.3} + CO_2 \rightarrow 4.4\ CO + 0.9\ H_2O + 1.15\ H_2$
4	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3\ H_2$
5	Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

Table 3.4 : Reaction scheme for PKS catalytic steam gasification with *in-situ* CO_2 capture

Eq.No	Name	Reaction
1	Char gasification	$C_{4.4}H_{5.9}O_{2.6} + 1.8\ H_2O \rightarrow 4.75\ H_2 + 4.4\ CO$
2	Methanation	$C_{4.4}H_{5.9}O_{2.6} + 8.45\ H_2 \rightarrow 4.4\ CH_4 + 2.6\ H_2O$
3	Boudouard	$C_{4.4}H_{5.9}O_{2.6} + CO_2 \rightarrow 4.4\ CO + 2.95\ H_2$
4	Methane Reforming	$CH_4 + H_2O \rightarrow CO + 3\ H_2$
5	Water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
6	Carbonation	$CO_2 + CaO \rightarrow CaCO_3$

Steam gasification modeling usually consist of five main reactions; char gasification, methanation, Boudouard, methane reforming and water gas-shift to represent the steam gasification process [4,12,16]. However, carbonation reaction is included in the present study to increase the hydrogen yield from the product gas using CO_2 sorbent [1,6,14,15,17]. The mol fraction of each gas component (CO, CH_4, H_2 and CO_2) is calculated using the kinetic parameters of six reactions assumption.

To determine the rate of reaction for each reaction, the first order assumption is used with respect of every component concentration [1,18]. The first order reaction of two species is simply defined as [19]:

$$r_i = k_i C_A C_B \qquad [13]$$

where r_i is the rate of reaction i, C_A is the concentration of reactant A , C_B is the concentration of reactant B and k_i is the rate constant for the reaction i. Using the first order assumption for every component concentration, equation 14-16 are developed for the reaction involving char of EFB. The rates are presented as following:

$$r_1 = k_1 C_{C_{3.4}H_{4.1}O_{3.3}} C_{H_2O} \qquad [14]$$

$$r_2 = k_2 C_{C_{3.4}H_{4.1}O_{3.3}} C_{H_2} \qquad [15]$$

$$r_3 = k_3 C_{C_{3.4}H_{4.1}O_{3.3}} C_{CO_2} \qquad [16]$$

Applying the same principle the rate of char gasification, methanation and Boudouard reaction for PKS, the rates are presented by Equation 17-19.

$$r_4 = k_4 C_{C_{4.4}H_{5.9}O_{2.6}} C_{H_2O} \qquad [17]$$

$$r_5 = k_5 C_{C_{4.4}H_{5.9}O_{2.6}} C_{H_2} \qquad [18]$$

$$r_6 = k_6 C_{C_{4.4}H_{5.9}O_{2.6}} C_{CO_2} \qquad [19]$$

The rate of methane reforming reaction is calculated using Equation 20.

$$r_7 = k_7 C_{CH_4} C_{H_2O} \tag{20}$$

For water gas shift reaction, Equation 21 is used for this reversible reaction [1,6,16].

$$r_8 = k_8 \left(C_{CO} C_{H_2O} + \frac{C_{CO_2} C_{H_2}}{K_W} \right) \tag{21}$$

Meanwhile, the rate of carbonation reaction is presented by Equation 22.

$$r_9 = k_9 C_{CaO} C_{CO_2} \tag{22}$$

The rate of reaction for every reaction rely on the reaction constant and the concentration of reactant. The reaction constant is defined by Arrhenius equation where it is directly proportional to the pre-exponential factor and temperature [20]. The Arrhenius constant for respective reaction, k_i is shown by Equation 23.

$$\mathrm{k}_i = \mathrm{A}_i e^{E_i/RT_i} \tag{23}$$

where A_i is pre-exponential factor, E_i is the activation energy, T_i is the gasifier temperature and R is the ideal gas constant. The overall volumetric rate, R_i for each gas species are calculated based on the stoichiometric approach [21]. The volumetric rate for gas-phase components in EFB steam gasification coupled with in-situ CO_2 adsorption are given by Equation 24-27 [1].

$$R_{H_2} = 2.15\, r_1 - 8.05\, r_2 + 1.15\, r_3 + 3\, r_7 + r_8 \tag{24}$$

$$R_{CO} = 3.4\, r_1 + 4.4\, r_3 + r_8 - r_9 \tag{25}$$

$$R_{CH_4} = 3.4\, r_2 - r_7 \tag{26}$$

$$R_{\mathrm{CO_2}} = - r_3 + r_8 - r_9 \tag{27}$$

On the other hand, the volumetric rate for gas-phase species in PKS steam gasification are shown by the following equations.

$$R_{H_2} = 4.75\, r_4 - 8.45\, r_5 + 2.95\, r_6 + 3\, r_7 + \; r_8 \tag{28}$$

$$R_{CO} = 4.4\, r_4 + 4.4\, r_6 + r_8 - r_9 \tag{29}$$

$$R_{CH_4} = 4.4\, r_4 - r_7 \tag{30}$$

$$R_{\mathrm{CO_2}} = - r_6 + \; r_8 - \; r_9 \tag{31}$$

3.4 Kinetic Model Parameter Fitting

The kinetic parameter for the EFB steam gasification can be retrieved from the literature [1] since limited information on the experimental data. The experimental data provided is only at equilibrium value, not a data against experimental time. On the other hand, due to limited source for the kinetic data for PKS steam gasification, the calculation of reaction kinetic parameters for six reactions are needed. Using the experimental data for PKS catalytic steam gasification coupled with in-situ CO_2 capture, the kinetic parameter for the reactions (Table 3.5) are generated. Figure 3.2 demonstrate the flowchart of the minimization approach for kinetic model parameters. Conceptually, the residual error, RSS is calculated to minimize the residuals between the model predictions, y_m and the experimental results, y_e as shown by Equation 32 [22].

$$RSS = \sum_{i=1}^{N} \left(\frac{y_e - y_m}{y_e} \right)^2 \tag{32}$$

Where i is the number of available data points.

Beside the minimization approach, the kinetic parameters are calculated by the particle swarm optimization (PSA) and hybrid particle swarm optimization method followed by Levenberg –Marquardt algorithm [22]. Using the initial assumption value for the pre-exponential factor, A_i and the activation energy, E_i, the kinetic parameters model will compare the value generated by the model and it is later verified with the value from the experimental work.

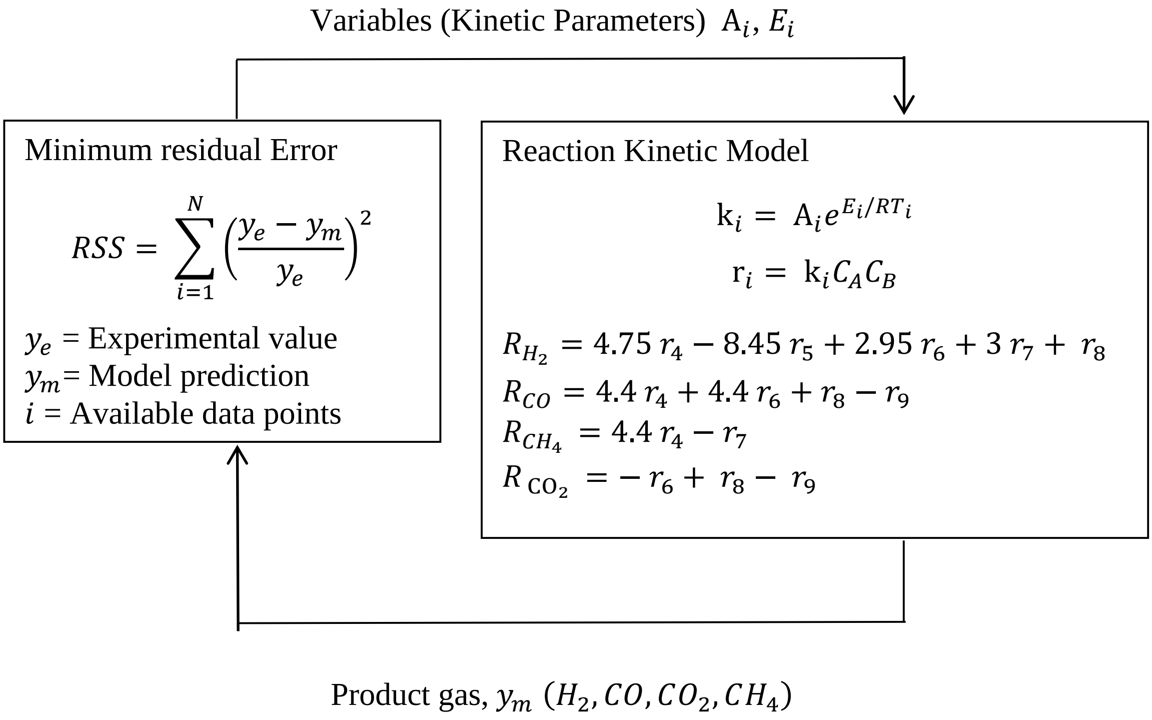


Figure 3.2 : Flowchart for Residual Minimization Approach for Kinetic Model Parameters Fitting Approach for PKS steam gasification

The sum squared deviation is used to represent the mean error between the model prediction, y_m and the experimental data, y_e for product gas composition (CO, CH_4, H_2 and CO_2) [1,6]. The deviation analysis is performed using Equation 33-35.

$$RSS = \sum_{i=1}^{N} \left(\frac{y_e - y_m}{y_e}\right)^2 \tag{33}$$

$$MRSS = \frac{RSS}{N} \tag{34}$$

$$Mean\ Error = \sqrt{MRSS} \tag{35}$$

Here RSS is the residual sum squared, $MRSS$ is the mean value of RSS, N is the total number of data points and i is the available data points.

3.5 Performance Indicator

The performance of the biomass gasification process for hydrogen production is evaluated based on kinetics parameters and simulation of reaction kinetics model. To indicate the performance of the gasifier, the mol fraction of gas-phase components are calculated based on Equation 36.

$$mol\ \%_i = \frac{mol_i}{total\ mol\ of\ product\ gas} \times 100\% \qquad [36]$$

The mol fraction of hydrogen and carbon dioxide gas are the main concern in this research. The mol fraction of hydrogen is theoretically increases with increasing temperature and steam/biomass ratio.

3.6 Mass and Energy Balance

The mass and energy balance equations are really important to develop a mathematical model. These equations become a framework for the behavior and dynamics of the components involved in the system. Many mathematical models are develop for the steam gasification process [1]. The mass balance equations of the components in the gasifier are calculated based on assumption of no accumulation of mass in the system. The mass flow rate of the system is defined as [6],

$$\sum m_i = \sum m_o \qquad [37]$$

where m_i is the mass flow rate of components into the system and and m_o is the mass flow rate leaving the system. The mass balance at the gasifier is defined as,

$$m_{char} + m_{CaO} + m_{H_2O} = m_{H_2} + m_{CH_4} + m_{CO} + m_{CO_2} \qquad [38]$$

Further details regarding the mass balance equation for every component is presented in Appendix A. Meanwhile, the energy balance equation is develop with the inclusion of enthalpy of formation, H_f and the change of enthalpy, ΔH. The enthalpy change, ΔH is calculated based on the difference of temperatures in the gasifier with the standard temperature.

$$\Delta H = \int_{T_1}^{T_2} C_p dT \qquad [39]$$

Based on Eq. 39, the value of the enthalpy change is depends on the specific heat capacity of components, C_p. The heat capacity and standard heat of formation for the components is tabulated in the Table 3.5.

Table 3.5 : Heat capacity and standard heat of formation for the components [1,23]

Component	Heat Capacity, C_p (J mol^{-1} K)	H$_f$ (J mol^{-1})
H_2O	$72.43 + (10.39 \times 10^{-3})T - (1.50 \times 10^{-6})T^2$	-2.413×10^5
H_2	$27.01 + (3.51 \times 10^{-3})T - (0.69 \times 10^5)T^{-2}$	0
CO	$28.07 + (4.63 \times 10^{-3})T - (0.26 \times 10^5)T^{-2}$	-1.105×10^5
CO_2	$45.37 + (8.69 \times 10^{-3})T - (9.62 \times 10^5)T^{-2}$	-3.935×10^5
CH_4	$14.15 + (75.5 \times 10^{-3})T - (18 \times 10^{-6})T^2$	-7.487×10^4
CaO	$41.84 + (2.03 \times 10^{-2})T - (4.52 \times 10^5)T^{-2}$	-6.356×10^5
$CaCO_3$	$82.34 + (4.975 \times 10^{-2})T - (12.87 \times 10^5)T^{-2}$	1.207×10^6

The heat of formation, H_f of components is used to calculate the heat of reaction, $H_{r,273\,K}$ at standard temperature [20]. The heat of reaction, $H_{r,273\,K}$ is given as,

$$H_{r,273\,K} = \sum n_i H_{f,i}(product) - \sum n_i H_{f,i}(reactant) \qquad [40]$$

Where n_i is the mol of component i and $H_{f,i}$ is the heat of formation of component i. Since the gasifier is heat up to the gasifier temperature, T_r, the heat of reaction, H_s is defined as,

$$H_s = \sum n_i \bar{C}_{p,i} \Delta T(product) - \sum n_i \bar{C}_{p,i} \Delta T(reactant) \qquad [41]$$

Where $\bar{C}_{p,i}$ is the specific heat capacity for component i and ΔT is the temperature difference. Therefore, the net heat required for a reaction is,

$$\Delta H = H_s + H_{r,273\ K} \qquad [42]$$

Thus, the relation of energy balance equation for the steam gasification is displayed as [1],

$$\sum H_i + Q_r = \sum H_o \qquad [43]$$

where H_i is the enthalpy given to the system, Q_r is the heat energy required for the gasification process and H_o is the energy loses from the system.

