SIMULATION OF AUTOTHERMAL REFORMER FOR PRODUCTION OF LIQUID FUEL FROM NATURAL GAS

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SIMULATION OF AUTOTHERMAL REFORMER FOR PRODUCTION OF LIQUID FUEL FROM NATURAL GAS

by

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LIST OF SYMBOLS

T_{ATR}	Reactor temperature
P_{ATR}	Reactor Pressure
$\dot{n}_{steam,inlet}$	Feed steam molar flowrate
$\dot{n}_{oxygen,inlet}$	Feed oxygen molar flowrate

LIST OF ABBREVIATIONS

ATR	Autothermal reforming
BOTP	Bottom product stream for ATR reactor model
GTL	Gas-to-liquid process
H_2/CO	Syngas ratio
INLET	Inlet stream for ATR reactor model
OXYGEN	Inlet oxygen stream for ATR reactor model
Peng-Rob	Peng-Robinson property method
REQUIL	Equilibrium reactor model
Syngas	Synthetic gas
TOPP	Top product stream for ATR reactor model

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SIMULASI REFORMASI AUTOTERMA DALAM PENGHASILAN BAHAN BAKAR CECAIR DARI GAS ASLI

ABSTRAK

Penghasilan bahan bakar cecair dari gas asli mendapat perhatian di seluruh dunia. Di kilang, salah satu operasi unit yang digunakan adalah reaktor reformasi autoterma (ATR) yang berfungsi untuk menukar gas asli (metana) menjadi gas sintetik yang terdiri daripada hidrogen dan karbon monoksida. Operasi unit ini perlu dikaji sebelum pelaksanaannya dalam industri sebenar. Dalam kajian ini, model REQUIL dalam ASPEN Plus V10 digunakan untuk mensimulasikan ATR. Keputusan simulasi yang diperoleh dibandingkan dengan data simulasi dari literatur. Keputusan simulasi yang diperoleh oleh ASPEN Plus menunjukkan bahawa ia boleh diterima kerana nilai simulasi mematuhi literatur dengan rentang kesilapan antara 0.72% hingga 9.45%. Analisis sensitiviti pada model REQUIL ATR menunjukkan bahawa suhu reactor (800 K hingg 2000 K), tekanan reaktor (20 bar hingga 50 bar), kadar aliran molar wap suapan (200 kmol/jam hingga 3000 kmol/jam) dan kadar aliran molar oksigen suapan (500 kmol/jam hingga 3000 kmol/jam) mempunyai pengaruh yang signifikan terhadap penukaran metana dan nisbah gas sintetik. Penukaran metana didapati meningkat apabila suhu reaktor, kadar aliran molar wap suapan dan kadar aliran molar oksigen suapan meningkat. Sementara itu, ia menurun ketika tekanan reaktor meningkat. Lain-lain, nisbah gas sintetik didapati menurun ketika meningkatkan suhu reaktor, tekanan reaktor, kadar aliran molar wap suapan dan ia menurun ketika meningkatkan kadar aliran molar oksigen suapan.

SIMULATION AND OPTIMIZATION OF AUTOTHERMAL REFORMER FOR PRODUCTION OF LIQUID FUEL FROM NATURAL GAS

ABSTRACT

The production of liquid fuels from natural gas is gaining attention worldwide. In the plant, one of the unit operation used is autothermal reforming (ATR) reactor which serves to convert natural gas (methane) to syngas that consist of hydrogen and carbon monoxide. This unit operations need to be studied before its implementation in real industry. In this work, REQUIL model in ASPEN Plus V10 was used to simulate an autothermal reforming (ATR) reactor. The simulated results obtained were first compared with the simulation data from literature. The simulated results obtained by ASPEN Plus showed that it is acceptable since the simulation values corroborated the literature with errors range of 0.72% to 9.45%. Sensitivity analysis on the REQUIL ATR model showed that reactor temperature (800 K to 1300 K), reactor pressure (20 bar to 50 bar), feed steam molar flowrate (200 kmol/hr to 3000 kmol/hr) and feed oxygen molar flowrate (500 kmol/hr to 3000 kmol/hr) have significant effects on the conversion of methane and syngas ratio. The methane conversion was increases when the reactor temperature, feed steam molar flowrate and feed oxygen molar flowrate were increase. While, it was decreases when the reactor pressure was increase. The syngas ratio was decrease when increasing the reactor temperature, reactor pressure, feed steam molar flowrate and it was decreases when increasing the feed oxygen molar flowrate.

CHAPTER 1

INTRODUCTION

1.1 Natural Gas

Natural gas is a mixture of hydrocarbons, mainly methane which is the main component others than ethane, propane, butane and pentane. In addition, natural gas usually contains small or large amounts of non-hydrocarbon gasses such as carbon dioxide, nitrogen, hydrogen sulphide, and helium. Natural gas can be used with crude oil ("associated gas") or found in reservoirs where no oil exists ("non-associated gas"). Table 1.1 show the composition of methane and other components in natural gas that being used as feedstock for liquid fuel production plant (Mezni, 2017).

Natural gas as cleanest burning petroleum based fuel compared to oil and coil that can be as alternative energy in the future. Natural gas is commonly used across all sectors such as industrial, residential, electric generation, commercial and transportation sectors. It also has much lower environmental impact than others hydrocarbons fuels (Demirbas, 2006)., Converting natural gas into liquid phase can be more easily transported compared to natural gas in gas phase since it is difficult to transport in form of gas (Wood et al., 2012).

