THERMAL ASSESSMENT OF HYDROGEN PRODUCTION UNIT FROM ETHANOL STEAM REFORMING

MEK SRILOMSAK

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF ENGINEERING IN AUTOMOTIVE ENGINEERING

(INTERNATIONAL PROGRAM)

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KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG

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ABSTRACT

Hydrogen is an energy carrier for the future. Unlike fossil fuel, hydrogen burns cleanly, without emission of any toxic pollutants. It can also be applied in the petroleum and chemical industries e.g. hydrodesulfurization process (HDS). Hydrogen can be converted from any sources of hydrocarbon fuel. A renewable fuel source such as ethanol is an interesting alternative for producing of hydrogen. The feasibility in using ethanol as it is a potential and sustainable alternative energy to substitute fossil fuel because it is cultivated from the revolving planted crops. In this study, ethanol is used as a fuel in hydrogen production. Ethanol mixed water is vaporized, then fed into a reactor for producing of hydrogen by the steam reforming and water gas shift reactions. Combustion of LPG which using of porous media materials as a heat transfer media was used as a heat source for the reactions. The hydrogen production system is investigated for the energy input and output by an energy balance equation which is calculated by using experimental data of the unit. The hydrogen production system consumed 5.39 kW of energy in practice, while 3.98 kW of energy is required in theory. Therefore, the efficiency of the hydrogen production unit is 73.88%. Finally, the high efficiency of the unit states that the ethanol steam reforming is a feasible technology for a production of hydrogen.

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This thesis could not be complete without the assistance of many persons to whom I would like to express my sincere appreciation.

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MEK SRILOMSAK

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NOMENCLATURE

ΔH	Heat of reaction	kJ/mol
$\dot{m}$	Mass flow rate	kg/s
h	Enthalpy	kJ/kg
$\dot{W}$	Work input rate	kW
$\dot{E}$	Energy rate	kW
$\dot{Q}$	Heat rate	kW
$\dot{Q}_{loss}$	Rate of heat loss	kW
η	Efficiency	%

Acronym

LPG	Liquefied Petroleum Gas
GS	Gas chromatography
SMR	Steam reforming of methane
ESR	Steam reforming of ethanol
WGS	Water-gas shift
MFC	Mass flow controller
MEM	Mass flow meter
A/F ratio	Air-Fuel ratio
S/C ratio	Steam to Carbon ratio
STP	Standard conditions for temperature and pressure
CAD	Computer-Aided Design

CHAPTER 1

INTRODUCTION

1.1 Significance and Background

Renewable hydrocarbon energy sources are of wide interest nowadays such as ethanol. Ethanol can be produced from agricultural products which are abundant throughout Thailand, since we are an agricultural country. Remarkably, it strengthens the nation's energy stability and stabilizes the price of agricultural crops for farmers. Hydrogen is a primary energy carrier for the future, also it can be utilized in processes of petroleum refinery in petro chemical industries. It can be derived from any form of hydrocarbon, thus ethanol is an alternative fuel which can be a fuel supply for a production of hydrogen. In order to produce hydrogen, steam reforming is an energy-efficient and cost-effective process.

Hydrogen production from ethanol steam reforming is a reaction which converts an ethanol mixed with water to product containing hydrogen and carbon dioxide. Porous media burner was utilized to be a heat source of high temperature about 700-900°C which is required for endothermic reaction of the reforming process. The burner has ability to be stabilized under wider operating condition compare to free flame combustion, and can evenly distribute furnace temperature all along the longitudinal height in order to maintain an optimum condition for the catalytic reaction of the steam reforming process. Since ethanol steam reforming has high energy efficiency and is environmentally friendly, it is potentially attractive in producing hydrogen.

To study the energy utilization for production of 20 liters/minute hydrogen output from an ethanol steam reforming at the National Metal and Materials Technology Center (MTEC), the hydrogen production from ethanol steam reforming pilot-scale unit was developed. The main units in the hydrogen production system are reforming reactor, and porous media furnace. First, the porous media furnace is heated up until 700-900°C by using Liquefied Petroleum Gas (LPG) as a fuel. Then, ethanol mixed water is vaporized before feeding into the reforming reactor, which placed inside

a porous media furnace, for producing hydrogen as an output via a reforming process. Finally, a mass flow meter and a gas chromatography (GC) is used in total product measurement, and analytical chemistry for separating and analyzing compounds, respectively. Overview of the process is shown in Figure 1.1. The study of energy conversion is necessary. Energy balance is investigated to determine the energy input and output of sub-units and overall system.

