

SIMULATION AND OPTIMIZATION OF A BUTANE AUTOHERMAL REFORMER FOR FUEL CELL APPLICATIONS

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Abstract. Hydrogen (H₂) production is gaining popularity among researchers for a better future environment. Hydrogen, which is known as the cleanest fuel, is also an excellent candidate to replace existing fuels. Its high flammability and energy produced with no side product make it even more popular. In this study, a steady-state model simulation is developed to describe a butane fuel processor by autothermal reforming (ATR) to provide H₂ for fuel-cell application. The objective of the study is to develop a general steady-state simulation of an H₂ production plant for fuel cell application using butane as the feedstock. The scope of the study includes stoichiometric mathematical analysis, base case steady-state simulation, base case simulation validation, the design of heat integration, carbon monoxide (CO) clean-up processes which contains water gas shift (WGS) and preferential oxidation (PrOx) reactors and plant wide optimization. The simulation has been run in Aspen HYSYS 2004.1 in steady-state mode in which optimization was done to generate more H₂ as well as CO reduction. The butane fuel processor was optimized at Oxygen-to-Carbon (O/C) ratio of 2.18 and Steam-to-Carbon (S/C) ratio of 4.6 to produce 39.2 % of H₂ and has achieved 78.1 % efficiency, while CO clean-up units was capable to reduce the CO concentration down to 10 ppm.

Key Words: Butane, Autothermal Reforming, Proton Exchange Membrane Fuel Cell, Aspen HYSYS, Simulation and Optimization

1.0 INTRODUCTION

Hydrogen as an energy carrier in proton exchange membrane fuel cell (PEMFC) offers perhaps the largest potential benefits in terms of reduced emissions of pollutants and greenhouse gases. Moreover, no side products are involved in the electrochemical conversions of H₂ with zero emission of hazardous species, for instance volatile organic compound (VOCs), nitrogen oxides (NO_x) and carbon oxides (CO) [1]. When it is used as fuel, it will only produce water. It is such a good option as a fuel because H₂ is colourless, odourless and extremely flammable and also the smallest and simplest member of the family of chemical elements compared with other fuel such as hydrocarbons, alcohols, or coals [2].

However, it is difficult to store and handle hydrogen directly as a kind of on-board fuel. For practical fuel cell systems hydrogen gas has to be generated from locally available fuels, most commonly hydrocarbons. The objective of this study is to simulate and optimize the on-board hydrogen production for fuel cell vehicle from hydrocarbon feedstock. This study is important since the on-board conversion of hydrocarbon feedstock

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into hydrogen is more efficient and much better than having hydrogen in pressurized vessels or in cryogenic state for safety reasons.

The text is organized as follows: the major thermochemical reforming of butane, the reaction scheme and clean up are presented in the following section. Section 2 describes the methodology of butane fuel processor. The results and discussions will be discussed in more details in Section 3. Finally, in Section 4 some conclusions and recommendations will be drawn.

1.1 Reforming of butane

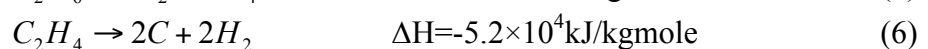
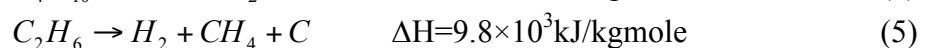
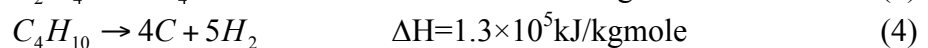
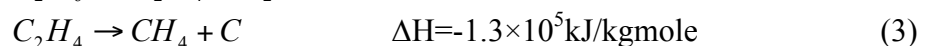
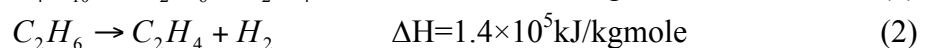
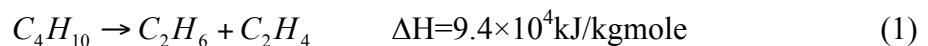
There are three major thermochemical reforming techniques used to produce hydrogen from hydrocarbon fuel, i.e., steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). Steam reforming is probably the most common and traditional method for producing hydrogen on industrial scale. In this process, steam reacts with fuel in the presence of a catalyst to produce hydrogen, carbon dioxide, and carbon monoxide. Though this process can yield high concentration of hydrogen (up to 70% on a dry basis), it is strongly endothermic [3]. Hence, the reformer needs external heat to be supplied through the reactor wall to perform the fuel reforming. The overall configuration of steam reformer with heat exchangers makes the reforming system very bulky and heavy, which is not suitable for a mobile fuel cell system.