Table 1.1: The composition of components in natural gas (Mezni, 2017)

Name	Formula	Volume (%)
Methane	CH_4	>85
Ethane	C_2H_6	3 – 8
Propane	C_3H_8	1 – 2
Butane	C_4H_{10}	<1
Pentane	C_5H_{12}	<1
Carbon dioxide	CO_2	1 – 2
Hydrogen sulphide	H_6S	<1
Nitrogen	N_2	1 – 5
Helium	He	<0.5

Natural gas can be used to produce synthesis gas, a mixture of hydrogen and carbon monoxide as an intermediate step for production of liquid fuels using Fischer-Tropsch synthesis.

1.2 Types of Reformers in Production of Synthesis Gas

There are three types of reformers can be used for production of synthesis gas as an intermediate step for production of liquid fuels. The determination of specific reformers depends on the use of downstream (specifications of produces synthesis gas) and economic issues such as the availability of feedstock which is natural gas. Steam reformer, steam reforming for production of synthesis gas by involving the reaction of hydrocarbons (methane in natural gas) with water (steam) in the presence of catalyst. Partial oxidation reformer, partial oxidation occurs where a hydrocarbon (methane in natural gas) reacts with air (oxygen) is partially combusted in a reformer to produce synthesis gas without presence of catalyst. Catalytic partial oxidation (CPOX) is an attractive option to produce synthesis gas from natural gas because presence of catalyst. Autothermal reformer, autothermal reforming is the combination of partial oxidation and steam reforming for production of synthesis gas.

Commonly, in production of liquid fuel, the steam reformer is being used for production of synthesis gas. But, when using the steam reformer, the amount of carbon monoxide produces is too low for further process. The combination of steam and autothermal reformer take attractive method to be used for production of synthesis gas for liquid fuels production because carbon monoxide produced can be raised by adding autothermal reformer. Thus, the process of autothermal reforming needs to be studied about its efficiency to convert the natural gas into syngas before its implementation in industrial scale. With the development of computer with simulation software such as

ASPEN Plus V10. It is possible to study the simulation of ATR process with desired end-product characteristics. Improvement of quality and yield the desired product can significantly performed with proper optimization as well as to make the process safe for environment and prevent any accident and explosion.

1.3 Problem Statement

This research is study on synthesis gas production from natural gas for liquid fuels production application. There is a lack of simulations for methane reforming in recent studies. Synthesis gas production via the ATR of methane give more attention compared to conventional reformer that being used in industry. The simulation-based study using software is more effective compared to experimental based due to time consuming to collect the data. Therefore, this work tries to simulate the ATR by using ASPEN Plus V10 to achieve higher synthesis gas production for liquid fuels production plant. In order to see the yield of synthesis gas produced from ATR reactor that suitable for liquid fuels production plant, it is important to understand the effect of certain operating parameters such as feed temperature, reactor pressure, steam-methane feed ratio and oxygen-methane feed ratio on the conversion and yield values. With ASPEN Plus V10, sensitivity analysis tool can be used for quick study of sensitivity of process performance to change in the input operating variables. This enables a wide range of manipulating variables to be studied at a time, after which a set of results can be tabulated and plotted using Microsoft Excel 2013. The optimum conditions of feed also need to be studied in order to produce higher yield of synthesis gas.

A simulation of autothermal reforming is scarce in the recent study for that reason a general simulation study of liquid fuel production plant had been carried out. Higher yield and better quality of syngas are needed to maximize the production of

liquid fuels in the industry. The production of syngas is influenced by various factor such as reforming reactor temperature and pressure, steam molar flowrate supply to the reactor and oxygen molar flowrate supply into the reactor. Hence, simulation is carried out to predict the syngas production using autothermal reforming reactor and study the effects of reactor temperature, reactor pressure, feed steam molar flowrate and feed oxygen molar flowrate on the reforming system. Simulation model can help to predict the performance of autothermal reforming in industrial scale.

1.4 Objectives

1. To simulate the autothermal reformer (ATR) using equilibrium reactor (REQUIL) model in ASPEN Plus V10.

2. To investigate the effect of reactor temperature, reactor pressure, feed steam molar flowrate and feed oxygen molar flowrate on the conversion of methane and yield of hydrogen and carbon monoxide by using sensitivity tool in ASPEN Plus V10.

1.5 Scope of Study

In this work, simulation-based work was done to simulate the autothermal reformer in synthesis gas production using ASPEN Plus V20. Unlike previous experimental works done by other researchers, this study focused on simulation-based approach rather than experimental in order to study the various operating variables on the conversion of methane and yield of synthesis gas.

Firstly, ASPEN Plus V10 was used to develop a simulation flow sheet for the equilibrium reactor (REQUIL) model for ATR process. The simulation results obtained were then compared with those reported in the literature. If the simulation results obtained was comparable and valid with the literature, sensitivity analysis was

then conducted on the operating variables such as feed temperature, reactor pressure, steam-methane feed ratio and oxygen-methane feed ratio. Using the sensitivity analysis tool, the effect of operating variable mentioned above on the yield of synthesis gas was studied in order to obtain the optimum set of operating conditions for the autothermal reforming process.

1.6 Organization of Thesis

The following are the content for each chapter in this study:

Chapter 1 outlines the general information about the natural gas, types of reformer in the industry, problem statement, objectives and scope work of this research.

Chapter 2 discusses literature review regarding the previous research on simulation of ATR reactor, the reaction mechanism involve in ATR reactor and the parametric study was been discussed in this Chapter.

Chapter 3 covers the materials and methodology of the research. It includes step to develop simulation flow sheet for the equilibrium reactor (REQUIL) model in ATR process followed by the sensitivity analysis on operating variables such as feed.