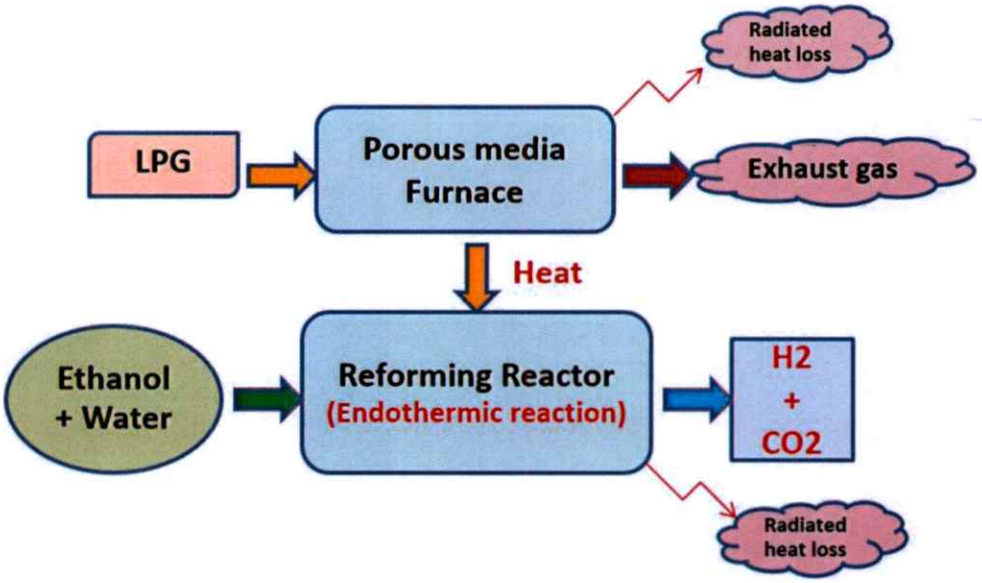


Figure 1.1 Flowchart of hydrogen production from ethanol steam reforming system

1.2 Objectives

To study, design, and develop a pilot scale prototype of hydrogen production unit and to assess an energy budget for the production of 20 liters/minute hydrogen output of the hydrogen production unit from ethanol steam reforming.

1.3 Scope of Work

1.3.1 Develop a pilot scale unit of hydrogen production from ethanol steam reforming using a porous media-LPG burner as a heat source.

1.3.2 Develop a calculation procedures of the hydrogen production system to investigate the energy conversion and efficiency of the unit.

1.4 Expected Benefits

1.4.1 Understanding the processes of hydrogen production from ethanol steam reforming and porous media burner.

1.4.2 Developing a mathematical model for an energy assessment of the hydrogen production unit.

1.4.3 Developing a high efficiency unit for production of hydrogen by using a renewable feedstock.

CHAPTER 2

LITERATURE REVIEW

Alternative energies have become magnificent choices instead using of natural resources that derived from fossil fuel during the past few decades. In term of hydrogen production, one of the most promising resources is ethanol which can be produced from agricultural products which are abundant throughout the country like Thailand.

2.1 Ethanol

Ethanol is a renewable energy resource which has its structural formula CH_3CH_2OH. It is often abbreviated as C_2H_5OH, C_2H_6O or Et-OH. Presently, it is widely accepted that Ethanol has a potential as sustainable alternative energy because it is cultivated from the revolving planted crops.

To blend ethanol with gasoline, we obtain "gasohol fuel" which now becomes more popular as its price is cheaper than pure gasoline. Remarkably, a use of gasohol can help reducing polluted substances and also imported fuel from overseas. Moreover, it strengthens the nation's energy stability and stabilizes the price of agricultural crops for farmers. Therefore, ethanol is an important part for the national (Thailand) economic development. A potential of ethanol production from agricultural products in Thailand is approximately 12.295 million liters per day of Bioethanol (in the year 2011) from 47 factories; approximately from sugarcane (86%), cassava (11%), and molasses (3%). (Siamphakdee 2011)

In order to produce hydrogen, hydrogen gas can be generated through a steam reforming process which is most widely adopted in industries. Hydrogen can be produced from many kinds of hydro-carbon substances not only with fossil fuels but also renewable material such as ethanol.

2.2 Hydrogen & Use of Hydrogen

Hydrogen is considered as a primary energy carrier for the future. Unlike fossil fuel, hydrogen burns cleanly, without emission of any toxic pollutants. Hydrogen can also be applied in the petroleum and chemical industries. The most significant application of hydrogen is to apply into the processing of fossil fuel, and in the production of ammonia. In a petrochemical plant, the main consumption of hydrogen include hydrodesulfurization (HDS), and hydrocracking units. Hydrogen may be obtained from fossil fuel feedstock (such as natural gas, or methane), but these types of feedstock are not sustainable.

2.3 Hydrogen Production

Hydrogen is very rare in the Earth's atmosphere (1 ppm by volume) because of its light weight, which enables it to escape from the Earth's gravity. However, hydrogen is still the third most abundant element on the Earth's crust (Argonne National Laboratory. 2003). Most of the Earth's hydrogen is in the form of chemical compounds such as hydrocarbons and water. Thus all hydrogen production processes are based on the separation of hydrogen from hydrogen-containing feedstock. The feedstock directs the selection of the separation method. In this chapter, two main methods are proposed to separate hydrogen from the feedstock; those are thermo-chemical and biological methods. A comparison of various hydrogen production technologies based on three main methods is summarized in table 2.1.

Table 2.1 Current technology for hydrogen production

Process	Status of current technology	Efficiency (%)	Cost relative to SMR
Thermo-chemical process			
Grid electrolysis of water	R&D	27	3-10

High-temp. electrolysis of steam (100-800 °C)	R&D	41-61	-
Methanol electrolysis	R&D	-	-
Steam methane reforming (SMR)	Mature	70-80	1
Partial oxidation of methane	Mature	70	1.8
Biological process			
Photo-biological	Early R&D	<1	1

(T-Raissi 2004)

From Table 2.2, the most interesting process is Steam Methane Reforming (SMR) because this technology is already mature in terms of research and development. Moreover, it provides the highest efficiency and the cheapest process when compared with others. However, the details and advantages of each process are described in the following section.