3.7 MATLAB Implementation

Based on the figure below, the mass and energy balance equations are implemented in the MATLAB file which is denoted by m.file. Figure 3.3 shows MATLAB simulation flowsheet for the biomass steam gasification model.

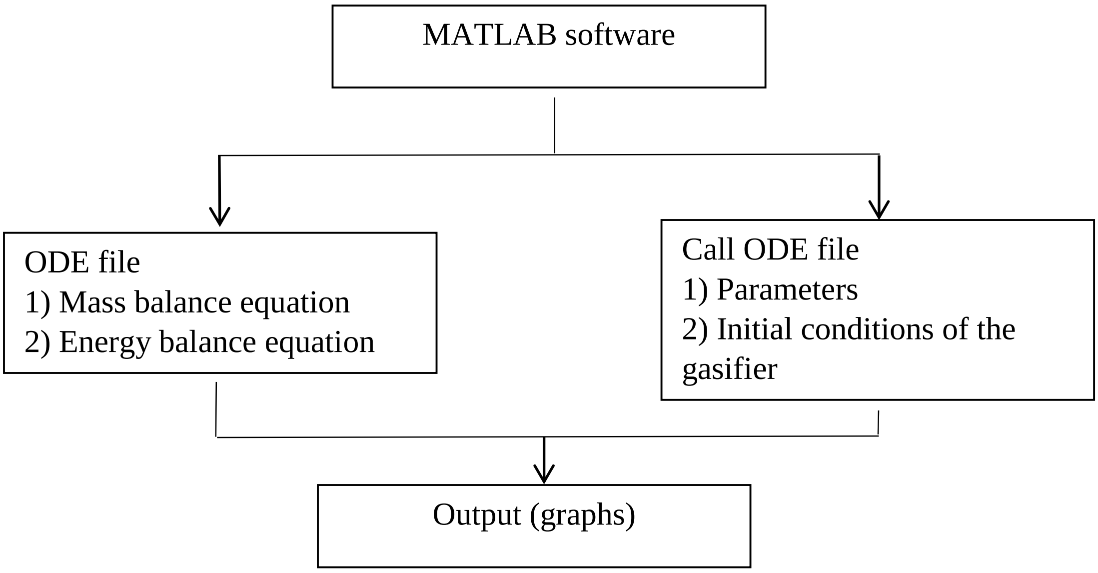
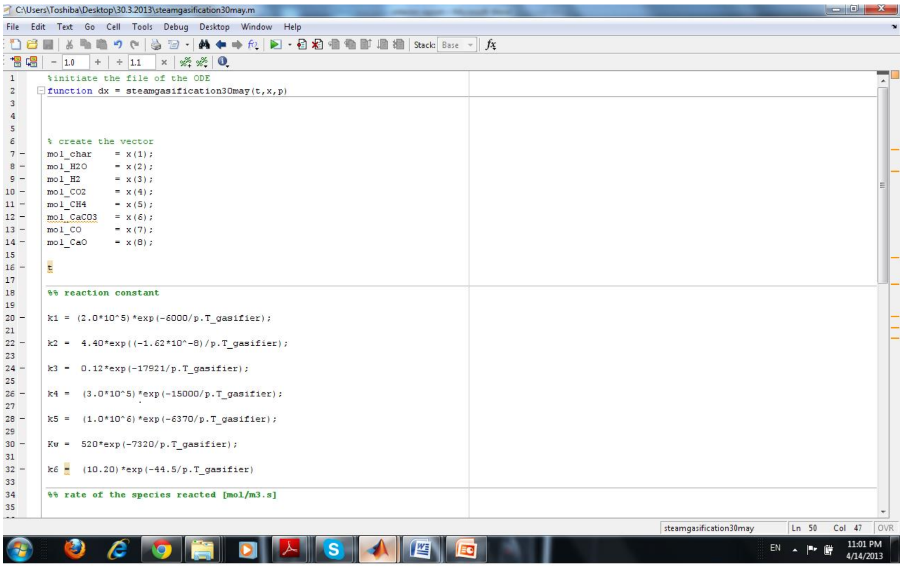


Figure 3.3 : MATLAB Simulation Flowsheet

Two files are created in *MATLAB* where one file was used to write the mass and energy balance equations and another m.file is functioned in addressing the constants and initial conditions of the simulation. In the Call ODE file, the initial conditions of the gasifier are consist of the simulation period, initial mass of gas phase components and reactor pressure and temperature.The figure below shows the implementation of mass balance equation in MATLAB.



```
%initiate the file of the ODE
function dx = steamgasification30may(t,x,p)



% create the vector
mol_char    = x(1);
mol_H2O     = x(2);
mol_H2      = x(3);
mol_CO2     = x(4);
mol_CH4     = x(5);
mol_CaCO3   = x(6);
mol_CO      = x(7);
mol_CaO     = x(8);

t

%% reaction constant

k1 = (2.0*10^5)*exp(-6000/p.T_gasifier);

k2 =  4.40*exp((-1.62*10^-8)/p.T_gasifier);

k3 =  0.12*exp(-17921/p.T_gasifier);

k4 =  (3.0*10^5)*exp(-15000/p.T_gasifier);

k5 =  (1.0*10^6)*exp(-6370/p.T_gasifier);

Kw =  520*exp(-7320/p.T_gasifier);

k6 =  (10.20)*exp(-44.5/p.T_gasifier)

%% rate of the species reacted [mol/m3.s]

```

Figure 3.4 : Mass Balance Equation Implemented in MATLAB

The ODE (ordinary differential equation) solver is selected to compute the mass and energy balance equations. Depending on the initial conditions of the gasifier, the ode solver will execute the results from the simulation in the graph form. Later, the graphs will be analyzed and documented. In order to determine the precision of the model, we will vary the operational parameters of the gasifier. The manipulated variables are stated as the following:

- Temperature of the gasifer
- Steam/biomass ratio
- Residence time

The H_2 yield from the product gas is the main priority in the result section. A high purity of H_2 concentration is expected in the system with the presence of CaO as CO_2 sorbent.

3.8 Work Progress

Key milestones or performance indicators are really important to ensure this project is at the good track. The key milestones need to be achieved at the requested time in order to meet the objectives of this research. Below are the simple illustration of the Gantt chart and Key Milestones of this project.

3.8.1 Gantt Chart

Activities	FYP 1														FYP 2													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Critical literature review on of steam gasification in fluidized bed reactor	🟦	🟦	🟦	🟦	🟦																							
Development of mass and energy balance equations for EFB						🟦	🟦	🟦	🟦	🟦																		
Implementation of mass and energy balance equations into EFB into MATLAB											🟦	🟦	🟦	🟦														
Development of mass and energy balance equations for PKS															🟦	🟦	🟦	🟦	🟦									
Implementation of mass and energy balance equations into PKS into MATLAB																				🟦	🟦	🟦	🟦	🟦				
Data analysis and documentation																									🟦	🟦	🟦	🟦

3.8.2 Key Milestones

Activities	FYP 1														FYP 2													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Finishing the critical review for steam gasification coupled with CO_2 capture					■																							
Completed mass and energy balance equation for EFB										■																		
Completed implement mass and energy balance equation for EFB in MATLAB and model validation														■														
Completed mass and energy balance equation for PKS																			■									
Completed implement mass and energy balance equation for PKS in MATLAB and model validation																								■				
Data analysis and documentation																												■

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results simulated via developed reaction kinetics model and using rate parameters from various literatures for the EFB and the reaction constants developed using a hybrid particle swarm optimization method for the PKS steam gasification. The results was next validated with the experimental results of palm waste catalytic gasification. The discussion continues with comparison of this model results with the previous developed model.

To study the catalytic adsorption steam gasification with in-situ CO_2 capture of EFB and PKS for hydrogen production, the simulation were carried out with the effect of temperature ranging between 800 to 1000 K. Due to the limited information on kinetic parameter for the PKS steam gasification in the literature, this chapter also provides the discussion on the reaction kinetics parameters calculated for the reactions involving PKS based on the experimental data.

The extensive range of variables (temperature, steam/biomass ratio and sorbent/biomass ratio) has been investigated on product gas composition and hydrogen purity for both EFB and PKS. The range of variables is listed in the Table 4.1**.** The range of temperature has been selected based on the carbonation reaction [31] whereas steam/biomass ratio and sorbent/biomass ratio are selected based on Inayat et al’s initial parameters in their model [6].

The results for the EFB and PKS simulations were studied based on the different value of initial parameters and the discussions of the results were made based on the theoretical information.

Table 4.1 : Range of operating variables for modelling work

Basis	Value
Steam/biomass ratio	1.4-1.6-1.8-2.0-2.2
Sorbent/biomass ratio	0.7-0.8-0.9-1.0-1.1
Temperature (K)	873K to 1023 K
Pressure (atm)	1

4.2 Reaction Kinetic Modelling of EFB

4.2.1 Effect of Temperature on Product Composition

Initially, the kinetic parameters for the reactions (listed in Table 3.4**)** are used from literature and listed in Table 4.2. The kinetic model simulated with the effect of temperature on the product gas compositions along with validation using experimental data is presented in Figure 4.1**.** The developed model is validated using the experimental data of EFB catalytic steam gasification with *in-situ* CO_2 capture reported by Inayat et al [1,6] due to the proximity with current study. To ensure high consistency and accuracy of this developed model, the results for the modelling work are generated based on the similar initial conditions conducted in the experimental work by Inayat et al [6]. The simulation was conducted at the steam/biomass ratio of 2.0, sorbent/biomass ratio of 1 and 1 atm gasifier pressure. The major components of the product gas considered are H_2, CO_2, CO and CH_4 as investigated by Inayat et al [6].

Table 4.2 : Reaction kinetic parameters of EFB steam gasification reactions from Inayat et al [1]

No	Reaction Name	Kinetic Constant
1	Char gasification	$2.0 \times 10^5 \exp(-6000/T)$
2	Methanation	$2.345 \times 10^5 \exp(-13670/T)$
3	Boudouard	$1.19 \times 10^{-3} \exp(-16840/T)$
4	Methane reforming	$3 \times 10^5 \exp(-15000/T)$

5	Water gas shift	10^6 exp (-6370/T) K_w = 520 exp (-7230/T)
6	Carbonation	1.67 x 10^{-3} exp (-3485/T)

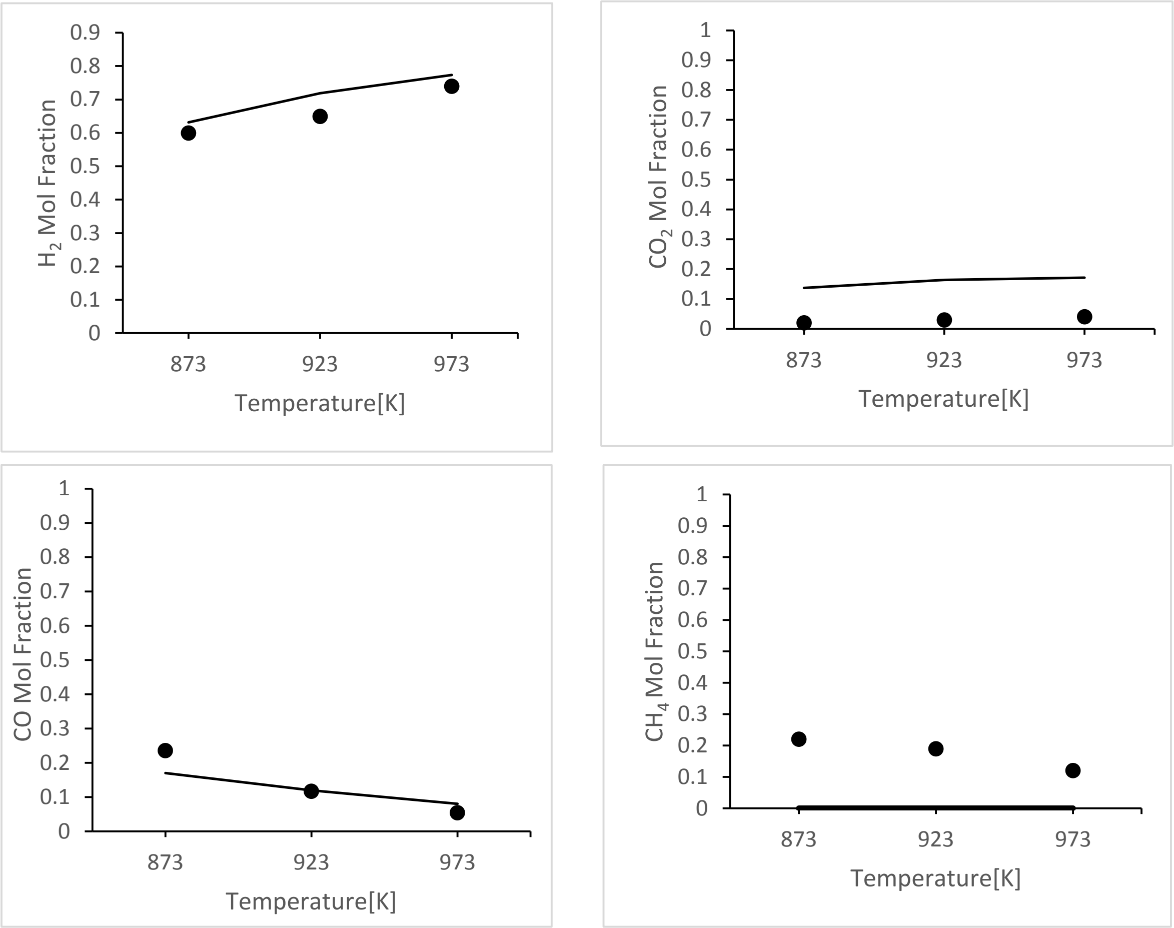


Figure 4.1: Effect of temperature on the product gas composition. Modelling (——), Experiment (●)

It is observed that the temperature range between 873 to 973 K, the hydrogen and carbon dioxide concentration generated by the model showing an increasing pattern similar to the experimental data. This model stated an increment of hydrogen concentration from 60 to 74 vol% while the experimental data stated 59 to 73 vol%. Therefore, the model predicts results with good agreement with those from the experimental work with 7.3 % mean error.