To overcome the heat transfer problem in steam reformer, POX has been often used as an alternative method to produce hydrogen or synthesis gas from hydrocarbons [4-5]. The process is exothermic and easily starts up upon ignition even without aid of a catalyst. It can raise the temperature to over 1000°C, which permits adiabatic operation and promotes SR of the remaining. However, POX produces high carbon monoxide concentration [6] that is undesirable for PEMFCs.

ATR [7] combines the thermal effects of the POX and SR reactions by feeding the fuel, water, and air together into the reactor. The two processes occur simultaneously in the presence of catalyst in the reactor. The thermal energy generated from POX is absorbed by SR and, hence, the overall temperature is lowered, which is favourable to water-gas shift reaction to consume carbon monoxide and produce more hydrogen. Hence, the auto thermal reformer is more compact and practical for use with mobile fuel cells.

1.2 Chemical reaction scheme of ATR

n-butane conversion in the presence of steam and oxygen affects the hydrogen yield. The reactions occur in ATR are fuel cracking, steam reforming oxidation as well as carbon gasification. Fuel cracking occur based on the reaction below, butane is cracked into ethane, ethylene, methane, and carbon and also able to produce H₂.



Steam reforming of the fuel occurs when there is enough steam to convert fuel into CO and H₂ based on the reactions below:



Aforementioned, oxidation is one way to supply heat and also water. The reactions below show how autothermal reforming will take place.



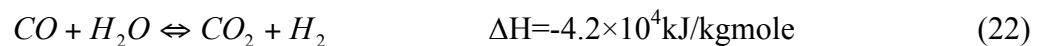
Carbon gasification may occur since carbon formation is expected to be high. Based on reactions below carbon can be converted into CO₂ and CO.



1.3 CO clean-up section

CO clean-up section includes WGS and PrOx reactions. At present, the research efforts concentrate in developing a system to reduce CO at an acceptable level for PEMFCs condition. The amount of CO in the outlet stream of the fuel processor is expected to be less than 10 ppm in order to prevent the anode catalyst to be poisoned [8-9]. The study was conducted under pressure ranging between 1 and 5 bars in a fixed bed steel reactor with a stream containing H₂ (46%), CO₂ (25%), CO (100 ppm) and N₂.

The reaction involved in the WGS reactors is



Steinberg [10] claimed that Reaction 22 can behave in either forward shift or reverse shift depending on the operating temperature. At temperatures lower than 250°C, the forward shift will occur in which CO is converted to CO₂ whereas the reverse shift will occur at temperatures greater than 500°C.

In PrOx reactor, the remaining CO can be reduced based on the reaction below



The use of chemical steady-state process simulator has become an integral part of the evaluation of the performance of hydrogen production systems. Steady-state simulation of conversion of n-butane into hydrogen fuel using Aspen HYSYS was rarely investigated.

Some researchers have simulated hydrogen production system for fuel cell using other than n-butane as a feedstock [1, 7, 11-13]. The process simulation package Aspen HYSYS 2004.1 has been used along with conventional calculations in this study to optimize the steady-state simulation of hydrogen fuel processor using n-butane.

2.0 METHODOLOGY OF BUTANE FUEL PROCESSOR

The general description of hydrogen production is sketched in Figure 1 where the raw material; butane, steam and air are fed into the ATR reactor at 100°C. The feeds are heated at this temperature to ease the conversion of butane. Since ATR consists of exothermic reactions, part of butane is combusted to produce heat and water.

After the reforming process in ATR reactor, all the vapour products are brought to the CO cleaning unit that comprises of WGS section and PrOx reactors. WGS section has three equilibrium reactors in which different temperature approach introduced to each reactor namely High Temperature Shift (HTS), Medium Temperature Shift (MTS) and Low Temperature Shift (LTS). Figure 1 also shows that air was fed into the last reactor, PrOx reactor at a certain flow rate to convert the remaining CO until the concentration reached 10 ppm. The reactions occurred in CO cleaning unit is exothermic. Therefore, cooling process is necessary before feeding into the next reactors.

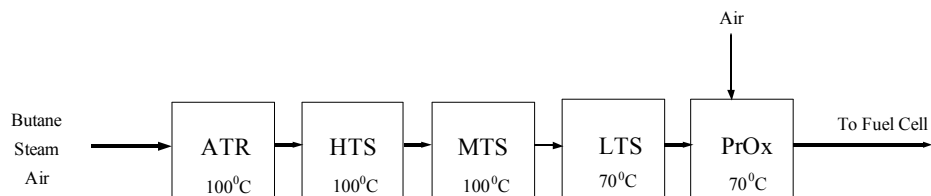


Figure 1 Butane ATR fuel processor

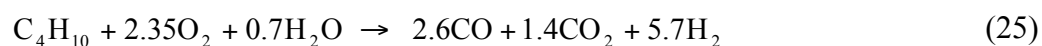
The use of chemical flow-sheeting software has become an integral part of the evaluation of the performance of fuel processor systems [1, 7, 11-13]. The steady-state simulation of Aspen HYSYS process modeling tool has been utilized along with conventional calculations.