Chapter 4 presents the results and discussion of the simulation results. The simulated data is first compared with those reported in the literature. The effect of operating variables such as feed temperature, reactor pressure, feed steam molar flowrate and feed oxygen molar flowrate are also studied.

Chapter 5 concludes all the findings obtained in this study. Recommendation to improve the current research results are also presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This Chapter discussing the previous research that has been done on simulation of reforming technologies. Other than that, the reaction mechanism was discussed to observe the chemical reaction that probably involve in autothermal reforming technologies. Lastly, the main parametric study was been discussed in this Chapter which are temperature, pressure, steam-methane feed ratio and oxygen-methane feed ratio on various observed parameter. In addition, effect of hydrogen and carbon dioxide in the feed mixture also been discussed.

2.2 Simulation of Reforming Technologies

Borio and Pina (2006) has studied the simulation of ATR as two reactor in series which are combustion zone and catalyst bed with the proposed mathematical model. A one-dimensional heterogeneous model of the catalyst bed is used to calculate the axial fluctuations in composition, temperature, and pressure of the process gas stream. The temperature and composition of the gas that exits the combustion chamber, as well as the temperature and concentration profiles along the catalyst bed and gradients inside the catalyst particle, are all predicted by the model. The influence of feed composition such as steam-carbon ratio and carbon dioxide content in the hydrocarbon stream was studied (Borio, 2006).

Xu Hao et al. (2008) has studied the simulation analysis of gas-to-liquid process using ASPEN Plus. The ATR was simulated using Gibbs reactor model. Adiabatic reactor and ideal gas behaviour of hot gases and perfect mixing of reactant was assumed for the reactor model. Effect of varying the pressure, oxygen, carbon dioxide and steam

in the feed stream were studied toward syngas ratio and efficiency of energy for ATR. This study also observed the other parameter such as unreacted hydrocarbons, syngas composition and carbon dioxide produced (Hao et al., 2008).

Zahedi et al. (2009) has proposed the mathematical of kinetic model for autothermal reformer that consisting two distinct sections which are a combustion section (non-catalytic partial oxidation and catalytic bed section (catalytic steam reformer). For kinetic model, one dimensional heterogeneous reactor model are used for the second section. The results were compared with the experimental data obtained from Christensen and Primdahl (1994). The operating conditions used to simulate ATR were at temperature of 700 K, pressure of 21 bar, the steam-methane ratio of 0.6, the oxygen-methane ratio of 0.59. The effect of operating parameter such as temperature, pressure, carbon dioxide-methane ratio and steam-methane ratio were studied toward syngas ratio (Zahedi et al., 2009).

Wu and Tungpanututh (2012) has studied the optimization of autothermal reforming for hydrogen production system using methane as the feedstock with low carbon dioxide emission. There are five major process units consider in the methane ATR process. At room temperature, three two-phase streams of methane, water, and air (oxygen) are well mixed, with two molar ratios of water-to-methane and oxygen-to-methane. A heater pre-heats the mixed stream, which then flows into the autothermal reforming (ATR) reactor at the specified inlet temperature. The adiabatic reactor with packed catalysts were assumed in the system. The main reaction used were complete combustion, steam reforming and water-gas shift reactions to simulate the ATR. The ASPEN HYSYS was used to simulate the ATR reactor model (Wu & Tungpanututh, 2012).

Giwa and Giwa (2013) was studied the hydrogen production using steam reforming of methane. Methane reforming bas been simulated using ASPEN Plus. Then, the results was analysed and optimized with aid of the software. The model was developed using equilibrium reactor (REQUIL) model for replicate the steam reforming. Two model was developed which are steam reformer with and without mixer to study the effect of mixing the reactant to the reactor. They discovered that the result for both model are same for mole fractions of the process components. The sensitivity analysis was studied with varying the reactor temperature, reactor pressure, inlet water volumetric flowrate and inlet methane volumetric flowrate. The optimization study was been done to vary operating variable that having high yield of hydrogen produced among the others components of the process. The result show that the mole fraction of hydrogen is 0.7432 present at the top product with operation condition at the reactor temperature of 964.89 ^{o}C , reactor pressure of 1 bar, the volumetric flow rate of feed water and the volumetric flow rate of feed methane were approximately 0.0172 L/min and 0.0353 L/min, respectively. The model use in ASPEN Plus was able to represent the steam reforming process very well (Giwa & Giwa, 2013).

Wutthithanyawat and Srisiriwat (2014) has developed the mathematical modelling and simulation of ATR using ethanol as feedstock. They consider the ATR is thermally self-sustaining that it required no heat sources from external. Some assumptions were made up for their mathematical model such as no reaction kinetic is available means using the minimization of Gibbs free energy to simplify the calculation of mass balance, the ethanol completely converted and adiabatically reactor was considered. No pressure drop and gas behaviour also been considered in their work. They conclude that the ATR temperature can be controlled by controlling air flowrate. However, because the largest disturbance, the feed temperature, has a significant impact

on the ATR temperature, the feed temperature can be configured as a separate controlled variable, with the proportion of heating power as the manipulated variable (Wutthithanyawat & Srisiriwat, 2014).

Ayodele and Cheng (2015) has studied the process modelling, thermodynamics analysis and optimization of three types of reformer which are dry reforming, partial oxidation and autothermal methane reforming for hydrogen and syngas production. The ASPEN HYSYS has been utilized to simulate all types of reformers using Gibbs reactor (RGIBBS) as the reactor model. The simulation works was conducted at the temperature range of 200 ^{o}C to 1000 ^{o}C and pressure of 20 bar as same as industrial process. The gas fed ratio into Gibbs reactor is 1:1:1 for methane, carbon dioxide and oxygen respectively. The optimum condition were obtained at CH_4/CO_2 of 0.634, CH_4/O_2 of 0.454 and temperature at 800 ^{o}C to achieved higher conversion of methane and yield of syngas. The syngas ratio vary from 1 to 2 for ATR reforming reaction is suitable for several chemical product (Ayodele & Cheng, 2015).