2.3.1 Thermo-chemical Method

2.3.1.1 Electrolysis process

Water electrolysis

This process produces high-purity hydrogen as high as 97.7% (Austin 1984). The process can be performed by passing direct electric current through an aqueous solution of alkaline and decomposing the water to hydrogen and oxygen as shown in Figure 2.1. The involved reactions are indicated in reactions (2.1) to (2.3).

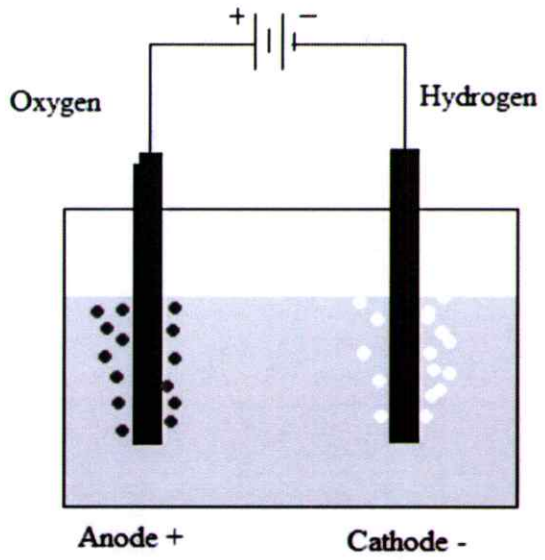


Figure 2.1 Basic of configurations of water electrolysis

Anode (oxidation): $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ (2.1)

Cathode (reduction): $4H^+_{(aq)} + 4e^- \rightarrow 2H_{2(g)}$ (2.2)

Overall reaction: $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$ (2.3)

From Figure 2.1, the black dots are oxygen bubbles generated at the anode of the cell because; water decomposes to proton, oxygen and gives off four electrons as indicated in Reaction (2.1). Generated hydrogen gas is the white dots produced at the cathode as indicated in Reaction (2.2). Molecules of water receive electron and to form hydrogen.

The water electrolysis process is divided into two types, low temperature and high temperature processes operating at 333-343 K and 373-1123 K, respectively. The efficiencies of these processes are about 32% for low temperature (Austin. 1984), and 41-61 % for high temperature.

The advantage of water electrolysis is CO_2-free process because the reactant involves only water which does not contain carbon in its molecule. The main disadvantage of this method is its low energy efficiency.

Methanol electrolysis

The major cost for producing hydrogen by water electrolysis method is electrical energy while oxygen produced from the process is not so valuable. An alternative way to reduce energy consumption in electrolytic process is to use methanol solution. The main reason is that an operating voltage of methanol electrolysis process is lower than the water electrolysis process by about three times. It is about 0.3 volt for methanol and higher than 1.4 volt for water (Jeffries-Nakamura 2002). The electrical energy used in methanol electrolysis is less than a half of water electrolysis in producing a given amount of hydrogen so the efficiency of methanol process is three times higher than the water electrolysis process (NASA Tech Briefs 1999). A schematic diagram for methanol electrolysis process is shown in Figure 2.2 and corresponding reactions are indicated as follows:

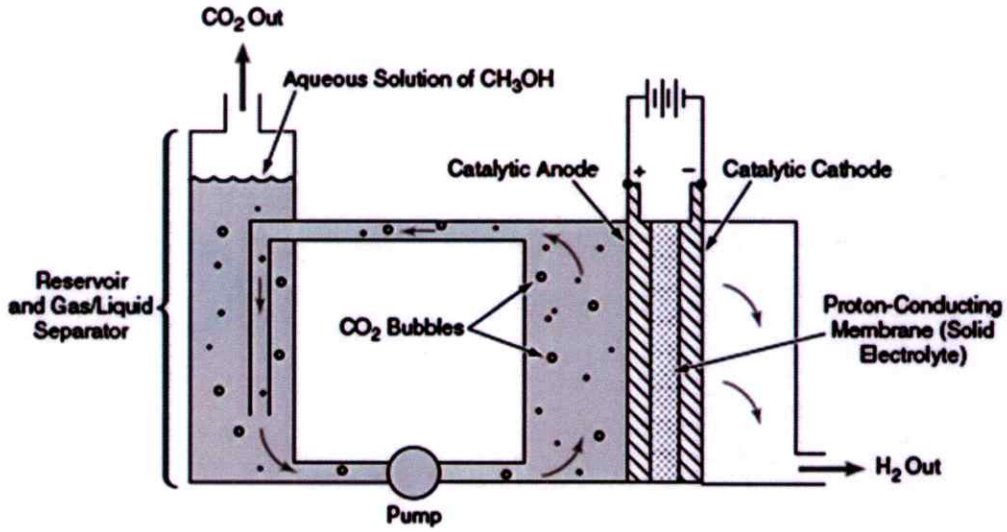


Figure 2.2 Schematic diagrams of methanol electrolysis apparatus (NASA Tech Briefs 1999)

Anode: $$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (2.4)$$

Cathode: $$6H^+ + 6e^- \rightarrow 3H_2 \quad (2.5)$$

Overall: $$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (2.6)$$

These reactions can be obtained at the temperature between 278– 393 K. At the anode, methanol reacts with water to give off hydrogen ions and carbon dioxide, which can be further separated and purified to be a valuable product. The proton was conducted through the membrane to the cathode and combined with electron to give hydrogen.