For all cases, all reactors for WGS are simulated to operate under equilibrium conditions and for ATR and PrOx reactors are simulated using conversion reactor. The pressure is kept constant at 1 atm. The S/C, O/C ratios and operation temperatures of reactors are changed parametrically to determine the best operation parameters. The simulator is capable to calculate the steady-state product compositions taking into account the incoming stream compositions under the defined operation conditions.

The aim is to convert as much as the H₂ in the fuel into H₂ gas at acceptable yields in the efficient manner while decreasing CO. Lower S/C ratios favor soot and coke formation, which is not desired in catalytic steam and ATR processes. A wide S/C ratio range has been selected to see its effect on H₂ yield and CO formation. A similar approach has been adopted for O/C ratio.

3.0 RESULTS AND DISCUSSIONS

From Eqs. (1-22) the overall reaction is obtained as below



With a basis of 100 kgmole/h of n-butane feed flow rate, the calculated feed water is 70 kgmole/h, while air flow rate was determined by:

$$\text{Air Molar Flow kgmole/h} = \frac{\text{Moles Oxygen Needed}}{\text{Oxygen Mole Fraction in Air}} \times 100 \text{ kgmole/h} \quad (26)$$

Thus, air molar flow needed was 1119 kgmole/h. The reformat gas, which contains H₂, CO and CO₂ were 570, 260 and 140 kgmole/h, respectively.

3.1 Base case simulation and validation

Figure 2 illustrates the conversion of butane in the ATR reactor in Aspen HYSYS simulator environment. Raw materials, n-butane, water (steam) and air were channelled to the ATR reactor by heating them to 100°C. The composition of n-butane and water were pure while the air was composed of 0.21 mole fraction of oxygen and 0.79 mole fraction of nitrogen.

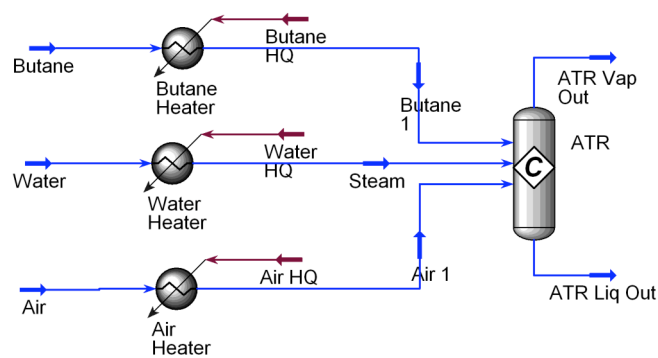


Figure 2 Base case simulation model

Table 1 shows the differences between output mole fractions of simulated case and calculated case. Whereby, the calculated case was obtained from the overall stoichiometric reactions as shown in reaction 25. At inputs flow rates of 1119 kgmole/h for air and 70 kgmole/h water, the errors of ATR output components mole fractions were minimum. These results indicate that the base case simulation developed using Aspen HYSYS 2004.1 was valid and can be considered as a real plant for further analysis.

Table 1 Validation of base case simulation.

| Components | Input Flow rate (kgmole/h) | Output Mole Fraction | | |
|------------------|-------------------------------|----------------------|-----------|--------|
| | | Calculated | Simulated | Error |
| n-Butane | 100 | 0 | 0 | 0 |
| Ethane | 0 | 0 | 0 | 0 |
| Ethylene | 0 | 0 | 0 | 0 |
| Methane | 0 | 0 | 0 | 0 |
| Carbon | 0 | 0 | 0 | 0 |
| H ₂ O | 70 | 0 | 0.0069 | 0.0069 |
| CO | 0 | 0.1402 | 0.1472 | 0.0070 |
| CO ₂ | 0 | 0.0755 | 0.0686 | 0.0069 |
| H ₂ | 0 | 0.3074 | 0.3005 | 0.0069 |
| Oxygen | 235 | 0 | 0 | 0 |
| Nitrogen | 884 | 0.4768 | 0.4768 | 0 |

3.2 ATR reactor optimization

Aspen HYSYS 2004.1 can investigate the whereabouts of the optimized point by running a case study that manipulate air molar flow rate to show two independent variables which is H_2 and ATR liquid molar flow rates. These two variables were selected because it was important to achieve no ATR liquid flowed out the ATR reactor and obtaining the highest possible H_2 generation. Substances that formed in liquid was actually carbon. This condition occurred because of insufficient water. From Figure 3 where optimization of air flow rate was done, we can see that ATR liquid out was nil when air flow at 1102 kgmole/h. The combustion of the fuel which produce water was sufficient to secure carbon formation. This point was taken though H_2 molar flow was at maximum when air molar flow ranging from 1000 to 1100 kgmole/h.