Based on the plots above, the concentration of monoxide decreases with the increase of the gasifier temperature and in this model, the concentration decreases from 0.254

mol fraction to 0.054. Similar concentration pattern also shown by the experimental data where it states a concentration reduction from 0.161 to 0.047 mol fraction. The overall difference between the model and the experimental reading for the carbon monoxide purity is 30 %.

The increases of hydrogen and carbon dioxide concentration with the increases of temperature can be explained by Le Chartelier's principle. The char gasification and methanation reactions are promoted by the heat supplied. Therefore, the usage of steam and the carbon monoxide produced via char gasification and Boudouard reactions encourage the water gas shift reaction; produces carbon dioxide and hydrogen gas.

Meanwhile, the small amount of methane gas produces in the reactor is due to the methane reforming reaction in which the methane gas becomes a reactant for the production of carbon monoxide and hydrogen. The concentration of methane decreases with the increase of temperature as the methane reforming reaction due to the rate of consumption of methane gas is much higher in the methanation reaction than the rate of production of methane in the methane reforming reaction.

High concentration of hydrogen is yields both in experimental and model works due to the presence of the calcium oxide in the reactor. Through the carbonation reaction, the concentration of carbon dioxide reduces thus increase the purity of hydrogen.

The difference of the results between experimental and modelling works is due to the ignorance of tar production in the model. Due to the complexity of tar composition, tar formation in the process are negligible as the calculation of tar content will lead to an increasing amount of error for final product composition [1,11]. Others, the kinetic data is gained from several literatures which uses different type of biomass. Therefore, it shows slight difference on the gas components when being compared to the EFB steam gasification experimental results.

This model also being compared to the Inayat et al's model which is among the current model available for the steam gasification of EFB with in-situ carbon dioxide capture by calcium oxide. For comparison purpose, both simulations were conducted at biomass feed rate of 0.072 kg/h, steam/biomass ratio of 3.0 and sorbent to biomass ratio of 1.0. The results are shown by Figure 4.2.

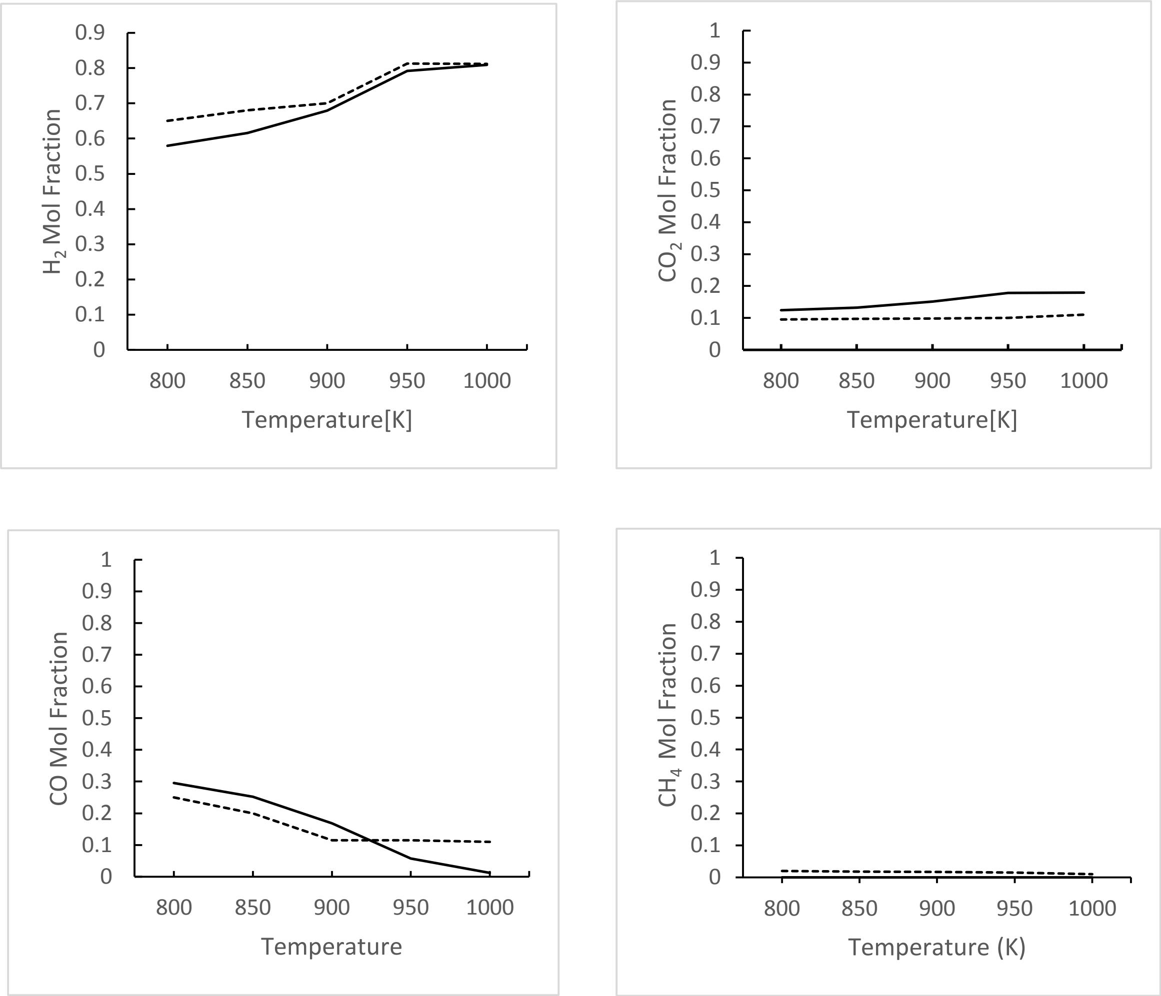


Figure 4.2: Effect of temperature on the product gas composition between Inayat et al and this model. This model (—), Inayat et al’s model (----)

Inayat et al [6] use different approach in their steam gasification model. They used *fmin* approach while this model use ODE (ordinary differential equation) approach for model estimation. Therefore, the compositions of product gas is different with the one in this model as they used different reaction parameters although all the gaseous components showing similar trends. However, the assumptions of the model and the initial conditions were made similar for comparison purpose.

Based on the figure above, the hydrogen production increases with the increase of temperature as more heat supplied at high temperature as explained by Le Chartelier’s principle. Both model predict closely the composition of hydrogen gas at high temperature where the highest amount of hydrogen present in the gasifier at 950 K with 81.3 % mol.

Both model also indicate small amount of methane gas despite the increase of temperature of gasifier. The small amount of methane can be explained by the methane reforming reaction where methane reacted together with steam to produce carbon monoxide and hydrogen gas. The amount of methane present is averagely at 0.015 mol fraction indicated by Inayat ‘s model while this model also predict small amount of methane averagely 0.013 mol fraction.

Since Inayat’s model includes the carbonation reaction, the percentage of carbon dioxide in the gasifier is almost similar to the values estimated by this model with percentage difference of 6.13 %. The presence of CaO in the gasifier allows the carbonation reaction to take place, reducing the concentration of carbon dioxide from the gas products.

4.2.2 Effect of Sorbent in the Gasifier

The simulation also conducted without the presence of carbonation reaction; no absorbent is included in the model and the simulation conducted using the initial conditions similar to the previous cases. The comparison between the hydrogen and carbon dioxide concentration in the simulation is conducted with and without the the presence of calcium oxide as shown by the Figure 4.3 below.

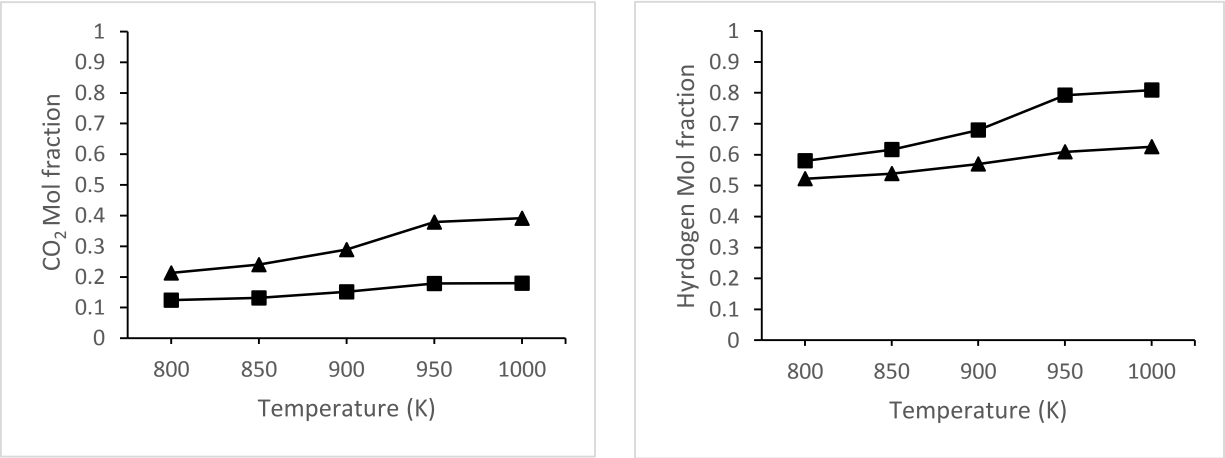
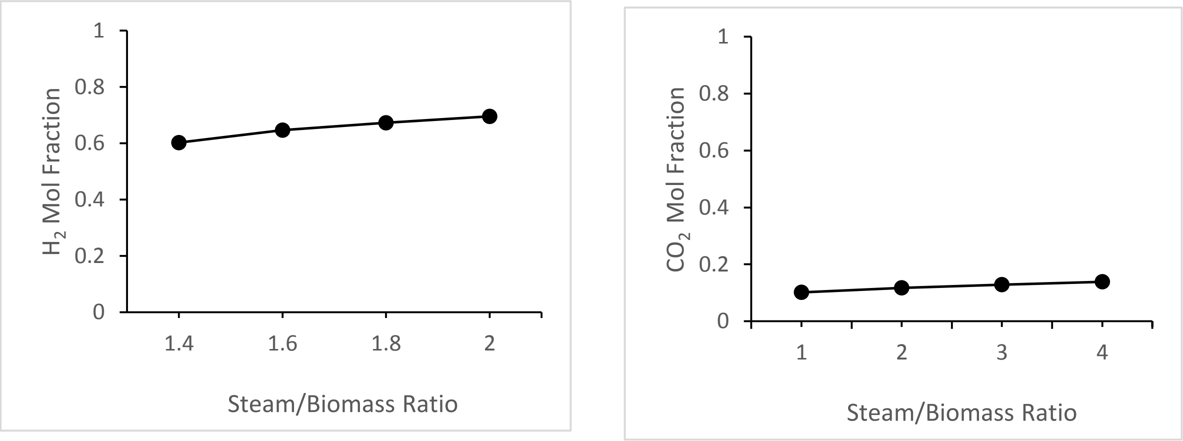


Figure 4.3 : The composition comparison of hydrogen and carbon dioxide in the simulation with and without the presence of calcium oxide. With calcium oxide (■). Without calcium oxide (▲)

The hydrogen concentration is much higher in the simulation where calcium oxide is being used as carbon dioxide sorbent than the one without it. The presence of calcium oxide promoted the carbonation reaction in which the carbon dioxide is absorbed to form solid calcium carbonate. This reaction reduces the concentration of carbon dioxide from the product gas despite the increases of gasifier temperature and promotes the hydrogen production through water-gas shift [15]. Based on the figures above, there is a significant difference between the concentrations of hydrogen gas on both situation with an average percentage difference of 21.3 % and 49.3 % reduction for the carbon dioxide. Mahishi et al [32] reported their thermodynamic studies showed that the use sorbents has the potential to enhance the equilibrium hydrogen yield of conventional gasification by 19 % and reduce the equilibrium carbon dioxide content of product gas by 50.2 %. Similar result also reported by Kinoshita and Turn [33] in their gasification experiment in fluidized bed reactor where the hydrogen yield increases by 15 vol.%.