2.3.1.2 Steam Methane Reforming (SMR) process

Steam methane reforming is a process that converts methane to synthesis gas consisting mainly of CO and H_2. The conventional feedstock for this process is natural gas or biogas. This is one of the most common method to produce commercial bulk hydrogen as well as the hydrogen used in industrial synthesis of ammonia. It is the least expensive method (W. Crabtree et al. 2004). Steam reacts with methane to yield carbon monoxide and hydrogen as indicated in Reaction (2.7) (Hoang. D.L. 2005) at high temperature of 973-1373 K and in the presence of a nickel-based catalyst. Then, the water-gas shift reaction further takes place to convert CO, and an excess H_2O to H_2 as indicated in Reaction (2.8). The Enthalpy changes as indicated in Reactions (2.7) to (2.9) were calculated at standard temperature of 298 K (Xu 1989).

SMR: $CH_4 + H_2O \rightarrow CO + 3H_2$ *(ΔH = +206.1 kJ/mol CH_4)* (2.7)

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ *(ΔH = -41.15 kJ/mol CO)* (2.8)

Overall: $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ *(ΔH = +165.0 kJ/mol CH_4)* (2.9)

From the heat of overall reaction as indicated in Reaction (2.9), the SMR reaction is an endothermic reaction. Then, this process requires extensive amount of heat from an external source to maintain the reaction. To reduce the external heat requirement, a limited amount of oxygen is added to the steam methane reformer. Oxygen reacts with methane to yield CO, H_2O and heat. This reaction is called partial oxidation of methane. The process involves steam methane reforming and partial oxidation of methane which will be described in the next section.

2.3.1.3 Partial oxidation process or autothermal reforming

From an energy intensity process, SMR, the partial oxidation process is conducted to substitute the external heat supplied by introducing limited amount of oxygen to methane and steam. Combustion of oxygen and some of methane in the reactor generates heat to supply SMR and water-gas shift reaction. Because of limited amount of oxygen, it reacts with methane yielding synthesis gas while carbon monoxide is converted to carbon dioxide and hydrogen by a water-gas shift reaction.

Total combustion: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ *(ΔH = -802 kJ/mol CH_4)*

(2.10) Partial oxidation: $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ *(ΔH = -36 kJ/mol CH_4)* (2.11)

A large amount of heat produced by exothermic reactions ((2.10) and (2.11)) is high enough to sustain the amount of heat consumed by endothermic reaction of SMR process (Equation (2.9)). The overall heat of reaction for SMR and partial oxidation reaction is still exothermic reaction then the excess heat can be recovered by preheating the feedstock. The disadvantage of this partial oxidation process is the lower yield of hydrogen as oxygen comes from air so hydrogen that comes out from this reactor is diluted with nitrogen.

The difference between partial oxidation process and auto-thermal process is that the partial oxidation (PO) uses oxygen to react with methane to achieve H_2 and CO. Catalytic partial oxidation (CPO) is used to permit partial combustion reaction which occur at lower temperature to produce synthesis gas. This process operates at low steam/carbon ratio (S/C from 0 to 1) and gives H_2/CO ratio in a range of 1.6 to 1 in the production of synthesis gas (Halabi 2008). In contrast, auto thermal reforming (ATR) uses a burner followed by a catalyst bed with methane, steam and oxygen to produce synthesis gas with higher H_2 to CO ratios of 2 to 1 and it operates at relatively higher steam load (S/C > 1).

2.3.2 Biological Hydrogen production process

The thermo-chemical process requires extensive amount of energy from fossil fuel to produce hydrogen. However, for making hydrogen fully renewable energy, it requires a method which does not require energy intensively to produce hydrogen. A biological method is a method that produces hydrogen by some types of anaerobic metabolism which is produced by several microorganisms, via reactions catalyzed by iron- or nickel- containing enzymes in a microorganism. Most of this process can be operated at room temperature and atmospheric pressure, therefore; it needs less energy than the thermo-chemical process. Furthermore, hydrogen production by biological method uses waste material as a feedstock such as agricultural waste or waste water. From this method, it is a new option to produce hydrogen as a fully renewable energy.

The biological hydrogen production process can be classified into three mechanisms, first is the lighting process which occur by light and enzyme called hydrogenase, such as biophotolysis process of water by algae and cyanobacteria, or nitrogenase in photo-fermentation of organic substrate and water by photosynthesis bacteria. The second is the dark fermentation process. Hydrogen is produced without lighting. The third is a combination between photosynthetic and fermentation of bacteria by separating the system into two stages. The first stage is fermentation by which organic waste is fermented to organic acid. The second stage is photolysis process to convert organic acid to hydrogen. The combined system is advantageous as a reduction of light energy demand in photolysis process but increasing in hydrogen production.

Nevertheless, the disadvantage of the biological hydrogen production process is low efficiency; theoretically maximum hydrogen yield is up to 40%. Meanwhile, in practice the efficiency is less than 10% (Esper 2006).

From many kinds of hydrogen production technologies discussed above, the steam methane reforming process is the most cost effective process. It provides the highest efficiency and less complicated system than partial oxidation process. However, the steam methane reforming process is not sustainable

because the process requires a number of non-renewable energies from fossil fuel to produce hydrogen.