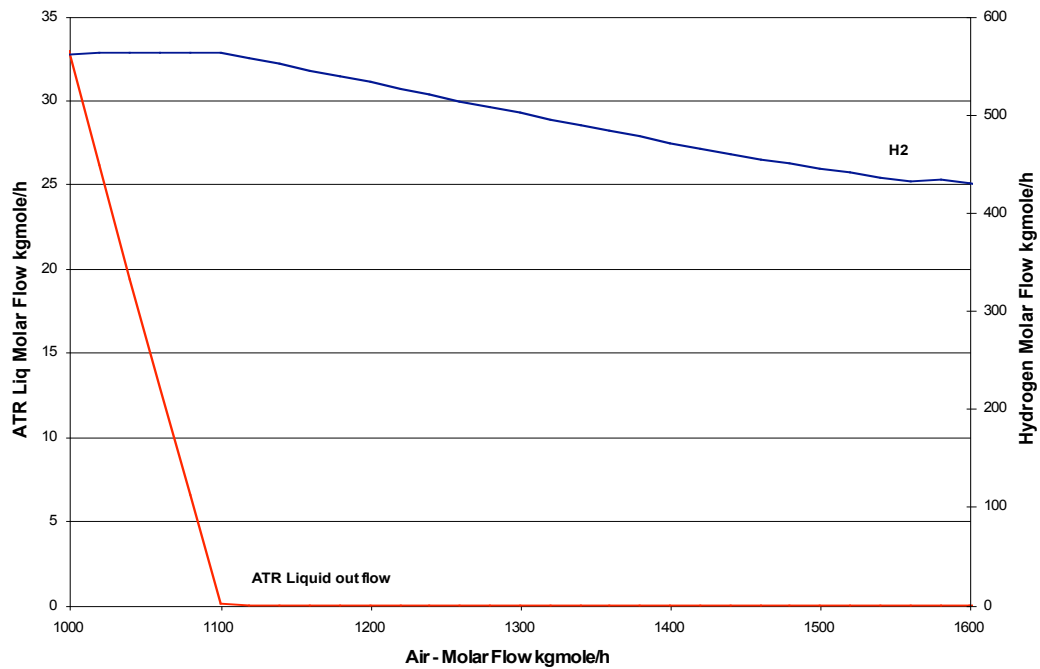


Figure 3 Optimization of ATR product stream

3.3 ATR reactor heat integration

Heat integration was required in order to minimize heating utility since the reactions occurred in ATR was highly exothermic. The heat from ATR Vap Out stream can be integrated with the raw materials streams to heat up the stream to $100^{\circ}C$. As a result, no external heating utility was required to heat the raw materials. The design of heat integration is shown in Figure 4.

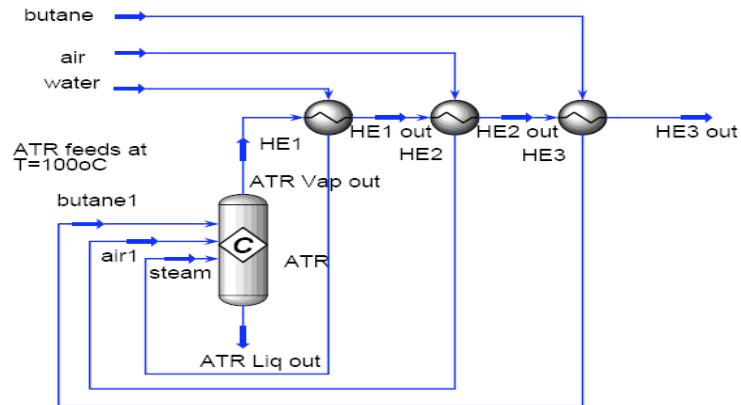


Figure 4 Heat integration design

3.3 WGS and PrOx

On-board fuel processor requires WGS section to clean the toxic gas CO that was produced in steam reforming and combustion reactions in ATR reactor. CO characteristic could poison fuel cell at certain concentration. Thus WGS section was needed to reduce the CO concentration to a certain concentration (ppm). Three equilibrium reactors were set up as WGS because the reaction involved in these reactors was reversible as shown in Eq. (22) and CO must be reduced at different temperature condition depending on the CO concentration level to avoid a reverse shift reaction to occur. Figure 5 shows the overall plant diagram with additional preferential oxidation unit.