4.2.3 Effect of Steam/Biomass Ratio to the Product Composition

The steam/biomass ratio is another critical variable to indicate the performance of EFB gasification. The compositions profile for each component in the product gas with respect to steam/biomass ratio at 800 K and sorbent/biomass ratio of 1.0 is plotted in the Figure 4.4.



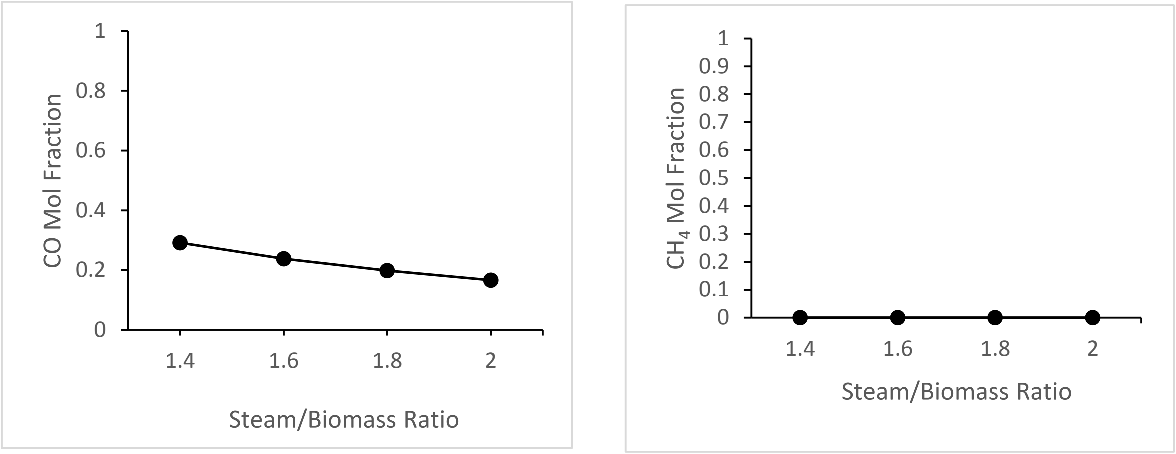


Figure 4.4: Effect of steam/biomass ratio on product gas composition (T=973 K, Sorbent/biomass ratio = 1.0)

The concentration of hydrogen gas increases with the increase of steam/biomass ratio. It increase from 60 to 70 % of hydrogen gas as larger amount of steam fed to the gasifier. This trend can be explained by the consumption of char and methane gas which produces more carbon monoxide and hydrogen. Excess steam in the gasifier allows the complete reaction in the char gasification reaction, methane reaction and water gas shift reaction. Therefore, the hydrogen concentration increases resulted from these series of reactions.

However, the carbon monoxide content is consistently reduced due to the excess steam which shift the equilibrium reaction of water gas shift reaction forward. Larger amount of steam/biomass ratio resulted the excess steam to react completely with carbon monoxide. Due to this reaction, more carbon dioxide gas is produced as indicated by Figure 4.4. However, only 0.02 increment of carbon dioxide gas mol fraction indicated despite the increase of steam/biomass ratio.

Based on the same reason for methane reforming reaction, methane amount also reduces when increasing steam/biomass ratio. Methane gas reacted with excess steam to form carbon monoxide and hydrogen gas. Similar trends also reported on the effect of steam/biomass ratio on product gas composition for biomass steam gasification with calcium oxide [21].

Based on the study on the operational parameters, the hydrogen gas stated the highest value at the gasifier temperature of 950K, steam/biomass ratio of 2.0 and sorbent/biomass ratio of 1.0. In these conditions, the production of hydrogen is 81.3 % mol.

4.3 Reaction Kinetic Modelling of PKS

4.3.1 Kinetics Parameters for Palm Kernel Shell (PKS) Catalytic Steam Gasification with In-situ CO_2 Capture

Table 4.3 lists the kinetics parameters i.e. pre-exponential factors (*A*) and activation energy (*E*) calculated for six reactions occurred in the gasification process using the minimization of the residual approach. The minimum value of the objective function obtained is 0.415.

Table 4.3: Kinetics constants determined using minimizing of residual approach

No	Reaction Name	Kinetic Constant
1	Char gasification	$7.701 \times 10^5 \exp(-106412/RT)$
2	Methanation	$1.771 \times 10^5 \exp(-136565/RT)$
3	Boudouard	$1.889 \times 10^5 \exp(-152600/RT)$
4	Methane reforming	$7.279 \times 10^5 \exp(-83602/RT)$
5	Water gas shift	$7.561 \times 10^5 \exp(-92149/RT)$
6	Carbonation	$1.817 \times 10^4 \exp(-77390/RT)$

The kinetic constants for all six reactions were gained from the model simulation utilizing particle swarm optimization method (PSO) and hybrid particle swarm optimization (HPSO). Particle swarm optimization is a heuristic optimization method and it starts with the randomly generated initial population called particles [22]. Figure below shows the distribution of particles in the parity diagram.

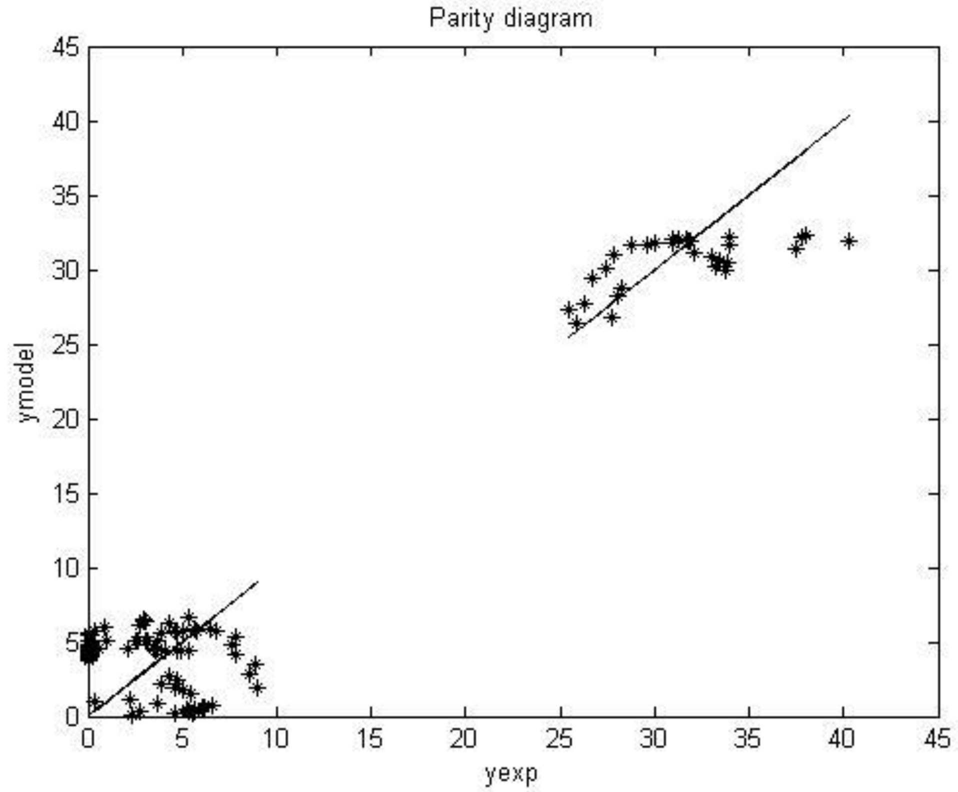


Figure 4.5 : Parity diagram

The particles are closely approaching the the straight line, indicating the model prediction values are closely similar to the experimental values. The discontinuation of the line and particles between the model and experimental values are due to insufficient data of the experimental data mostly the composition of gaseous components for the first six minutes of the PKS steam gasification experiments.

Using the kinetics constant listed in Table 4.3, the reaction kinetics model was validated with the experimental results conducted in Block P, Universiti Teknologi Petronas for the same feed rate of 500g /hr, steam/biomass ratio ratio of 2.0 and sorbent/biomass ratio of 1.0, pressure of 1 atm and temperature range of 873K to 1023K. The simulation was conducted for a period of an hour similar to the experimental work. Further discussion for model validation is reviewed in 4.3.2 and 4.3.3 sections.

4.3.2 Model Validation Based on the Effect of Temperature

Figure 4.6, 4.7 and 4.8 show the comparison results between the model and the experimental works for PKS catalytic steam gasification coupled with CO_2 capture by CaO at three different temperature; 873K, 948K and 1023K. These figures show the model predicts the gas compositions with similar trends and good agreement with those from the PKS steam gasification experiments. The mean error of product gas composition between model prediction and experimental results at gasifier temperature are 873K are 0.073, 0.091, 0.054 and 0.243 for H_2, CO, CO_2, and CH_4 respectively. The deviation is due the assumption used in the model; tar was not produced in the gasification process and all the gaseous components are not present in the gas phase of the reactor once the steam gasification simulation started.

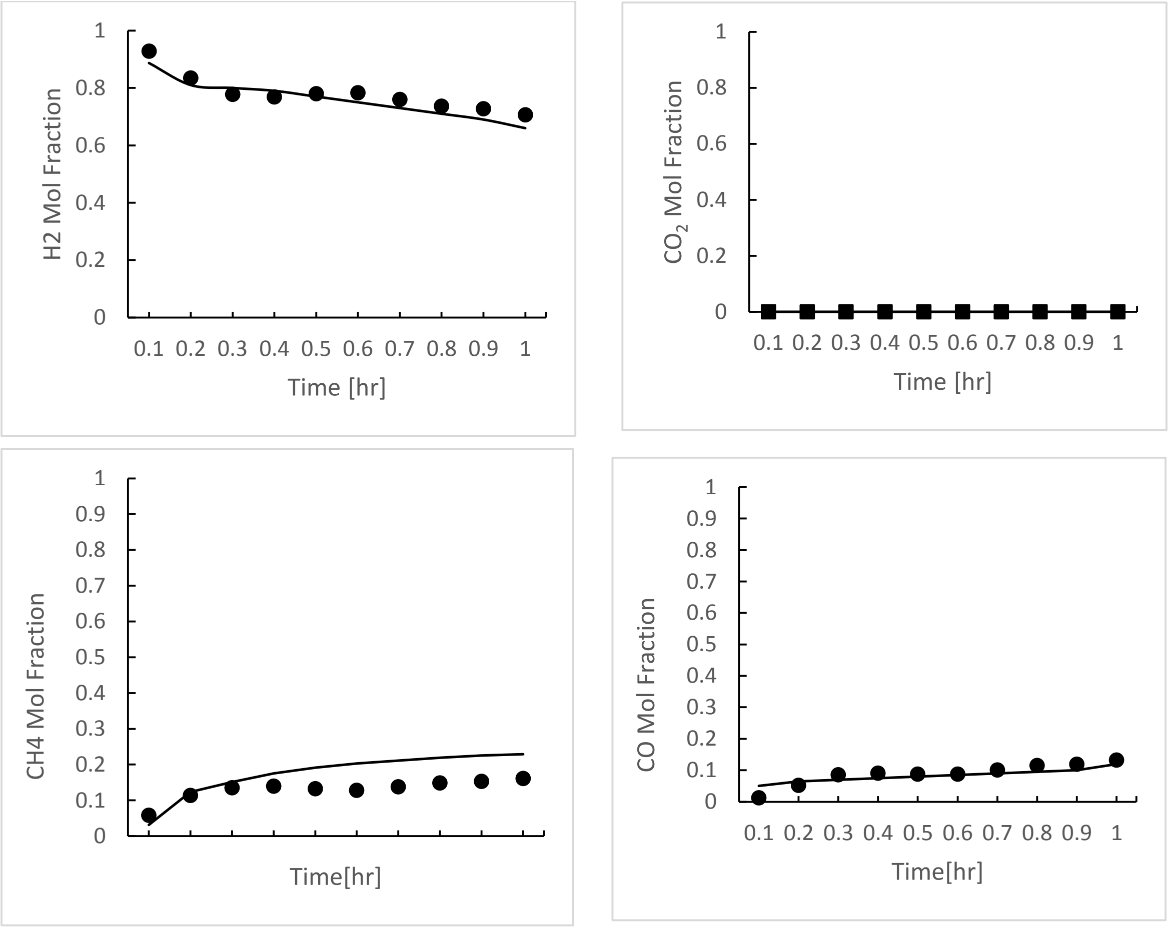


Figure 4.6: Model validation with effect of temperature at 873K on product gas composition. Modelling (—). Experiment (●).