Qasim et al. (2016) has studied the optimization study of syngas production. The syngas production process is simulated and optimized using ASPEN HYSYS V8.4 to increase its production. Two process were investigated which are the syngas process with recycle technique and heat integration and conventional design for syngas production. The natural gas and steam were fed into ATR model at temperature of 400 ^{o}C and 300 ^{o}C respectively with the pressure of 25 bar. The parameters such as molar flows and temperature and also composition of production rate of syngas and others components were observed along the reactor length (Qasim et al., 2016).

Jimmy et al. (2017) has studied the thermodynamic modelling of ATR using synthetic crude glycerol as the feedstock for hydrogen production. By solving the Gibbs free energy minimization issue based on the Peng-Robinson Stryjek-Vera (PRSV)

equation of state, the Gibbs reactor in ASPEN Plus was utilized to estimate the equilibrium compositions of synthesis gas products from the crude glycerol ATR reactor. Based on standard settings from earlier experimental work, the effect of operating temperature, S/SCG ratio, and O/SCG ratio on yield of hydrogen was investigated. They discovered the highest yield of hydrogen present at the high temperatures, high S/SCG ratio, and low O/SCG ratio for synthetic glycerol reforming. Maximum hydrogen is produced in thermoneutral conditions with a steam to SCG ratio of 3.6, an oxygen to SCG ratio of 0.75, and an adiabatic temperature of 927 K (Jimmy et al., 2017).

Ayad and El-Emam (2018) has studied the different reforming techniques in gas to liquid technology. Three types of reformer which are steam reforming, partial oxidation and autothermal methane reforming for syngas production. The simulation of all reforming techniques were utilized using ASPEN Plus V8.6. the simulation of reformers were done with equilibrium reactor (REQUIL) model which is an equilibrium-based calculation and Peng-Robinson property method was chosen for the property calculation. The operating conditions and parameters data were obtained form industry field. The effect of parameters such as temperature, feed steam and feed oxygen were studied toward syngas ratio. The syngas ratio was adjusted to 2 due to the ratio is suitable for the further process for GTL production (Ayad & El-Emam, 2018).

2.2.1 Summary of Simulation of Reforming Technologies

Table 2.1: Summary of simulation of reforming technologies

No	Author	Year	Types of Reformer	Parametric Study	Remark
1	Borio and Pina	2006	Autothermal reformer	Feed steam-carbon ratio Carbon dioxide content in the hydrocarbon stream	Two reactor in series which are combustion zone and catalyst bed.
2	Xu Hao et al.	2008	Autothermal reformer	Pressure reactor Feed oxygen Feed Carbon dioxide Feed steam	ATR was simulated using Gibbs reactor model. Adiabatic reactor and ideal gas behaviour of hot gases and perfect mixing of reactant.
3	Zahedi et al.	2009	Autothermal reformer	Temperature Pressure Carbon dioxide-methane ratio Steam-methane ratio	Mathematical of kinetic model for autothermal reformer that consisting two distinct sections which are a combustion section.
4	Wu and Tungpanututh	2012	Autothermal reformer	None	ASPEN HYSYS was used to simulate the ATR reactor model. The main reaction used were complete combustion, steam reforming and water-gas shift reactions to simulate the ATR.

5	Giwa and Giwa	2013	Steam reformer	Reactor temperature Reactor pressure Inlet water volumetric flowrate Inlet methane volumetric flowrate.	The model use in ASPEN Plus was able to represent the steam reforming process very well. The model was developed using equilibrium reactor (REQUIL) model.
6	Wutthithanyawat and Srisiriwat	2014	Autothermal reformer	Feed temperature	The feedstock used is ethanol. The minimization of Gibbs free energy has used to simplify the calculation of mass balance.
7	Ayodele and Cheng	2015	Dry reformer Partial oxidation reformer Autothermal reformer	None	The ASPEN HYSYS has been utilized to simulate all types of reformers using Gibbs reactor (RGIBBS) as the reactor model.
8	Qasim et al.	2016	Autothermal reformer	Feed molar flow rate Temperature	The syngas production process is simulated and optimized using ASPEN HYSYS V8.4.
9	Jimmy et al.	2017	Autothermal reformer	Operating temperature S/SCG ratio O/SCG ratio	The Gibbs free energy minimization, the Peng-Robinson Stryjek-Vera (PRSV) equation of state and the Gibbs reactor have used in ASPEN Plus
10	Ayad and El-Eman	2019	Steam reformer, Partial oxidation reformer Autothermal reformer	Temperature Feed steam Feed oxygen	The simulation of all reforming techniques were utilized using ASPEN Plus V8.6. Equilibrium reactor (REQUIL) model has choosen.