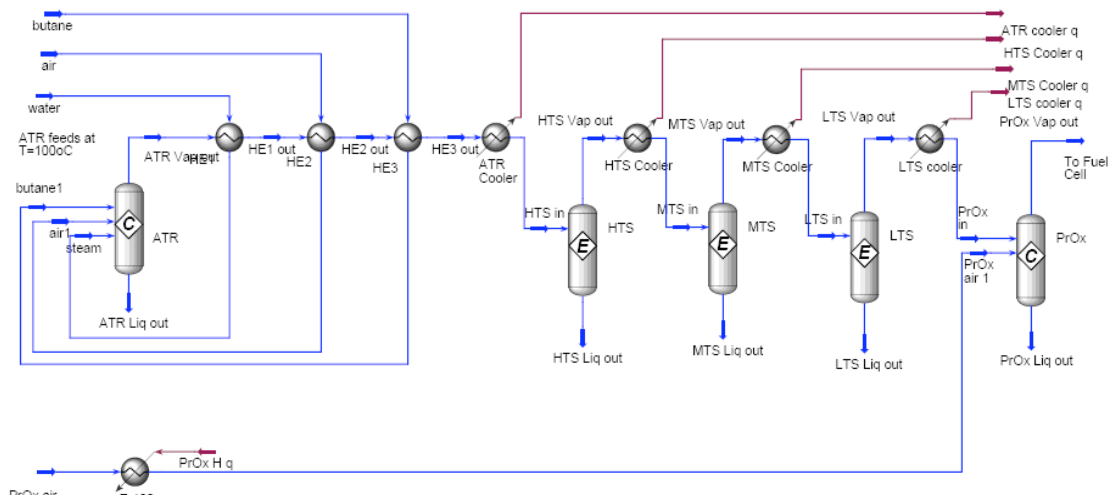


Figure 5 Overall plant diagram with additional preferential oxidation unit.

3.4 Plantwide optimization

Plantwide optimization was done by running a ‘Case Study’, one of the tools available in Aspen HYSYS, to investigate the CO concentration after LTS Vap Out stream. From Figure 6, LTS Vap out stream was expected to yield CO concentration of 100 ppm level. The target was acceptable because at low concentration entering PrOx reactor, the temperature would not changed significantly after the exothermic reactions occurred in PrOx reactor to minimize cooling duty.

This was done to obtain an optimum water flow by presetting the air molar flow to 1102 kgmole/h. From the figure also, we can see that the CO concentration was peaked at 70 kgmole/h of water. And then the CO concentration started to decrease as more water flowed in. The second line indicated a better view of the acceptable CO ppm level. The CO

ppm level has reached 10 ppm when water flow rate in which the optimized water flows in was determined at 430 kgmole/h. The water flow can be extended up to 500 kgmole/h in order to reduce more CO concentration. Air flow can be further optimized from 1102 kgmole/h and below. This was due to the water has been added more than enough to prevent carbon formation.

3.5 PrOx air optimization

PrOx reactor is the last reactor cleaning unit before discharging the H₂ to the fuel cell. The main objective of this work was to obtain a concentration of CO as low as 10 ppm. Figure 7 shows the results were obtained by manipulating air input into the PrOx. Hence the required Air flow to PrOx was found to be 10 kgmole/h.