However, to make hydrogen more renewable, and also cost effective, it requires a method having high efficiency and with a renewable feedstock. In Thailand, ethanol is more suitable feedstock to supply to a hydrogen production than methane. The reason is that ethanol is a renewable energy resource and it can be produced by fermentation of agricultural waste such as cassava root, and sugarcane as mentioned earlier in this chapter

Therefore, an ethanol steam reforming process is an attractive technology to produce hydrogen by using ethanol as a feedstock.

2.3.3 Hydrogen Production via a Catalytic Steam Reforming of Ethanol

Steam reforming is an energy-efficient and cost-effective process. In addition to ethanol being used as a renewable resource, a steam reforming of ethanol is a promising choice in hydrogen-based energy system. The overall steam reforming reaction of C_2H_5OH could stoichiometrically be represented as follows (Velu, et al. 2002).

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad (\Delta H^\circ_{298} = +347.4\ kJ/mol) \qquad (2.12)$$

However, there are many reaction pathways that could occur in the ethanol steam reforming process, depending on the catalysts used; some such reactions are shown in Figure 2.3.

A breakdown of the reactions is given as follows:

1) C_2H_5OH dehydration to ethylene (C_2H_4) and water, followed by polymerization of C_2H_4 to form coke (Llorca, Homs, et al. 2004).

Dehydration: $$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (2.13)$$

Polymerization: $C_2H_4 \rightarrow coke$ (2.14)

2) C_2H_5OH decomposition or cracking to CH_4, followed by steam reforming (Fatsikostas and Verykios 2004).

Decomposition: $C_2H_5OH \rightarrow CH_4 + CO + H_2$ (2.15)

Steam reforming: $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$ (2.16)

3) C_2H_5OH dehydrogenation to acetaldehyde (C_2H_4O), followed by decarboxylation or steam reforming of C_2H_4O (Cavallaro 2000):

Dehydrogenation: $C_2H_5OH \rightarrow C_2H_4O + H_2$ (2.17)

Decarbonylation: $C_2H_4O \rightarrow CH_4 + CO$

(2.18)

Steam reforming: $CH_2O_4 + H_2O \rightarrow 3H_2 + 2CO$

(2.19)

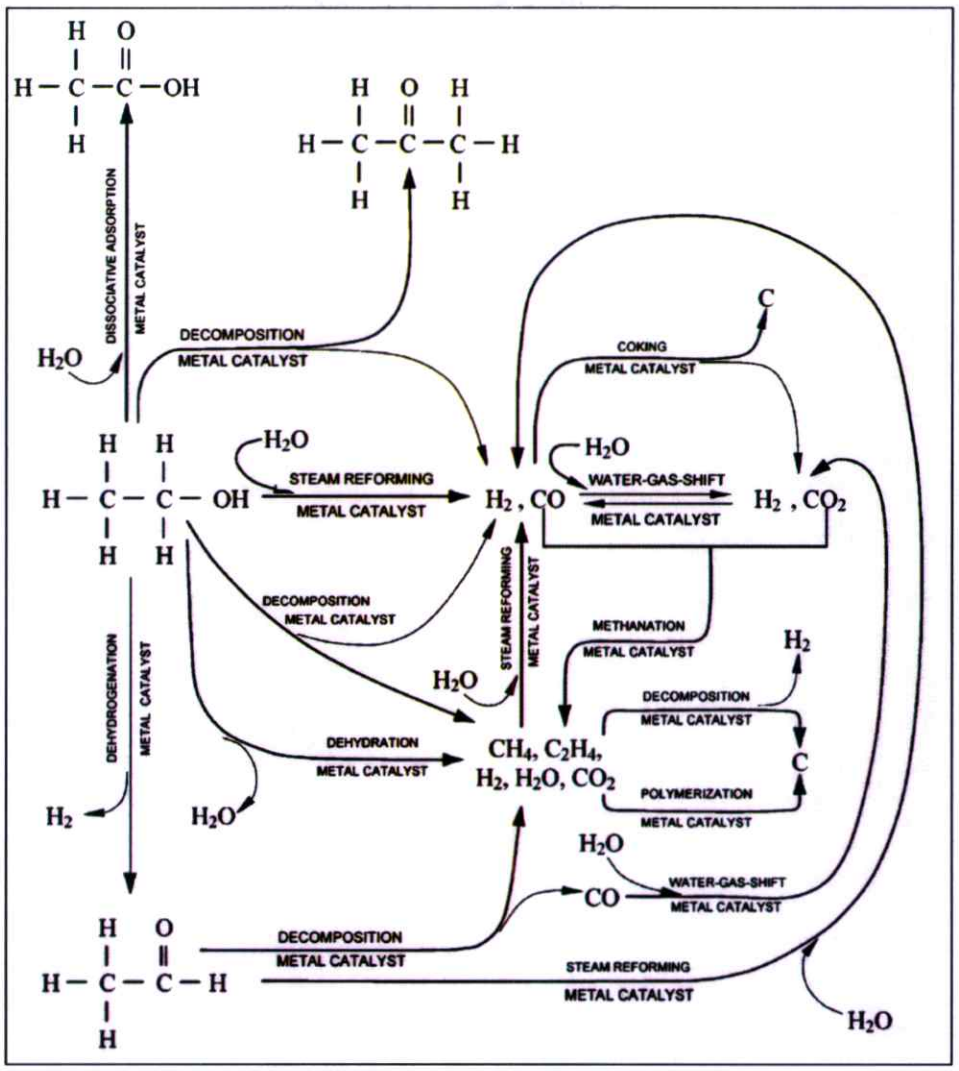


Figure 2.3 Reaction pathways that can occur during ethanol steam reforming over metal catalysts (Agus Haryanto 2005)