2.3 Reaction Mechanism

Natural gas can be reform into synthesis gas in several reaction. Since the methane found as the major component in natural gas, the set of reaction involved is shown in Table 2.1 (Azarhoosh et al., 2016). Appropriate values must be selected for all parameters of the rate constant and rate equation such as activation energies. Reaction mechanism is the most important data that needed before performing any simulation. De Groote and Froment (1996) has proposed a reaction mechanism for the simulation of methane reforming which are included nine reactions. It are listed as follows (Froment, 1996):

Complete Combustion:	$CH_4 + 2O_2 \leftrightarrow CO_2 + 4H_2$	(2.1)
Partial Combustion:	$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2$	(2.2)
Steam Reforming:	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(2.3)
	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	(2.4)
Water Gas Shift Reaction:	$CO + H_2O \leftrightarrow CO_2 + H_2$	(2.5)
Carbon Dioxide Reforming:	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	(2.6)
Boudouard Reaction:	$2CO \leftrightarrow C + CO_2$	(2.7)
Methane Cracking:	$CH_4 \leftrightarrow C + 2H_2$	(2.8)
Carbon Gasification by Steam:	$C + H_2O \leftrightarrow CO + H_2$	(2.9)
Carbon Gasification by Oxygen:	$C + O_2 \leftrightarrow CO_2$	(2.10)

The reactions are all non-elementary in nature. Solid carbon is involved in the last four reactions, as can be seen. Most modelling work skips the last four reactions since the quantity of solid carbon present in the end product is usually very minimal, if not zero. Since the reactor simulation is related to the ATR of methane into synthesis

gas with supported of nickel (Ni) catalyst, the rate of equation of total combustion, steam reforming and water gas shift reaction must be combined in the calculation (Azarhoosh et al., 2016). Trimm and Lam (1980) have studied a kinetic equation for the complete combustion of methane with supported Pt/Al_20_3 catalyst, adjusting the corresponding adsorption parameters for Ni (D. L. Trimm and C. W. Lam., 1980).

2.4 Parametric Study

The study on effect of operating parameter such as temperature, pressure, steam-methane feed ratio and air(oxygen)-methane feed ratio was important to investigate the good quality of syngas produce. In addition, the effect of hydrogen and carbon dioxide content in the feed mixture also be studied.

2.4.1 Effect of Temperature on Syngas Production

Effect of reactor temperature was studied to obtain the good quality of syngas produced in ATR reactor. Lamb et al. (2020) discovered the generally ATR reactor temperature was operated at 950 ^oC to 1050 ^oC (Lamb et al., 2020). Rowshanzamir et al. (2012) was investigated the increase inlet temperature in the range of 450 ^oC to 700 ^oC will increased the mole fraction of hydrogen and carbon monoxide. The increase in activity of steam reforming reactions at higher inlet temperatures is mostly responsible for this. The water gas shift reaction was similarly degraded when the inlet temperature was increased. This resulted in a higher carbon monoxide content. The reformer's methane consumption was increased when the inlet temperature was increased. As expected, increasing the temperature of the feed gas resulted in higher temperatures in the reactor (Rowshanzamir et al., 2012).

2.4.2 Effect of Pressure on Syngas Production

Effect of reactor pressure was studied to obtained the good quality of syngas produced in ATR reactor. Lamb et al. (2020) discovered the generally ATR reactor pressure was operated at 30 bar to 50 bar (Lamb et al., 2020). Olsvik and Hansen (1998) was discovered the high pressure ATR (HP ATR). The purpose use HP ATR is to lower the cost of investment for plant by converting more gas per unit volume and eliminating the synthesis gas compression stage, more gas may be converted per unit volume. The performance of the ATR in the high pressure range of 70 bar to 100 bar is investigated using fluid flow models and combustion kinetic calculations (Olsvik & Hansen, 1998). Souza et al. (2005) was investigated the effect of pressure toward performance of ATR in term of conversion of methane in the range of 1 bar to 50 bar of pressure. Increasing the pressure give negatively impact to conversion of methane. In fact, the lowest pressure value yields higher methane conversion values (Souza & Schmal, 2005).

2.4.3 Effect of Steam-Methane Feed Ratio on Syngas Production

Effect of steam-methane feed ratio was studied to obtain the good quality of syngas produced with suitable ratio in ATR reactor. Lamb et al. (2020) discovered the generally ATR steam-methane feed ratio (S/C ratio) was operated at 0.5 to 1.5 (Lamb et al., 2020). Rowshanzamir et al. (2012) was investigated the effect of the S/C ratio on the temperature profile in the reformer, the steam-to-carbon ratio (S/C ratio) was decreased will increase the temperature along the reformer. At higher S/C ratio, hydrogen yield increased and carbon monoxide yield decreased (Rowshanzamir et al., 2012). Hoang et al. (2007) investigate the water-fuel (W/F) ratio give have significant effect on the reforming performance. They studied the conversion of fuel, dry hydrogen and carbon monoxide concentrations, and mole of hydrogen produced per mole of fuel supplied under different W/F ratio. The conversion of fuel was increased with increased

of W/F ratio. While, the dry hydrogen and carbon monoxide concentrations were decreased with increasing the W/F (Hoang & Chan, 2007).

2.4.4 Effect of Oxygen-Methane Feed Ratio on Syngas Production

Effect of air(oxygen)-methane feed ratio was studied to obtain the good quality of syngas produced with suitable ratio in ATR reactor. Lamb et al. (2020) discovered the generally ATR oxygen-methane feed ratio (O/C ratio) was operated at 0.6 to 1.0 (Lamb et al., 2020). Rowshanzamir et al. (2012) was investigated the effect of the O/C ratio on the methane outlet mole fraction. Increasing the O/C ratio will decrease the methane outlet mole fraction. The combustion reaction occurred at a high rate with a greater O_2/C ratio, and the majority of the methane was converted in the process. The steam content in the mixture would have no effect on the overall reactor product since steam reforming and water gas shift processes were demoted (Rowshanzamir et al., 2012). Hoang et al. (2005) investigate the air-fuel (A/F) ratio give have significant effect on the reforming performance. They studied the conversion of fuel, dry hydrogen and carbon monoxide concentrations, and mole of hydrogen produced per mole of fuel supplied under different A/F ratio. The conversion of fuel was increased with increased of A/F ratio. While, the dry hydrogen and carbon monoxide concentrations were decreased with increasing the A/F (Hoang & Chan, 2007).