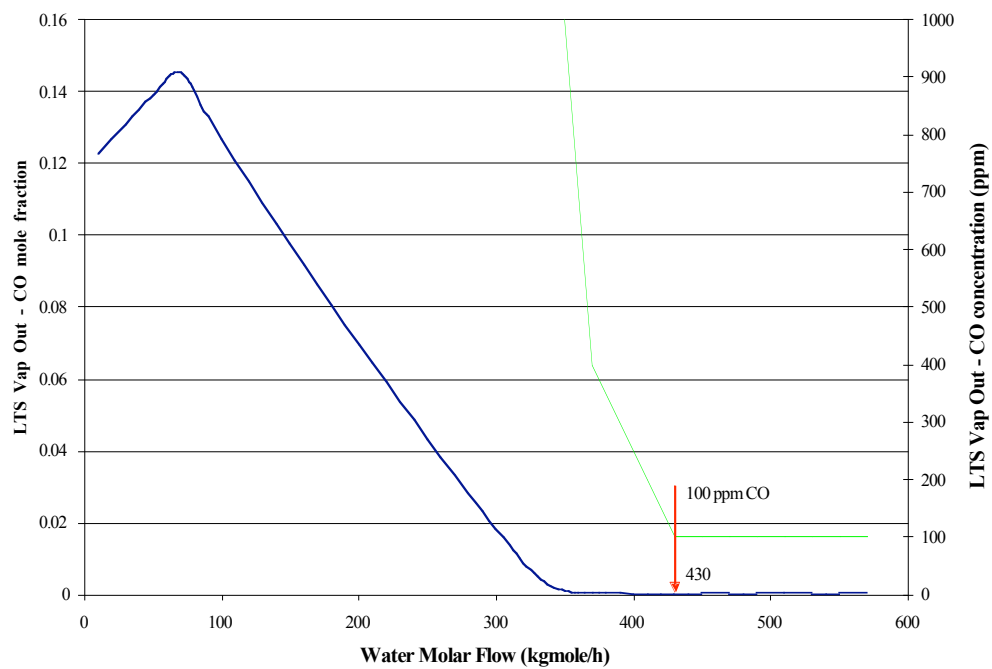


Figure 6 Water flow optimization

3.6 Further optimization

The purpose of this further optimization was to determine the best air flow by changing water flow i.e. increasing the Steam-to-Carbon ratio (S/C). The result shown in Figure 8 indicates that the increasing of steam flow would require less air flow. Based on the optimized water flow of 430 kgmole/h, the S/C ratio was increased from 4.4, 4.6, 4.8, and 5.0. The results shows that at S/C = 4.4, CO concentration of 10 ppm was reached as air flow was fed at 1040 kgmole/h. For S/C = 4.6, the air flow dropped to 1000 kgmole/h. Next, for S/C = 4.8 and 5.0, the air flow required were obtained at 990 kgmole/h and 950 kgmole/h respectively. It can be concluded that air flow of 990 kgmole/h and S/C 4.8 were acceptable for the use of fuel processor. These values had taken consideration the required size for on-board fuel processor.

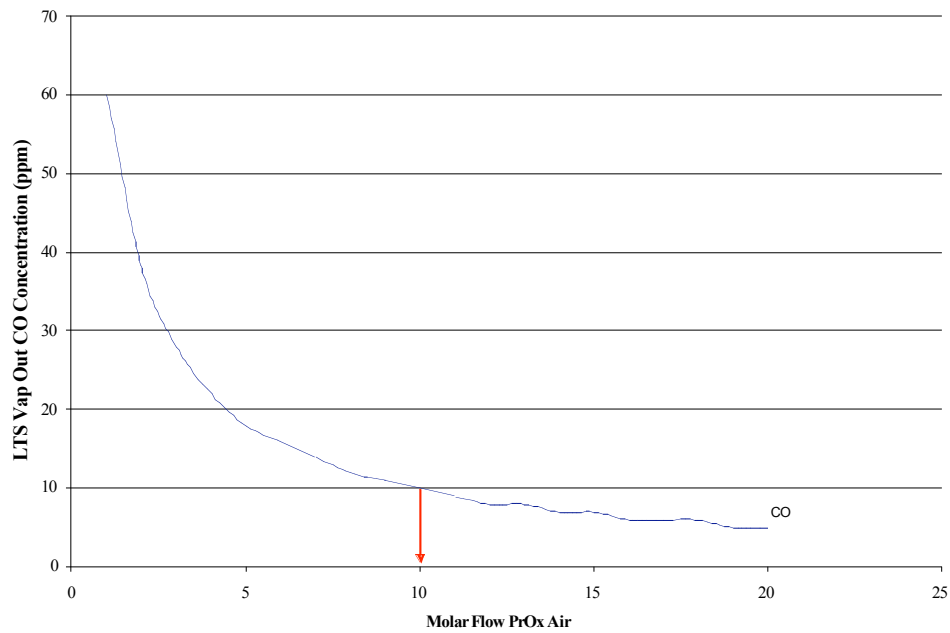


Figure 7 Effects of PrOx air flow to CO concentration.

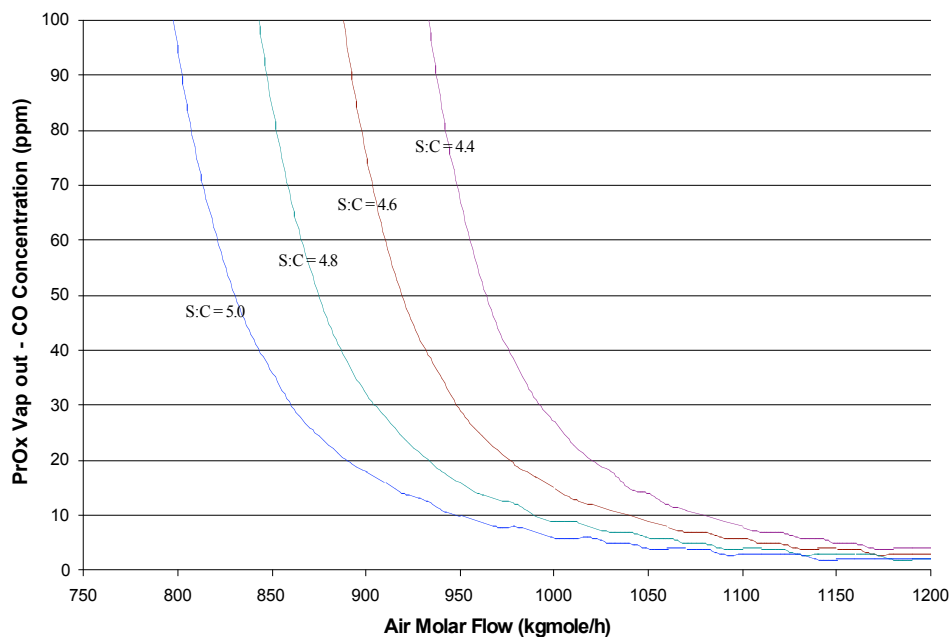


Figure 8 Steam-to-carbon and air flow effect to CO concentration.