4) C_2H_5OH decomposition to acetone (CH_3COCH_3), followed by steam reforming (Sheng and Idriss 2004):

Decomposition: $$2C_2H_5OH \rightarrow CH_3COCH_3 + CO + 3H_2 \qquad (2.20)$$

Steam reforming: $$CH_3COCH_3 + 2H_2O \rightarrow 5H_2 + 3CO \qquad (2.21)$$

5) Steam reforming of C_2H_5OH to syngas ($CO + H_2$) (Deluga, et al. 2004):

Steam reforming: $$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \quad (2.22)$$

6) Water gas shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2.23)$$

7) Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2.24)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2.25)$$

8) Coking from the decomposition of CH_4:

$$CH_4 \rightarrow 2H_2 + C \quad (2.26)$$

9) Coking from the Boudouard reaction:

$$CO_2 \rightarrow O_2 + C \quad (2.27)$$

10) Dissociative adsorption of water to form acetic acid (CH_3COOH) (Marino, et al. 2004):

Water adsorption: $$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2 \quad (2.28)$$

The purpose of the reforming processes is to obtain as much as possible of H_2 and CO_2 by cracking C_2H_5OH in the presence of steam over a catalyst. However, from the reaction scheme, it is clear that the overall reaction is very complex and involves

several potential products. Therefore, it is important to reduce the production of undesirable intermediate compounds. Reactions to avoid are those that lead to C_4 species and C_2H_4. The presence of C_2H_4 especially hinders the overall H_2 production reaction by inducing the pathways toward carbon production reaction and thus causing "coking" of the catalyst (Amphlett, et al. 1998).

Typically, a reforming process including with three main steps which are: steam reforming, WGS, and purification, as described in Figure 2.4.

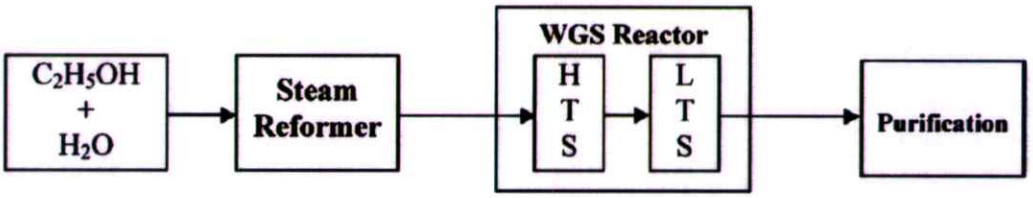


Figure 2.4 Scheme of steam reforming of ethanol. (Legend of abbreviations: WGS, water-gas shift; HTS, high-temperature shift; and LTS, low-temperature shift.) (Agus Haryanto 2005)

2.3.3.1 Steam Reforming

Steam reforming is the first step of the hydrogen production process. The process occurs with a catalyst at a temperature of ~ 1023-1073 K. In this stage, C_2H_5OH is introduced into a reformer or reactor, where the liquid is thermochemically broken down into shorter-chained carbonaceous species. These compounds would react with steam over the catalyst to produce a mixture of hydrogen and other compounds, such as carbon monoxide (CO), CO_2, C_2H_4O, C_2H_2, or CH_3COCH_3. Conversion of C_2H_5OH to H_2 may occur through the reactions depicted below:

$$C_2H_5OH + H_2O \Leftrightarrow CH_4 + CO_2 + 2H_2 \quad (\Delta H^\circ_{298} = 51.3\ kJ/mol) \quad (2.29)$$

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (\Delta H^\circ_{298} = 206.2\ kJ/mol) \quad (2.30)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (\Delta H^\circ_{298} = -41.2\ kJ/mol) \quad (2.31)$$

2.3.3.2 WGS Reaction

Almost all catalysts used for the steam reforming of C_2H_5OH produce CO (Frusteri, et al. 2004). The WGS reaction is an important step in the reforming process. During the WGS reaction, CO is converted to CO_2 and H_2 through a reaction with steam over a catalyst. CO is poisonous to the noble-metal catalysts, and therefore, the formation of CO is typically reduced by performing the reaction in excess steam. At the end of the WGS reaction, the CO concentration is between 0.5 mol % and 1 mol %. The chemical reaction for WGS is demonstrated in the reaction (2.31). This reaction is the basis for most industrial hydrogen production in the world. The WGS reaction is reversible, and, therefore, the reaction equilibrium shifts to the right and provides the formation of H_2 and CO_2 as products at lower temperature. At higher temperatures, the equilibrium shifts to the left, limiting the complete conversion of CO.