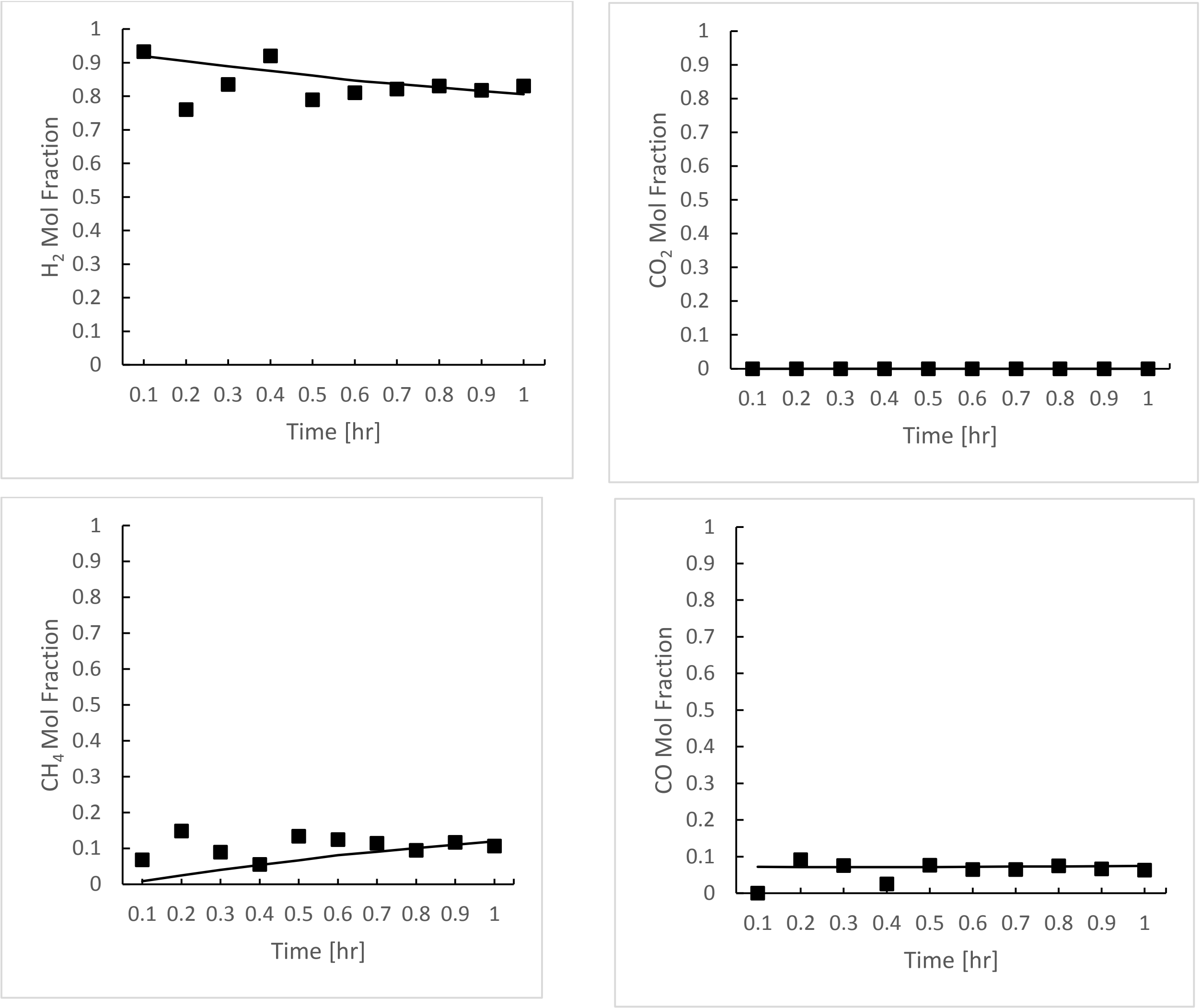
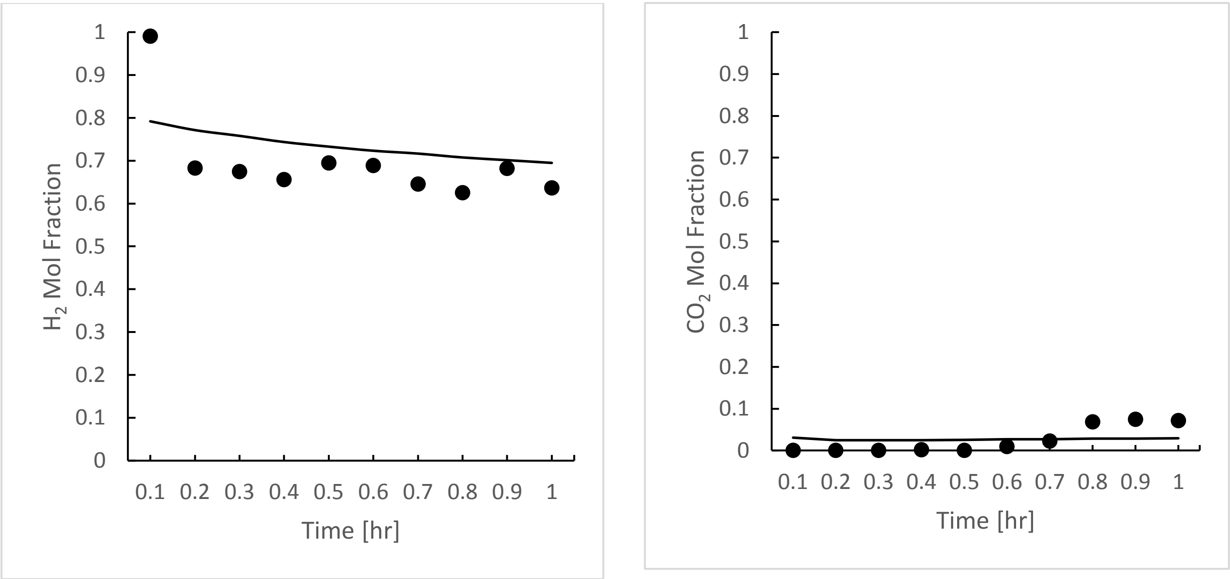


Figure 4.7: Model validation with effect of temperature at 948K on product gas composition Modelling (—). Experiment (■).



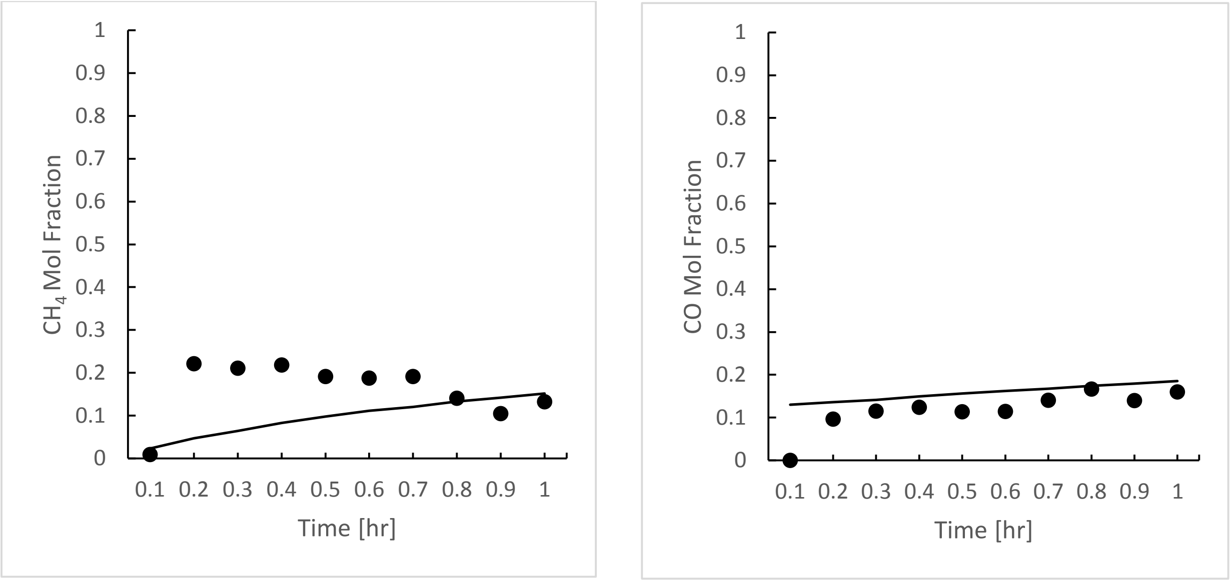


Figure 4.8: Model validation with effect of temperature at 1023K on product gas composition. Modelling (—). Experiment (●).

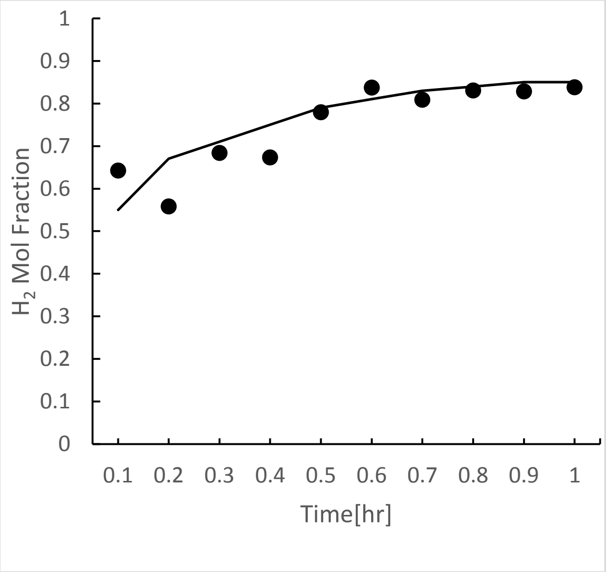
The mean error of product gas composition between model prediction and experimental results at gasifier temperature are 1023K are 0.118, 0.191, 0.123 and 0.241 for H_2, CO, CO_2, and CH_4 respectively. Overall, the model is linearize the dynamic of gas components on both temperature very well. At a simulation conducted at 873K, H_2 gas was produced in the range of maximum value of 0.932 and reduces gradually to 0.830 while the model prediction is 0.920 to 0.826. H_2 gas is produced largely within the first 6 minutes due to the high rate of production resulted from char gasification, Boudouard, methane reforming and water gas shift reaction. Similar trend of H_2 also reported in the simulation conducted at 948K and 1023 K where the model linearize the experimental data from a maximum value of 0.792 to 0.695 in 1023K simulation.

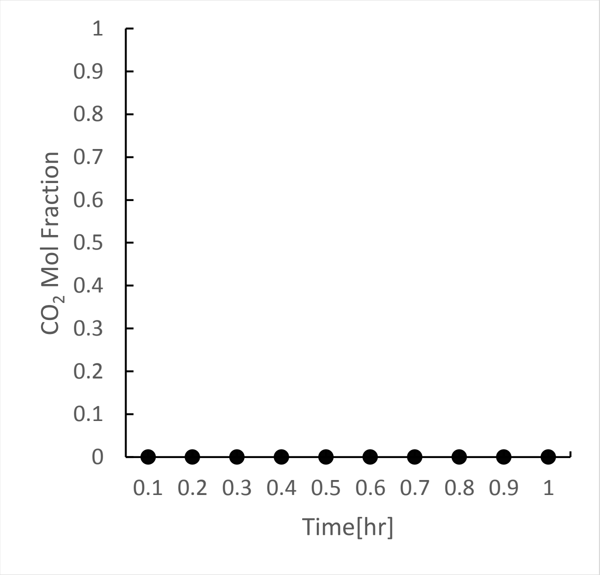
Across the simulation time of an hour, the CO_2 shows no presence in the gasifier at 873K and 948K due to the effectiveness of CaO to adsorp CO_2 gas to form $CaCO_3$. The adsorption of CO_2 is presented in the model by the carbonation reaction. At a higher temperature of 1023K, there is small amount of CO_2 present in the gasifier at a fraction range of 0.031 to 0.030. This trend can be explain by the higher rate of production of CO in Boudouard reaction which affects the water gas shift reaction. Higher CO concentration promotes higher production CO_2 in the water gas shift reaction, exceeding the adsorption rate of CO_2 by CaO through the carbonation reaction.

For CH_4 gas, the model estimates fraction of this component from gas product at a range of 0.008 to final value of 0.112 across an hour simulation time at a gasifier temperature of 948K. CH_4 is produced in the gasifier resulted from the reaction of H_2 and PKS char through the methanation reaction. This reaction is promoted by nickel as the catalyst. The produced CH_4 is consumed in the methane reforming reaction, to form CO_2 and H_2. Despite the CH_4 consumption, the methanation reaction is more favourable at higher temperature, leaving more unreacted CH_4 in the gas product. This trend can be shown in Figure 4.5 where more CH_4 gas produced with a maximum value of 0.153 in the simulation conducted at 1023K compared to the one reported in 948K.

4.3.3 Model Validation Based on the Effect of Steam/Biomass Ratio

The compositions profile for each components in the product gas with respect to different value of steam/biomass ratio at 948K ranging from 1.5 to 2.5 are shown in Figure 4.9, 4.10 and 4.11. The simulation was conducted at constant temperature of 948K, sorbent/biomass of 1.0, pressure of 1 atm with a feed flow rate of 500g/hr. The simulation was conducted for a period of an hour, similar to the experimental works. The mean error of product gas composition between model prediction and experimental results at steam biomass ratio of 1.5 are 0.054, 0.145, 0.064 and 0.165 for H_2, CO, CO_2, and CH_4 respectively.