3.7 Temperature and components profiles

The temperature profile of the fuel processor is demonstrated in Figure 9. With 2.18 of O/C and 4.6 of S/C ratios, the outlet temperature of ATR reactor was about 726.6°C which was integrated with raw materials streams as the heat source. There were three heat exchangers where water was heated first then air and butane. In the last heat exchanger (HE3), the temperature has dropped to 391.1°C.

To enter the WGS and PrOx reactors the streams were then cooled to 100°C, 100°C, 70°C and 70°C by passing it through ATR cooler, HTS cooler, MTS cooler, LTS cooler, respectively. The reactions occurred in HTS release heat excessively where the HTS inlet temperature was at 100°C while the outlet increased to 252.3°C. In the MTS, the inlet

temperature was also 100°C, whereas the outlet temperature was slightly increased of about 115.6°C. LTS and PrOx outlet temperatures were also increased a little. The increasing temperature occurred because of the exothermic nature of WGS reaction. PrOx outlet temperature was readily to provide for fuel cell as the temperature was in the range of 60-100°C.

Figure 10 shows the components profile of each vapour outlet stream. With 2.18 of O/C and 4.6 of S/C ratios the production of H₂ after autothermal reforming of butane was about 580 kgmole/h while 280 kgmole/h of CO was largely produced. At HTS Vap Out, H₂ had increased significantly from 580kgmole/h to 836 kgmole/h, while CO had dropped drastically from 280 kgmole/h to 27 kgmole/h. A slight increase of H₂ at MTS Vap Out and LTS Vap Out was observed in contrary with CO that decreased slightly in both streams. At PrOx Vap Out, CO obtained was below 10 ppm. H₂ was slightly decreased due to H₂ oxidation in the PrOx reactor. The purity of H₂ obtained was about 39.2%.

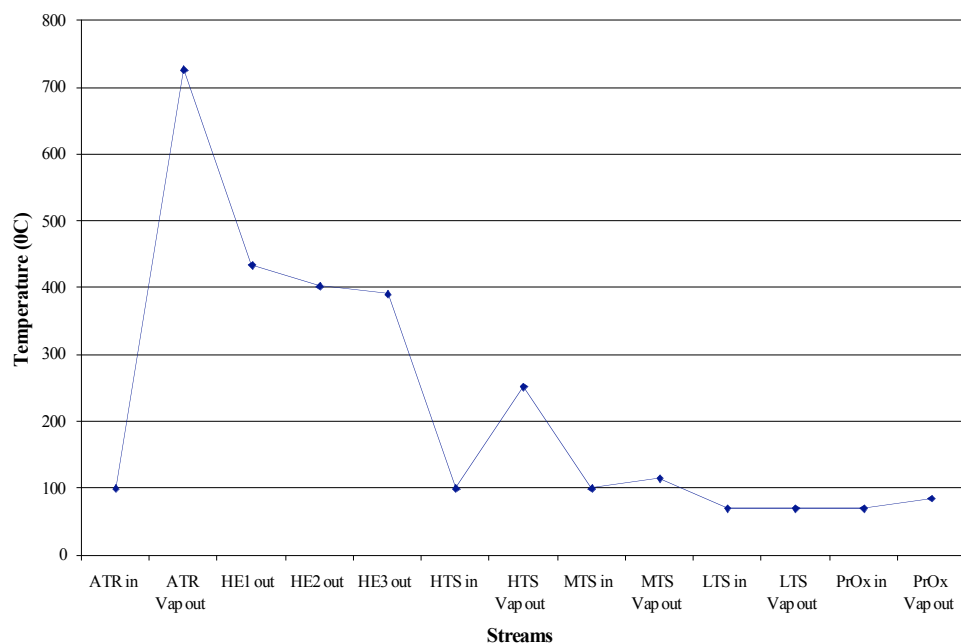


Figure 9 Temperature profiles of the fuel processor.

3.8 Fuel processor efficiency

The efficiency of fuel processor is defined according to Eq. 26 below, where its definition was stated at [14].

This definition considers the dimensionless number of moles of hydrogen (η) produced out of each mole of hydrocarbon fuel supplied, including the fraction of input fuel supplied to the hydrocarbon burner for heating purposes in oxidation mode.