Normally, WGS reactors use metallic catalyst in a heterogeneous gas-phase reaction with CO and steam. Although equilibrium favors formation of products at lower temperatures, the reaction kinetics is faster at higher temperatures. Consequently, the catalytic WGS reaction is performed in two steps: high-temperature shift (HTS) and low-temperature shift (LTS). The HTS reactor generally operates at temperature of 623-643 K. To achieve higher conversions of CO to H_2, the gas leaving the HTS reactor is then cooled to 473-493 K and passed through a LTS reactor. Thereby, ~ 90% of the CO is converted to H_2 in the first HTS reactor and 10% of the remaining CO is converted in the LTS reactor.

2.3.3.3 Purification

Further reduction in the amount of remaining CO from the reforming can be achieved by catalytic methanation. Methanation reactor converts any residual carbon oxides back to CH_4 so that CO concentration becomes < 10 ppm. Note that H_2 would be consumed for the process, and the chemical reactions are shown below.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (\Delta H°_{298} = -251\ kJ/mol) \qquad (2.32)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (\Delta H°_{298} = -253\ kJ/mol) \qquad (2.33)$$

In addition to methanation, other methods could be used to purify H_2, such as pressure swing adsorption, cryogenic distillation, or membrane technology in which ~ 99.9% purity of H_2 can be produced, so that methanation is no longer needed (Adhikari and Fernando 2005).

The three processes i.e. steam reforming, WGS, and methanation—may occur simultaneously in a single steam reforming reactor (reformer), depending on the type of catalysts used. Different catalysts lead to different reaction pathways and different effluent compositions (Agus Haryanto 2005).

2.4 Porous media Burner

For hydrogen production from steam reforming process, a furnace design is one of the most important steps as expected to obtain the required temperature of about 700-900°C. It is required that the temperature should be evenly distributed within a specified region in order to maintain optimum condition for the catalytic reaction. Porous media material has an ability to absorb uncertainty of thermal loading of the raw gas, ability for heat retention and mixing buffer in the combustion process.

With this technology, the combustion taking place within the cavity of porous matrix can be stabilized under wider operating conditions. Accordingly, thermal NO_x is relatively lower compared to the conventional free flame combustion due to lower combustion temperature.

Previous literature pointed out the performance of the burner on ignition process. The ignition process can be discussed in three steps. 1) During a startup period ignition takes place within the flammability area. 2) After a porous domain is heated up to an auto-ignition temperature of a fuel, the gas mixtures is self-ignited, and 3) When the furnace temperature is heated up to the required temperature, mixture under rich

condition is fed at the bottom of the furnace; as a complete combustion with an additional stage air at the top area of a reactor is expected. Then significant heat from downstream is fed back to upstream region with heat transfer modes of radiation and conduction through the porous matrix (Jarruwat Charoensuk 2011).

CHAPTER 3

EXPERIMENTAL PROCEDURE AND EXPERIMENTAL SETUP

The experimental setup of hydrogen production from ethanol steam reforming mainly consists several steps as follows: the study of H_2 production reactor design concepts, mechanical design and installations of the hydrogen production unit, and search for the optimum operating conditions of hydrogen production unit. This study has investigated the mass and energy conservation of hydrogen production from ethanol steam reforming by collecting all data from an experiment on pilot scale of the hydrogen production unit.

In the first step, hydrogen production reactor design-concept studies are based on the simulation results from COMSOL program (Chemical Reaction Engineering Module). The optimum dimension of hydrogen production reactor is the one which can produce high yield of hydrogen product.

The second step, the simulation results are applied into the mechanical design process of the reactor. Mechanical and manufacturing designs are carried out using CATIA computer aided design (CAD) program; while, piping system diagram and unit components layout are made by using Microsoft Visio.

In the next step, after all reactor and unit components are installed, several experiments would be carried out to find suitable operating conditions of porous media burner by using LPG as a fuel. The porous media type of burner is applied to be a heat source for the steam reforming and water gas shift reactions in the hydrogen production process. The purpose of the experiments on the burner is to obtain the required temperature of about 700-900 °C with low exhaust gases emission in the startup and long term-operation periods.

The last step, long term operation of 100 hours of the hydrogen production from ethanol steam reforming is conducted using the optimum operating condition, then the energy conversion of all sub-units are determined whether they are

worthwhile or not for the hydrogen production system using ethanol steam reforming process.