2.4.5 Effect of Hydrogen Gas Content in the Feed Mixture

In autothermal reformers, no additional amount of hydrogen needed into it, because the amount of hydrogen in the feed from the downstream of steam reformers of 50 % is enough. The study show adding the hydrogen gas into feed mixture which are 10% of hydrogen added, the percentage of carbon efficiency is lower by about 6% and the conversion of methane also lower is about 3%. The mixture containing hydrogen caused the maximum temperature in catalyst bed is slightly lower. When the

hydrogen added into feed mixture, there is no carbon formation because of the endothermic methane cracking near the inlet of reactor. So, no temperature decrease and the reaction of combustion starts further upstream in the reactor. Other than that, the fraction of the catalyst bed that covered by carbon is smaller if the feed mixture containing hydrogen that can caused the catalyst bed is going to deactivate. In conclusion, presence of hydrogen in feed mixture prevent the methane cracking and it is not efficient for avoiding carbon deposition (Froment, 1996).

2.4.6 Effect of Carbon Dioxide Gas Content in the Feed Mixture

Presence of the carbon dioxide into feed mixture mainly reflected in the product ratio (H_2/CO ratio). It also caused the conversion of methane decrease, but increase the conversion towards carbon monoxide, thus it lead to a synthesis gas with lower product ratio. On other side, the product ratio in the effluent become higher when the steam is added. The desired product ratio in the effluent can be produced if adding the carbon dioxide or steam in the feed mixture. The desired product ratio in the effluent can also be achieved by changing the methane-oxygen feed ratio (Froment, 1996). Natural gas may contain a high amount of carbon dioxide which can be remove for further process to produce synthesis gas.

2.5 Syngas Ratio in Liquid Production Plant

Syngas ratio plays important role in the liquid fuels production or GTL plant. The appropriate syngas ratio should be determined with the requirement of the further process in the liquid fuel production plant. Cao et al. (2008) discovered the syngas with stoichiometric ratio at 2 or ranging from 1 to 2 was suitable in major syngas-based chemical production (Cao et al., 2008). Sangsong et al. (2020) was recommended the syngas ratio (H_2/CO) is 2 as a feedstock of Fischer-Tropsch synthesis for GTL

production for the condition of temperature (600 ^{o}C) and the $H_2O/(CH_4 + CO_2)$ ratio of 0.53 with the present of Nickel catalyst (Sangsong et al., 2020). Ayad and Fotouh (2019) was adjusted syngas ratio for the base case of ATR to 2 at a low steam-methane ratio and oxygen-methane ratio of 0.53 (Ayad & El-Emam, 2018). The syngas ratio is the favorable value that need to be consider when simulating the ATR reactor.

CHAPTER 3

METHODOLOGY

3.1 Overview of Research Methodology

In order to achieve the research objectives as stated in Chapter 1, a process model for autothermal reforming (ATR) reactor was developed using the ASPEN Plus V10 simulator. The model created was then be used to study the relationship of reactor temperature, reactor pressure, feed steam molar flowrate and feed oxygen molar flowrate towards the conversion of methane and ratio of hydrogen and carbon monoxide.

Firstly, a suitable reactor block in ASPEN Plus V10 simulator was chosen to simulate the data obtained from the literature. Suitable information and assumption were made up into account for the reactor block. The simulation data from the literature was used to validate the model in order to determine whether the model is comparable and valid for further study. If, the validation was succeeded, operating parameters which are reactor temperature, reactor pressure, feed steam molar flowrate and feed oxygen molar flowrate were manipulated using the Sensitivity Analysis Tool in ASPEN Plus V10 simulator.. A general flow of the methodology is shown in Figure 3.1.

3.2 Research Methodology Steps

Figure 3.1 shows the summary of methodology steps involved in this research work.