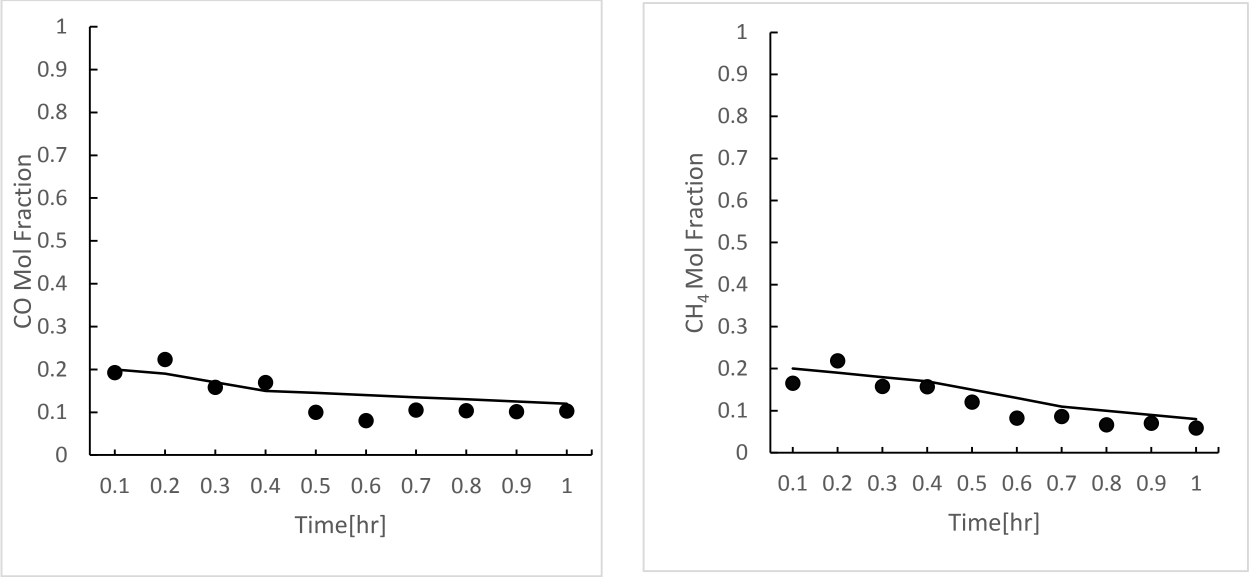


Figure 4.9: Effect of steam/biomass ratio of 1.5 on gas product composition (T=948K, Sorbent/biomass ratio = 1.0). Modelling (—). Experiment (●).

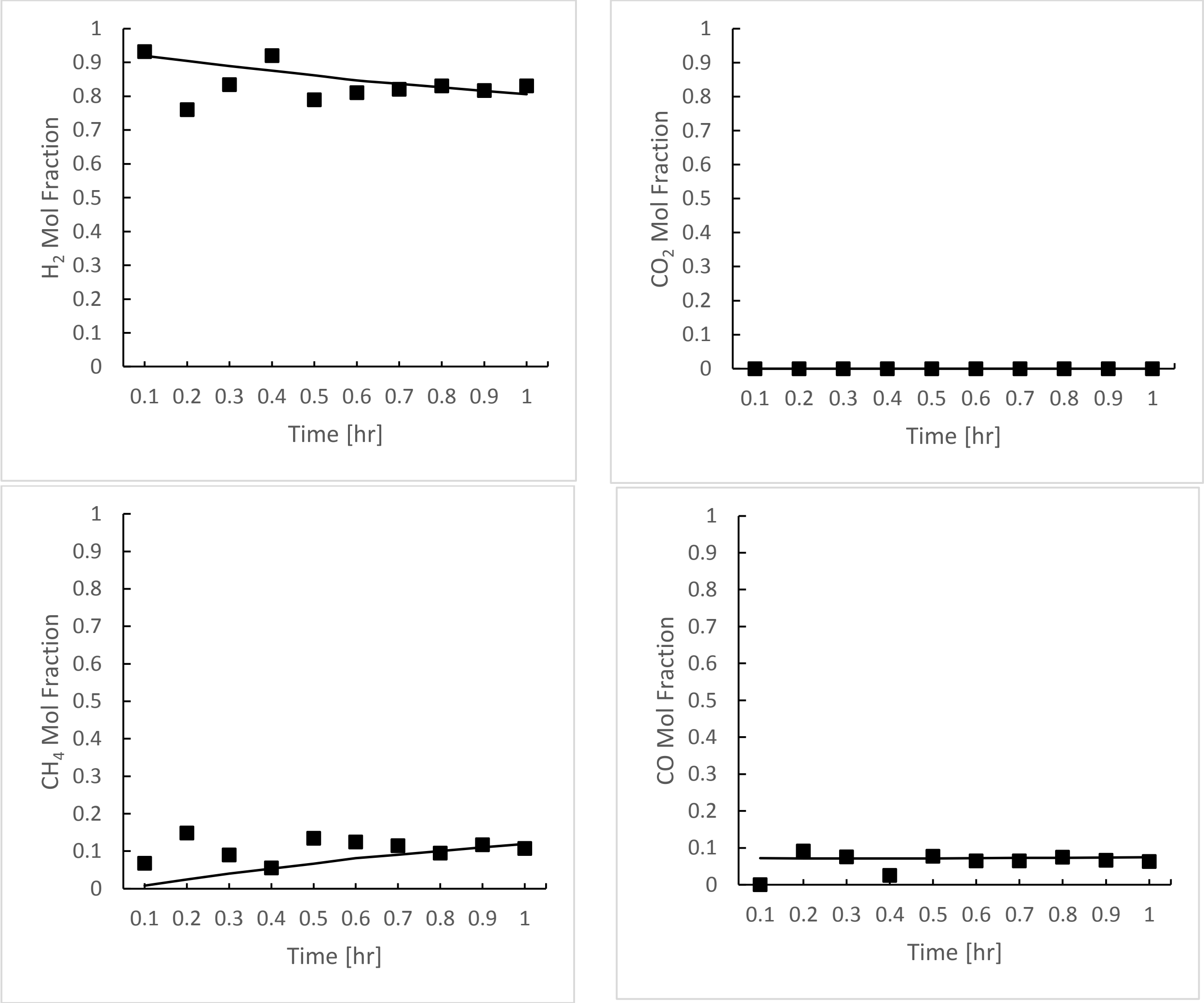


Figure 4.10: Effect of steam/biomass ratio of 2.0 on gas product composition (T = 948K, as Sorbent/biomass ratio = 1.0). Modelling (—). Experiment (■).

As shown by Figure 4.10, the model predicts well the composition of gas components in the simulation utilizing steam/biomass ratio of 2.0. The mean error of product gas composition between model prediction and experimental results at steam biomass ratio of 2.0 are 0.093, 0.052, 0.041 and 0.151 for H_2, CO, CO_2, and CH_4 respectively.

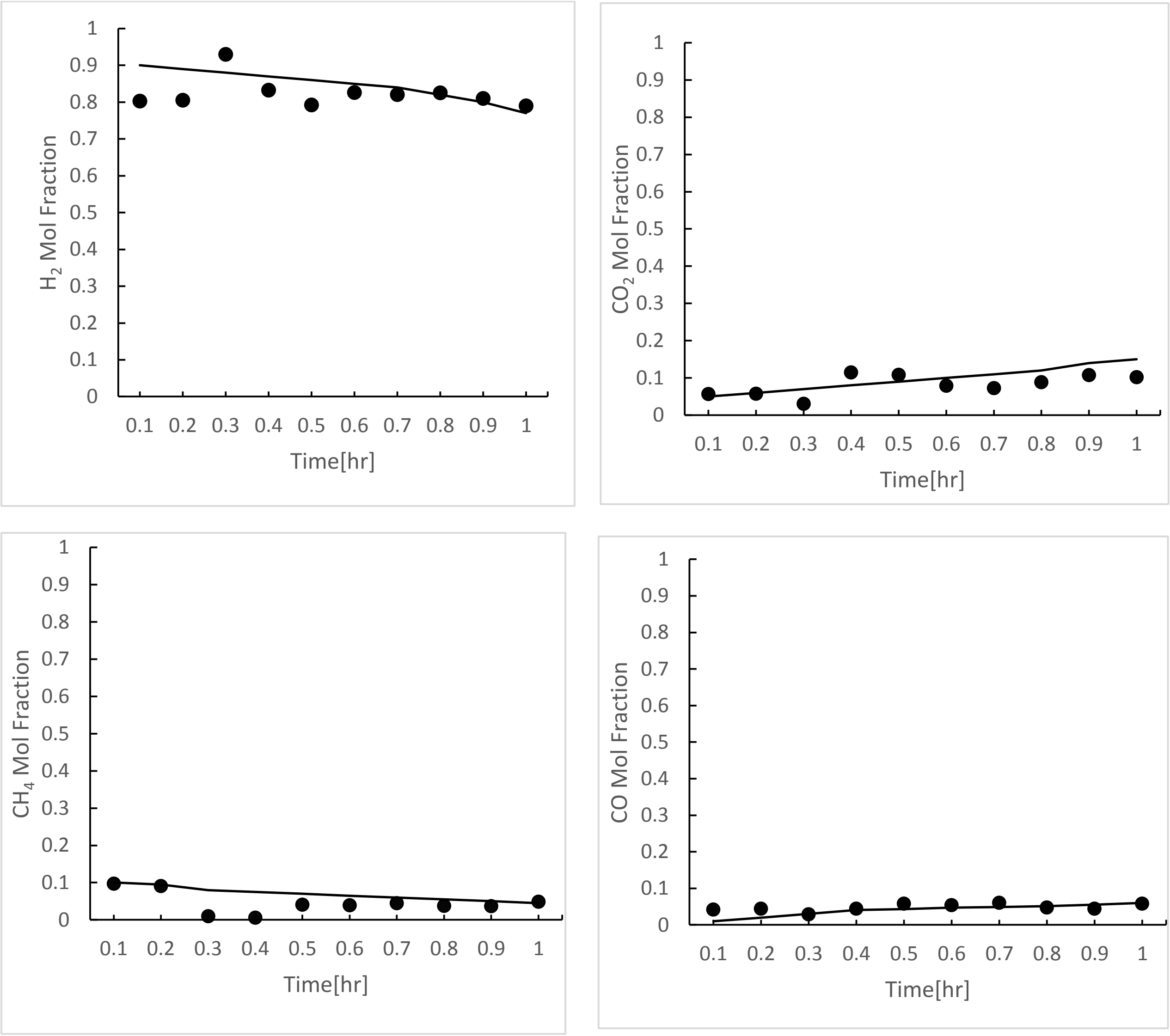


Figure 4.11: Effect of steam/biomass ratio of 2.5 on gas product composition (T = 948K, as Sorbent/biomass ratio = 1.0). Modelling (—). Experiment (■).

As shown by Figure 4.11, the model predicts well the composition of gas components in the simulation utilizing steam/biomass ratio of 2.5. The mean error of product gas composition between model prediction and experimental results at steam biomass ratio of 2.5 are 0.112, 0.072, 0.1613 and 0.149 for H_2, CO, CO_2, and CH_4 respectively. Overall from the kinetic results, the model perfectly linearize the experimental data for all gas components. At the simulation conducted at steam/biomass ratio of 1.5, H_2 gas increases gradually across the simulation time. This is due to the active conversion of PKS char to be converted to H2 gas through char gasification reaction. Longer experimental duration allowing more unconverted char to react to form gas products. Despite the experimental work and model simulation were conducted at different value of steam/biomass ratio, the dynamic of gas components across an hour period are not fluctuated much and show consistent readings.

To have a better view on the dynamic of gas components, the equilibrium values of components is plotted against the steam/biomass ratio. Figure 4.12 shows the behavior of gas components tested with different value of steam/biomass ratio.