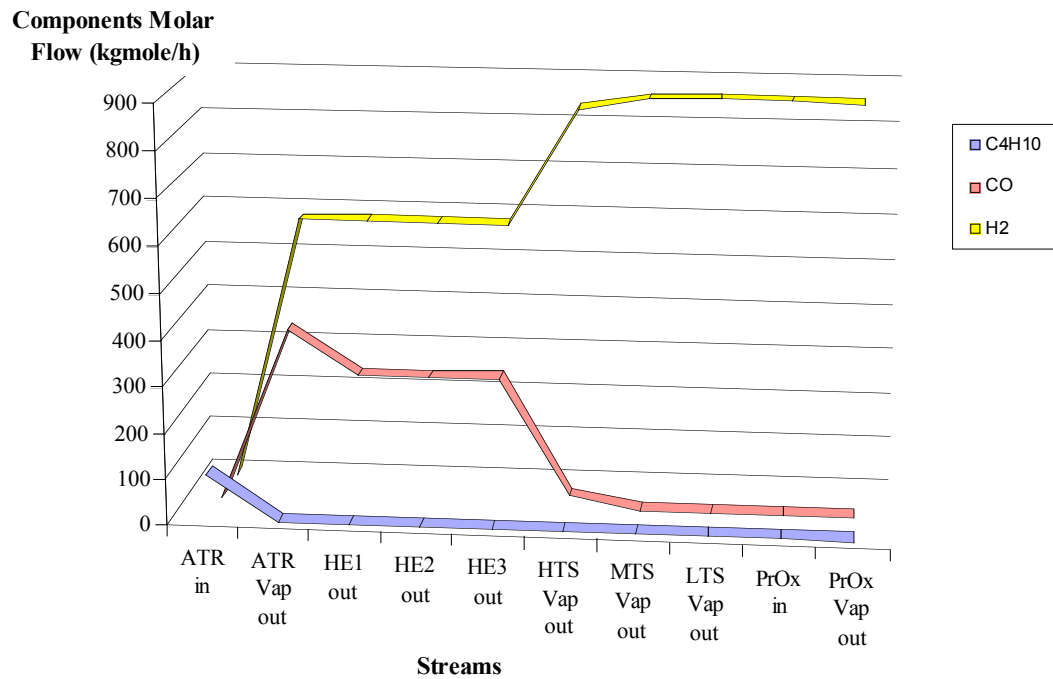


Figure 10 Components profiles

The values of efficiency presented in the following section can therefore be referred as the energetic efficiency of the complete the fuel processor system by comparing the energy available with the product hydrogen gas with the total energy supplied with the hydrocarbon fuel. Energy contents of hydrogen and hydrocarbon fuels are compared with respect to the lower heating value (LHV).

$$\text{Efficiency, } \eta \% = 100 \times \frac{n \times \text{LHV} (\text{H}_2)}{n \times \text{LHV} (\text{butane})} \quad (26)$$

Where, n is molar flow rate and LHV is lower heating value of the product hydrogen and butane can be obtained directly from Aspen HYSYS 2004.1 or by calculation that is expressed as below

$$\text{LHV} = \text{Yield (kgmole/h)} \times \text{Heat of combustion (kJ/kgmole)}$$

The LHV of H_2 is -2.419×10^5 kJ/kgmole while LHV of butane is 2.66×10^6 kJ/kgmole as determined by simulator. Therefore in this study, with the O/C ratio of 2.18 and S/C ratio of 4.6, the calculated fuel processor system efficiency was about 78.1 %.

4.0 CONCLUSIONS AND RECOMMENDATIONS

An optimized simulation model of a butane autothermal reforming has been developed to produce synthesis gas with higher hydrogen and lower carbon monoxide compositions, for mobile proton exchange membrane fuel cell applications. This study was performed with the assistance of Aspen HYSYS 2004.1, a commercial process simulator to develop a steady state model to investigate performance of the fuel processor. In this study, the fuel processor consists of the butane autothermal reformer section, clean-up section, and auxiliary units. The clean-up section consists of three WGS reactors; HTS, MTS and LTS; and one PrOx reactor. Several steps were considered to achieve the research objective. A

number of important observations were noted based on the analysis of results as presented in the previous section.

The contributions of this research to the simulation of hydrogen production plant for fuel applications, which also represent the new developments in this field, are the following:

- a. The hydrogen production plant for fuel cell application using autothermal reforming of butane in steady-state mode was successfully developed using Aspen HYSYS 2004.1.
- b. Optimized S/C and O/C ratios were 4.6 and 2.18 respectively, to produce 39.2% H₂ and CO concentration of less than 10 ppm.
- c. The efficiency of butane fuel processor was 78.1% based on the above optimized ratios.

In future works, it is recommended to study and integrate the following aspects:

- a. A real time dynamic simulation to investigate the dynamic behaviour of the butane fuel processor.
- b. H₂ purification must be studied to provide dry hydrogen entering fuel cell.
- c. Control structure design for better operability.

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