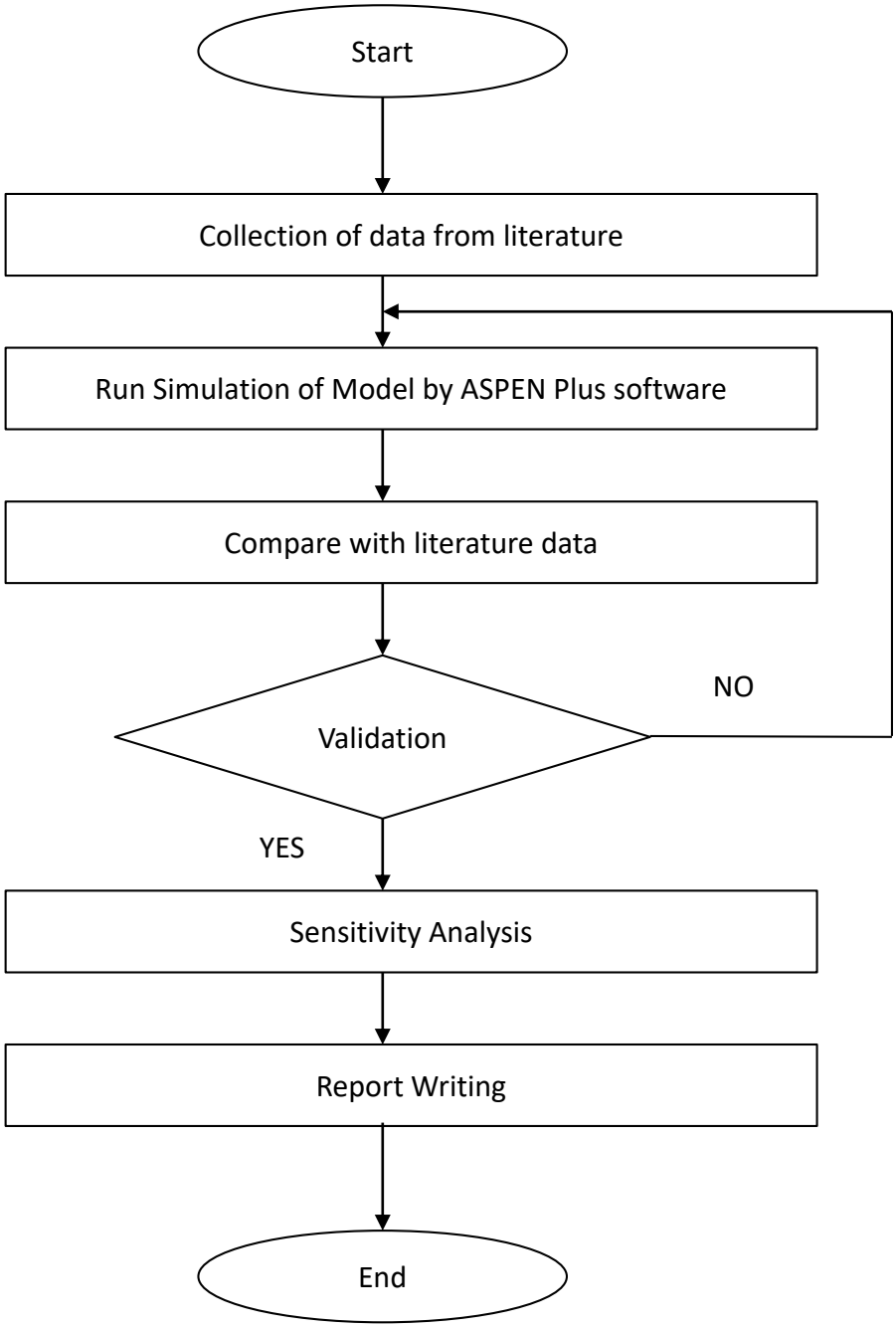

Figure 3.1: Methodology flow chart

3.2.1 Data Collection

The system considered in this simulation work was the autothermal reforming (ATR) reactor in the liquid fuels production gas. It is the reaction where the natural gas (assumed only methane consists in natural gas) feed into ATR reactor to produce syngas. The equation below show the reactions that occurs in the ATR reactor (Azarhoosh et al., 2016).

(i) Partial oxidation reforming reaction:

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H^o_{298} = -36\ kJ \cdot mol^{-1} \tag{3.1}$$

(ii) Steam reforming reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^o_{298} = 206.2\ kJ \cdot mol^{-1} \tag{3.2}$$

(iii) Water-Gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^o_{298} = -41.1\ kJ \cdot mol^{-1} \tag{3.3}$$

From the literature (Ayad & El-Emam, 2018), a process flowsheet based on autothermal reforming (ATR) reactor was designed with the operating conditions and parameter from industry data. The reactor used to simulate ATR is equilibrium reactor (REQUIL) model that available in ASPEN Plus V8.6 library which is equilibrium-based calculation. In this work, stand-alone ATR reactor is simulated using the same reactor model. Figure 3.2 is the process flow diagram for ATR obtained from the literature (Ayad & El-Emam, 2018). While, Figure 3.3 shows the REQUIL reactor model was chosen to model and simulate the ATR reactor for this work.