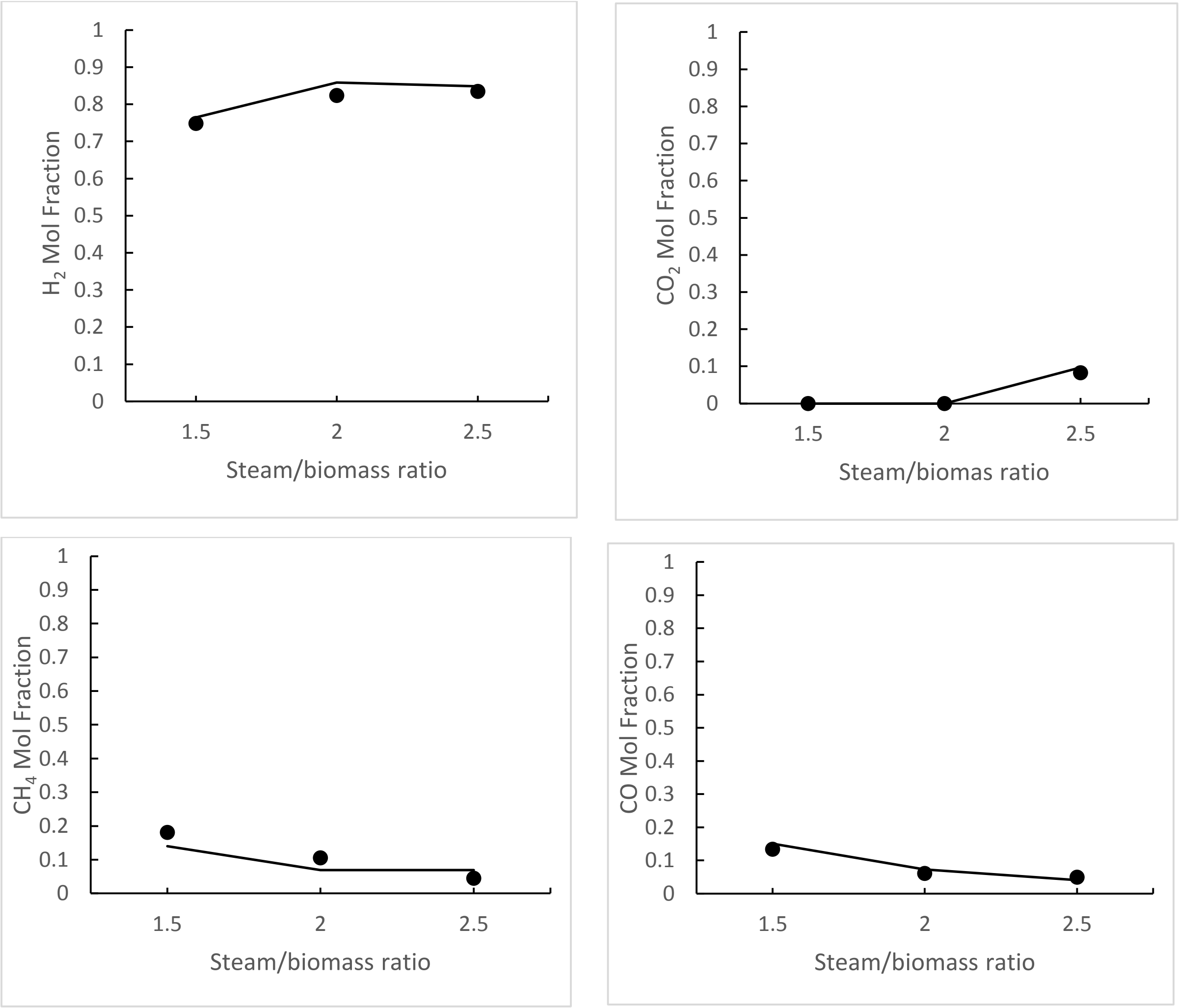


Figure 4.12 : Effect of steam/biomass ratio on product composition Modelling (—). Experiment (●).

H_2 gas production increases with the increase of steam/biomass ratio. The reason behind this is more steam is available to be reacted with PKS char and CH_4 gas to yield more H_2 gas in the char gasification and methanation reaction. Therefore, increase of steam/biomass ratio will increase the purity of H_2 gas. CO_2 gas meanwhile showing an increasing pattern with the increase of steam/biomass ratio. CO_2 gas is fully adsorbed by CaO in the steam/biomass ratio of 1.5 and 2.0 but present in the simulation conducted at 2.5 steam/biomass ratio. This is due to the higher rate of water gas shift reaction than the carbonation reaction, leaving some amount of unreacted CO_2. The rate of water gas shift reaction is more favourable with excess steam, allowing complete reaction of CO in the gasifier to be reacted to form CO_2 and H_2 gas.

For the dynamic of CH_4 gas with the increase rate of steam, CH_4 gas decreases gradually. This decreasing trend of CH_4 gas is due to the presence of excess steam in the gasifier, allowing complete reaction for the reaction between steam and CH_4 gas in the methane reforming reaction. Since CH_4 gas is the reactant in that reaction, this leads to the decrease of mol fraction of CH_4 from the product gas.

Based on the simulation on PKS steam gasification coupled with CO_2 capture, the hydrogen yield shows the highest amount of 84.5 % mol at the simulation conducted at 948 K. Only 77 % mol of hydrogen produced at the gasifier temperarature of 1023K due to deactivation of catalyst. The deactivation of catalyst reduces the rate of methane reforming reaction, significantly reduces the rate of hydrogen production. The best operating conditions for PKS steam gasification is at 948K, steam/biomass ratio of 2.5 and sorbent/biomass ratio of 1.0.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A first order reaction kinetic model has been developed for the prediction of the product gas composition from catalytic steam gasification of biomass coupled with CO_2 capture by CaO and was validated with the experimental data and other relevant literature [1,6]. From the model simulation, the hydrogen concentration increases with increasing gasifier temperature. Similar trends also reported in other literatures [1,6,12,13]. The model shows almost similar results for the hydrogen composition gained from experimental data. At steam/biomass ratio of 2.0, sorbent/biomass ratio ratio of 1.0, the hydrogen composition is 81.3 mol. % in EFB steam gasification coupled with CO_2 capture. The model also tested at different value of steam/biomass ratio and it shows an increasing amount of hydrogen production. The model also shows higher amount of gas composition H_2 in the simulation coupled with CO_2 capture than the simulation without CO_2 sorbent.

For PKS steam gasification, the hydrogen yield shows the highest amount of 84.5 % mol at the simulation conducted at 948 K. Only 77 % vol. of hydrogen produced at the gasifier temperarature of 1023K due to deactivation of catalyst. The deactivation of catalyst reduces the rate of methane reforming reaction, significantly reduces the rate of hydrogen production. The optimum operating conditions for PKS steam gasification is at 948K, steam/biomass ratio of 2.5 and sorbent/biomass ratio of 1.0.

5.2 Recommendations

It is recommended that the model includes the hydrodynamic calculations to investigate the effects of particle size, fluidization velocity, bed height, biomass flowrate, amount of catalyst on the gasification performance.

The integrated catalytic adsorptive steam gasification study can be extended to tar production under the influence of process variables i.e. temperature, steam/biomass ratio, and biomass type.

REFERENCES

[1] Inayat, A., Ahmad, M.M., Mutalib, M.I., and Yusup, S., (2011) "Process modeling for parametric study on oil palm empty fruit bunch steam gasification for hydrogen production" *Fuel Processing Technology,* 26-34.

[2] M.S. Umikalsom, A.B. Ariff, H.S. Zulkifili, C.C. Tong, M.A. Hassan, and M.I.A. Karim, "The treatment of oil palm empty fruit bunch fibre for subsequent use as sorbent for cellulose production by Chaetomium globasum Kunze," Biosource Technology, 62, 1-9, (1997)

[3] H. Yang, R. Yan, H. Chen, D. H. Lee, D. T. Liang, and C. Zheng, "Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases," Fuel Processing Technology, 87, 935-942, (2006)

[4] T. Y. Ahmed, M. M. Ahmad, S. Yusup, " Equilibrium model for steam gasification of palm kernel shell for hydrogen production" IEEE, (2011)

[5] A.A. Jaafar, M.M. Ahmad, "Torrefaction of malaysia palm kernel shell into value-added solid fuels," World Academy of Science, 60, (2011)

[6] Inayat, A., Ahmad, M.M., Yusup, S., and Mutalib, M.I., (2010) "Biomass steam gasification with in-situ CO_2 capture for enriched hydrogen gas production: A reaction kinetics modeling approach" *Energies,* 3, 1472-1484.

[7] J. Corella, and A. Sanz, "Modeling circulating fluidized bed biomass gasifiers. A pseudo-rigorous model for stationary state," Fuel Process. Tehnol, 86, 1023-1053, (2005)

[8] Zhang, Y., Jun, X., and Shen, L., (2009) "Simulation of methanol production from biomass gasification in interconnected fluidized bed" *Ind. Eng. Chem. Res*, 48, 5351-5359.

[9] B. Gobel, U. Henriksen, T. K. Jensen, B. Qvale, and N. Houbak, "The development of a computer model for a fixed bed gasifier and its use for optimization and control," Bioresource Tecnology, 98, 2043-2052, (2007)

[10] K. Laohalindanond, J. Heil, and C. Wirten, " The production of synthetic diesel from biomass," KTIML Sci. Tech. J., 6, 35-45, (2006)

[11] M.B. Nikoo, and N. Mahinpey, “Simulation of hydrogen production from biomass gasification in fluidized bed reactor using ASPEN PLUS,” Biomass Bioenergy, 32, 1245-1254, (2008)

[12] G. Schuster, G. Loffer, K. Weighl, H. Hofbauer, “Biomass steam gasification- an extensive parametric modelling study,” Biosource Tehnology, 77, 71-79, (2001)

[13] M. P. Arnavat, J. C. Bruno, A. Coronas, “Review and analysis of biomass gasification models, Renewable & Sustainable Energy Reviews , 14, 2841-2851, (2010)

[14] Acharya, B., Dutta, A., and Basu, P., (2010) “An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO” *International Journal of Hydrogen Energy,* 35(1), 1582-1589.

[15] Florin, N.H., and Harris, A.T., (2007) “Hydrogen production from biomass coupled with carbon dioxide capture: The implications of thermodynamic equilibrium” *International Journal of Hydrogen Energy,* 32, 4119-4134.

[16] A. Mountoris, E. Voutsas, and D. Tassios, “Solid waste plasma gasification: Equilibrium model development and exergy analysis” Energy Conversion and Management, 47, 1723-1737, (2006)

[17] Fujimoto, S., Yoshida, T., Hanaoka, T., Matsumura, Y., Lin, S.Y., Minowa, T., and Sasaki, Y., (2007) “A kinetic study of in situ CO_2 removal gasification of woody biomass for hydrogen production” *Biomass and Bioenergy,* 556-562.

[18] F. L.P. Resende, and P.E. Savage, “Kinetic model for noncatalytic supercritical water gasification of cellulose and lignin,” AIChE, 56, 2412-2420, (2010)

[19] H.S. Fogler, “Elements of chemical reaction engineering,” Prentice Hall, 2nd Edition, (1992).

[20] O. Levenspiel, “Chemical Reaction Engineering”, 3rd Edition, (1990)

[21] D. K. Lee, I.H. Baek, and W.L. Yoon, “Modeling and simulation for the methane steam reforming enhanced by in situ CO_2 removal utilizing the CaO carbonation for H_2 production,” Chemical Engineering Science, 59, 931-942, (2004)

[22] V. Kumar, and P. Balasubramanian, “Kinetic parameter estimation in hydrocracking using hybrid particle swarm optimization,” Fuel, 88, 2171-2180, (2009)

[23] J.M. Smith, H.C. Ness, and M.M. Abbott, “Introduction to Chemical Engineering Thermodynamics,” Mc. Graw Hill, (2005)

[24] F. Shafizadih, and P.P.S. Chin, “Thermal deterioration of wood,” ACS Symposium Series, 43, 57-81, (1977)

[25] L. Pengmei, T. Wang, Y. Fun, and Y. Chen, “Hydrogen-rich gas production from biomass catalytic gasification,” Energy & Fuels, 18, 228-233, (2004)

[26] P. Weerachanchai, M. Horio, and C. Tangsathitkulchai, “Effects of gasifying conditions and bed materials on fluidized bed steam gasification of wood biomass,” Biosource Technology, 100, 1419-1427, (2009)

[27] K. Umeki, K. Yamamotom, T. Namioka, and K. Yoshikawa, “High temperature steam-only gasification of woody biomass,” Applied Energy, 87, 791-798, (2010)

[28] Lasa, H., Salaices, E., Mazumder, J., and Lucky, R., (2011) “Catalytic steam gasification of biomass: Catalysts, thermodynamics and kinetics” *Chem. Rev.*, 111, 5404-5433.

[29] Hussain, A., Ani, F.N., Darus, A.N., Mokhtar, H., Azam, S., and Mustafa, A., (2006) “Thermochemical behavior of empty fruit bunches and oil palm shell waste in a circulating fluidized-bed combustor (CFBC)” *Journal of Oil Palm Research*, 60(1), 210-218.

[30] Basu, P., Biomass gasification and pyrolysis. Practical design and theory. UK : Elsevier, 2010, Imprint

[31] L.Han, Q. Wang, Y. Yang, C.Yu, M. Fang, and Z.Luo., (2011) “Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed,” International Journal of Hdyrogen Energy, 36, 4820-4829,

[32] M.R. Mahishi, and D.Y. Goswami, “An experimental study of hydrogen production by gasification of biomass in the presence of CO_2 sorbent,” Int. J. Hydrogen Energy, 32, 2803-2808, (2007)

[33] Kinoshita, C.M., Turn, S.Q. (2003)“ Production of hydrogen from bio-oil using CaO as CO_2 sorbent”. *Int. J. Hydrogen Energy*, 28, 1065-1071

[34] L.Han, Q. Wang, Y. Yang, C.Yu, M. Fang, and Z.Luo., (2011) “Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed,” International Journal of Hdyrogen Energy, 36, 4820-4829,

[35] Hirschkind, W., (1925) “Manufacture of hydrochloric acid from chlorine” *Ind. Eng. Chem*, 17(10), 1071-1073.

APPENDIX

1.1 Mass balance equations of EFB

The mass balance equation is develop using the equation below:

$$\begin{pmatrix} rate\ of\ mass \\ accumulation \end{pmatrix} = \begin{pmatrix} mass \\ flux\ in \end{pmatrix} - \begin{pmatrix} mass \\ flux\ out \end{pmatrix} + \begin{pmatrix} net\ rate\ of \\ chemical\ production \end{pmatrix}$$

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{reaction}$$

In this system, the mass balance equation is presented generally as,

$$\begin{pmatrix} rate\ of\ biomass \\ fed \end{pmatrix} + \begin{pmatrix} rate\ of\ mass\ of \\ steam\ fed \end{pmatrix} + \begin{pmatrix} rate\ of \\ CaO\ fed \end{pmatrix} = \begin{pmatrix} rate\ of\ mass\ of \\ product\ gas \\ leaving\ the\ gasifier \end{pmatrix}$$

$$\dot{m}_{C_{3.4}H_{4.1}O_{3.3}}{}^{s} + \dot{m}_{H_2O}{}^{g} + \dot{m}_{CaO}{}^{s} = \dot{m}_{H_2}{}^{g} + \dot{m}_{CO}{}^{g} + \dot{m}_{CO_2}{}^{g} + \dot{m}_{CH_4}{}^{g} + \dot{m}_{CaCO_3}{}^{s}$$

1.1.1 Mass balance equation of char ($C_{3.4}H_{4.1}O_{3.3}$)

Unit concentration = mol/m^3

$\dot{m}$ = *mol/hr*

m = mol

k =1/mol.hr

V = m^3

$C_{3.4}H_{4.1}O_{3.3} + 0.1\,H_2O \xrightarrow{k_1} 2.15\,H_2 + 3.4\,CO$

$C_{3.4}H_{4.1}O_{3.3} + 8.05\,H_2 \xrightarrow{k_2} 3.4\,CH_4 + 3.3\,H_2O$

$C_{3.4}H_{4.1}O_{3.3} + CO_2 \xrightarrow{k_3} 4.4\,CO + 0.9\,H_2O + 1.15\,H_2$

$$\frac{dC_{C_{3.4}H_{4.1}O_{3.3}}V^s}{dt} = -r_1V - r_2V - r_3V$$

$$\frac{dC_{C_{3.4}H_{4.1}O_{3.3}}V^s}{dt} = -\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}\mathrm{V} - \mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}\mathrm{V} - \mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\,\mathrm{V}$$

$$\frac{dC_{C_{3.4}H_{4.1}O_{3.3}}V^s}{dt} = -\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}\mathrm{V} - \mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}\mathrm{V} - \mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ \mathrm{V}$$

Assuming the reaction take place in the constant volume reactor,

$$\frac{dm_{C_{3.4}H_{4.1}O_{3.3}}}{dt} = \frac{d}{dt}C_{C_{3.4}H_{4.1}O_{3.3}}V = \frac{dC_{C_{3.4}H_{4.1}O_{3.3}}}{dt}V + \frac{dV}{dt}C_{C_{3.4}H_{4.1}O_{3.3}}$$

$$\frac{dV}{dt} = 0$$

$$\frac{dm_{C_{3.4}H_{4.1}O_{3.3}}}{dt} = -\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}\mathrm{V} - \mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}\mathrm{V} - \mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ \mathrm{V}$$

For a continuous batch reactor, the inclusion of dry biomass feed, $\dot{m}_{C_{3.4}H_{4.1}O_{3.3,in}}$ is needed. Therefore, the mass balance equation for char is as the following,

$$\frac{dm_{C_{3.4}H_{4.1}O_{3.3}}}{dt} = \dot{m}_{C_{3.4}H_{4.1}O_{3.3,in}} - \mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}\mathrm{V} - \mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}\mathrm{V} - \mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ \mathrm{V}$$

1.1.2 Mass balance of steam ($\mathbf{H_2O}$)

$$C_{3.4}H_{4.1}O_{3.3} + 0.1\,H_2O \overset{\mathrm{k}_1}{\rightarrow} 2.15\,H_2 + 3.4\,CO$$

$$C_{3.4}H_{4.1}O_{3.3} + 8.05\,H_2 \overset{\mathrm{k}_2}{\rightarrow} 3.4\,CH_4 + 3.3\,H_2O$$

$$C_{3.4}H_{4.1}O_{3.3} + CO_2 \overset{\mathrm{k}_3}{\rightarrow} 4.4\,CO + 0.9\,H_2O + 1.15\,H_2$$

$$CH_4 + H_2O \overset{\mathrm{k}_4}{\rightarrow} CO + 3\,H_2$$

$$CO + H_2O \overset{\mathrm{k}_5}{\leftrightarrow} CO_2 + H_2$$

$$\frac{dC_{H_2O}V^g}{dt} = -0.1\,r_1V + 3.3\,r_2V + 0.9\,r_3V - r_4V + r_5V$$

$$\frac{dC_{H_2O}V^g}{dt} = -0.1\left(\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) + 3.3\left(\mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) + 0.9\left(\mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ V\right) - \left(\mathrm{k}_4\mathrm{C}_{CH_4}\,\mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k}_5\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

Assuming the rate of volume changes is zero, thus,

$$\frac{dm_{H_2O}}{dt} = -0.1\left(\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) + 3.3\left(\mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) + 0.9\left(\mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\,V\right) - \left(\mathrm{k}_4\mathrm{C}_{CH_4}\,\mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k}_5\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

For a continuous batch reactor, the inclusion of dry biomass feed, $\dot{m}_{H_2O,in}$ is needed. Therefore, the mass balance equation for steam is as the following,

$$\frac{dm_{H_2O}}{dt} = \dot{m}_{H_2O,in} - 0.1\left(\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) + 3.3\left(\mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) + 0.9\left(\mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\,V\right) - \left(\mathrm{k}_4\mathrm{C}_{CH_4}\,\mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k}_5\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

1.1.3 Mass balance of hydrogen gas ($\mathbf{H_2}$)

$$C_{3.4}H_{4.1}O_{3.3} + 0.1\,H_2O \overset{\mathrm{k}_1}{\rightarrow} 2.15\,H_2 + 3.4\,CO$$

$$C_{3.4}H_{4.1}O_{3.3} + 8.05\,H_2 \overset{\mathrm{k}_2}{\rightarrow} 3.4\,CH_4 + 3.3\,H_2O$$

$$C_{3.4}H_{4.1}O_{3.3} + CO_2 \overset{\mathrm{k}_3}{\rightarrow} 4.4\,CO + 0.9\,H_2O + 1.15\,H_2$$

$$CH_4 + H_2O \overset{\mathrm{k}_4}{\rightarrow} CO + 3\,H_2$$

$$CO + H_2O \overset{\mathrm{k}_5}{\leftrightarrow} CO_2 + H_2$$

$$\frac{dC_{H_2}V^g}{dt} = 2.15\,r_1V - 8.05\,r_2V + 1.15\,r_3V + 3\,r_4V + r_5V$$

$$\frac{dC_{H_2}V^g}{dt} = 2.15\left(\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) - 8.05\left(\mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) + 1.15\left(\mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\,V\right) + 3\left(\mathrm{k}_4\mathrm{C}_{CH_4}\,\mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k}_5\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

$$\frac{dm_{H_2}}{dt} = 2.15\left(\mathrm{k}_1\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) - 8.05\left(\mathrm{k}_2\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) + 1.15\left(\mathrm{k}_3\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\,V\right) + 3\left(\mathrm{k}_4\mathrm{C}_{CH_4}\,\mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k}_5\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

1.1.4 Mass balance of carbon monoxide gas (CO)

$$C_{3.4}H_{4.1}O_{3.3} + \ 0.1\, H_2O \overset{\mathrm{k_1}}{\rightarrow} 2.15\, H_2 + \ 3.4\, CO$$

$$C_{3.4}H_{4.1}O_{3.3} + \ CO_2 \overset{\mathrm{k_3}}{\rightarrow} 4.4\, CO + \ 0.9\, H_2O + \ 1.15\, H_2$$

$$CH_4 + \ H_2O \overset{\mathrm{k_4}}{\rightarrow} CO + \ 3\, H_2$$

$$CO + H_2O \overset{\mathrm{k_5}}{\leftrightarrow} CO_2 + \ H_2$$

$$\frac{dC_{CO}V^g}{dt} = 3.4\, r_1V + 4.4\, r_3V + r_4V + r_5V$$

$$\frac{dC_{CO}V^g}{dt} = 3.4\left(\mathrm{k_1}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) + 4.4\left(\mathrm{k_3}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ V\right) + \ \left(\mathrm{k_4}\mathrm{C}_{CH_4}\ \mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k_5}\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

$$\frac{dm_{CO}{}^g}{dt} = 3.4\left(\mathrm{k_1}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2O}V\right) + 4.4\left(\mathrm{k_3}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ V\right) + \ \left(\mathrm{k_4}\mathrm{C}_{CH_4}\ \mathrm{C}_{H_2O}V\right) + \left(-\mathrm{k_5}\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V$$

1.1.5 Mass balance of carbon dioxide (CO_2)

$$C_{3.4}H_{4.1}O_{3.3} + \ CO_2 \overset{\mathrm{k_3}}{\rightarrow} 4.4\, CO + \ 0.9\, H_2O + \ 1.15\, H_2$$

$$CO + H_2O \overset{\mathrm{k_5}}{\leftrightarrow} CO_2 + \ H_2$$

$$CO_2 + CaO \overset{\mathrm{k_6}}{\rightarrow} CaCO_3$$

$$\frac{dC_{CO_2}\ V^g}{dt} = -\ r_3V + r_5V - r_6V$$

$$\frac{dm_{CO_2}{}^g}{dt} = -\ r_3V + r_5V - r_6V$$

$$\frac{dm_{CO_2}{}^g}{dt} = -\left(\mathrm{k_3}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{CO_2}\ V\right) + \left(-\mathrm{k_5}\mathrm{C}_{CO}\mathrm{C}_{H_2O} + \frac{\mathrm{C}_{CO_2}\mathrm{C}_{H_2}}{\mathrm{K_w}}\right)V - \left(k_6\mathrm{C}_{CO_2}\mathrm{C}_{CaO}\right)$$

1.1.6 Mass balance of methane gas ($\mathrm{CH_4}$)

$$C_{3.4}H_{4.1}O_{3.3} + \ 8.05\, H_2 \overset{\mathrm{k_2}}{\rightarrow} 3.4\, CH_4 + \ 3.3\, H_2O$$

$$CH_4 + \ H_2O \overset{\mathrm{k_4}}{\rightarrow} CO + \ 3\, H_2$$

$$\frac{dC_{\mathrm{CH_4}}V^g}{dt} = 3.4\, r_2V + r_4V$$

$$\frac{dm_{\mathrm{CH_4}}{}^g}{dt} = 3.4\, r_2V - \ r_4V$$

$$\frac{dm_{\mathrm{CH_4}}{}^g}{dt} = 3.4\left(\mathrm{k_2}\mathrm{C}_{C_{3.4}H_{4.1}O_{3.3}}\mathrm{C}_{H_2}V\right) - \left(\mathrm{k_4}\mathrm{C}_{CH_4}\ \mathrm{C}_{H_2O}V\right)$$

1.1.7 Mass balance of calcium carbonate ($\mathrm{CaCO_3}$)

$$CO_2 + CaO \overset{\mathrm{k_6}}{\rightarrow} CaCO_3$$

$$\frac{dm_{\mathrm{CaCO_3}}{}^{g}}{dt} = r_6 V$$

$$\frac{dm_{\mathrm{CaCO_3}}{}^{s}}{dt} = \left(k_6 \mathrm{C}_{CO_2} \mathrm{C}_{CaO}\right) V$$

1.2 Energy balance equations

$$\dot{m}_{gas} c_{p,g} \frac{dT_R}{dt} = \dot{m}_{C_{3.4}H_{4.1}O_{3.3}} c_{p,C_{3.4}H_{4.1}O_{3.3}} T_{in,C_{3.4}H_{4.1}O_{3.3}} + \dot{m}_{H_2O} c_{p,H_2O} T_{in,H_2O} + r\Delta H_{rxn} + \dot{Q}_{supplied} + \dot{m}_{gas} c_{p,g} T_{out}$$

$$\frac{dT_R}{dt} = \frac{\dot{m}_{C_{3.4}H_{4.1}O_{3.3}} c_{p,C_{3.4}H_{4.1}O_{3.3}} T_{in,C_{3.4}H_{4.1}O_{3.3}} + \dot{m}_{H_2O} c_{p,H_2O} T_{in,H_2O} + rV\Delta H_{rxn} + \dot{Q}_{supplied} + \dot{m}_{gas} c_{p,g} T_{out}}{\dot{m}_{gas} c_{p,g}}$$

1.2.1 For a batch reactor, the energy balance applied is,

$$\dot{m}_{gas} c_{p,g} \frac{dT_R}{dt} = r\Delta H_{rxn} + \dot{Q}_{supplied}$$

$$\frac{dT_R}{dt} = \frac{rV\Delta H_{rxn} + \dot{Q}_{supplied}}{\dot{m}_{gas} c_{p,g}}$$