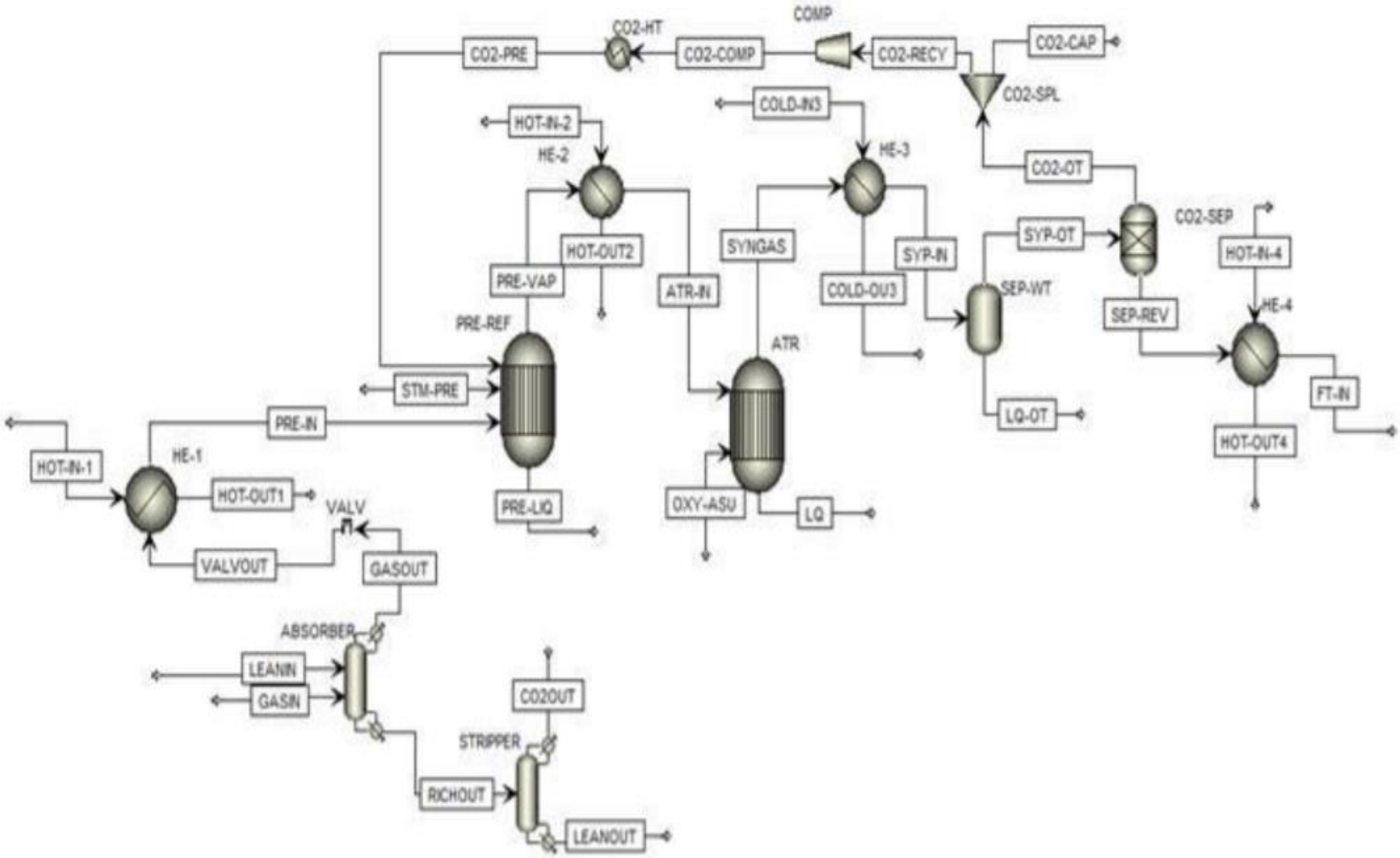

Figure 3.2: Process flow diagram for ATR in literature

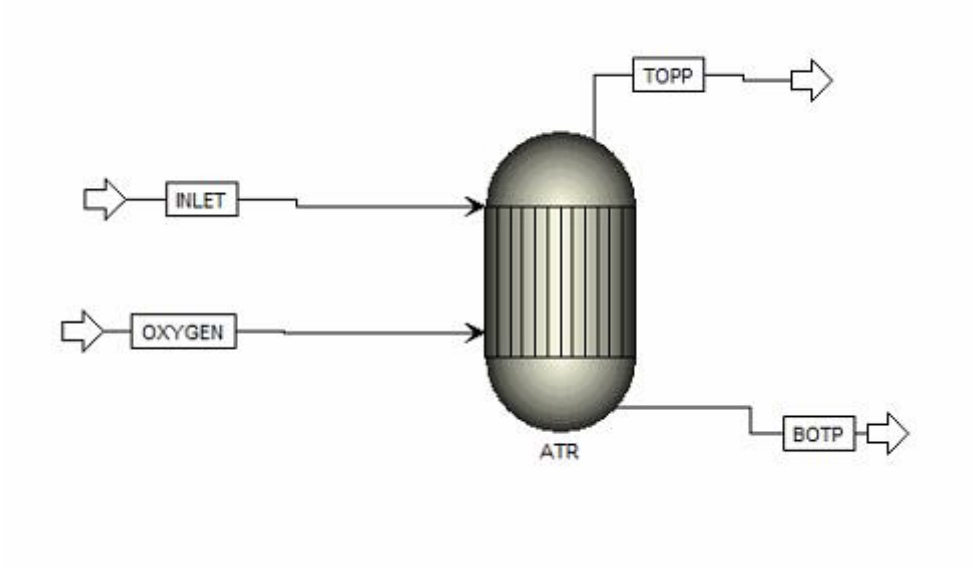

Figure 3.3: REQUIL reactor model used in the simulation

Peng-Robinson (PENG-ROB) property method was chosen for the simulation of autothermal reforming (ATR) reactor as it is suitable for high temperature and pressure reactor (Ayad & El-Emam, 2018). Since, this work is to simulate stand-alone ATR reactor, the composition of inlet ATR was obtained from the literature. The composition of components fed into ATR is from the outlet stream of pre-reformer in the literature. The calculation of composition for each components for inlet ATR were calculated in APPENDIX A with some assumption made up. The setup input to the REQUIL ATR block for ASPEN Plus simulation were as shown in the Table 3.1 and Table 3.2 below (Ayad & El-Emam, 2018);

Assumption made in the simulation of ATR reactor model are stated below,

1. The reactor is adiabatic and isothermal reactor, no pressure drop and temperature changes in the reactor.
2. No recycle stream is considered
3. No accumulation in the reactor (IN=OUT)

Table 3.1: Feed Specification (Ayad & El-Emam, 2018).

Species/Parameter	Value	Unit
INLET Stream		
Temperature	655	^{O}C
	928.12	K
Pressure	30	bar
Composition:		
Methane (CH_4)	2876.05	kmol/hr
Steam (H_2O)	222.37	kmol/hr
Carbon monoxide (CO)	281.68	kmol/hr
Hydrogen (H_2)	652.3	kmol/hr
OXYGEN Stream		
Temperature	200	^{O}C
	473.15	K
Vapour Fraction	1	
Composition:		
Oxygen (O_2)	1524.31	kmol/hr

Table 3.2: Reactor Specification (Ayad & El-Emam, 2018).

Species/Parameter	Value	Unit
Reactor Temperature	1300	K
Reactor Pressure	30	bar