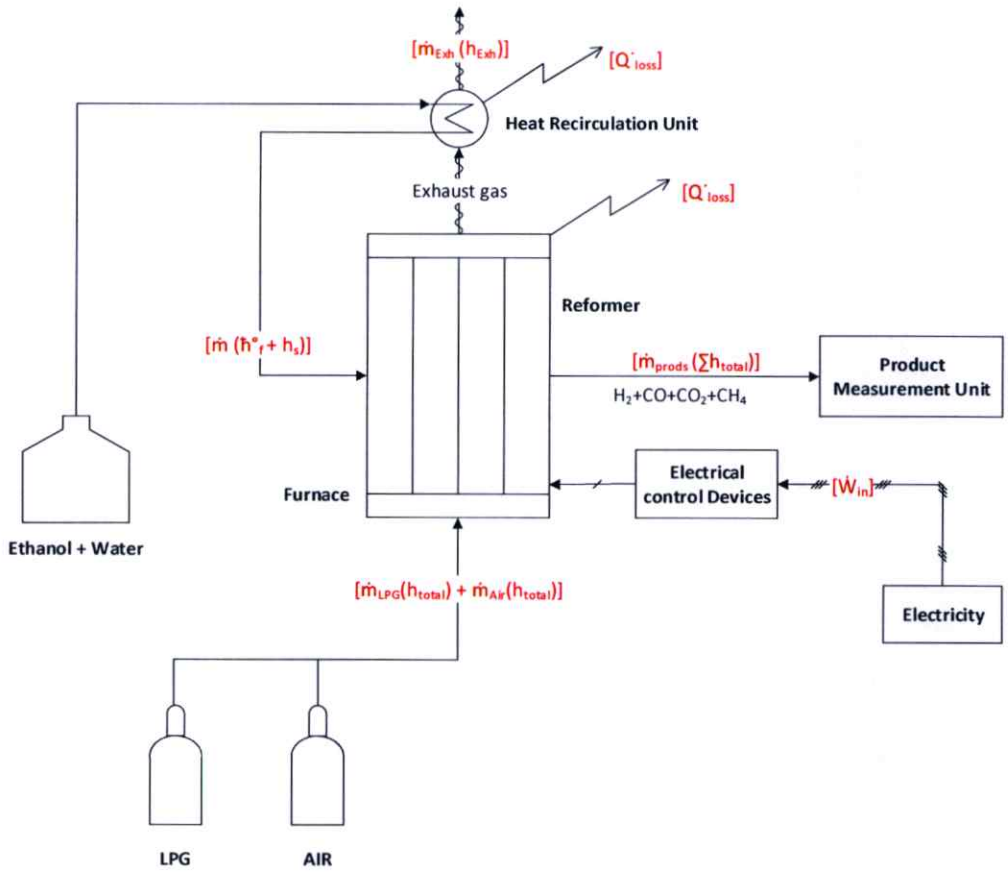


Figure 3.1 Hydrogen production from ethanol steam reforming system diagram

3.1 Hydrogen production reactor design-concept study

The hydrogen production design was based on hydrogen production from ethanol steam reforming lab scale results and chemical reaction simulation results. The main purpose is to find a design which can provide the highest yield of hydrogen production.

The simulation is conducted by using COMSOL program (Chemical Reaction Engineering Module) by (Jiwanurak 2014).

3.1.1 Sketch design

Several designs of the reactors were assessed by simulations of chemical reaction models. Figure 3.2 shows 2 types of the hydrogen production reactor created for the chemical reaction simulations.

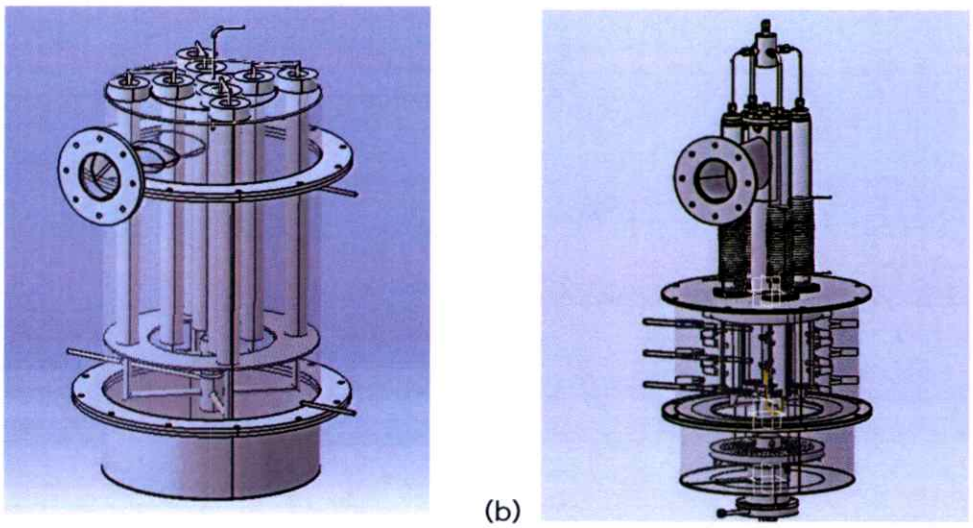


Figure 3.2 (a) Horizontal Cannula reactor design, (b) Vertical Cannula reactor design

Figure 3.2, (a) shows the Horizontal Cannula reactor design of hydrogen production reactor; 4 inner tubes are ethanol steam reforming (ESR) reactors, and the other 4 outer tubes are the water gas shift (WGS) reactors. The design is based on a criteria of heat transfer, by 4 ESR tubes receiving high heat at around 700-900°C from porous media burner at the inner area of the furnace. Then the reaction of WGS is continued in the outer section (see Figure 3.2(a)) thus receiving heat radiated from the inner zone.

Figure 3.2, (b) is the Vertical Cannula reactor design. The ESR and WGS reactors are designed to be attached together in vertical direction. This design criteria is to achieve a smaller size of reactors than the Horizontal one, while high yield of hydrogen product is obtained. The design includes 4 ESR tubes which are inserted inside the porous media domain at the bottom part of furnace, to receive high amount of heat (around 700-900°C). Then, the WGS reaction is continued in the upper part of

reactor. To achieve this, the middle part is equipped with a temperature control system to reduce the temperature after ESR to be appropriate for WGS reaction at around 250-400 °C.

3.1.2 Computer Simulation

The simulation results demonstrate that the vertical reactor (Figure 3.2(b)) can provide higher yield of hydrogen product than the horizontal one, although its overall size is smaller; the comparison of some simulated results are presented in Figures 3.3 – 3.6.

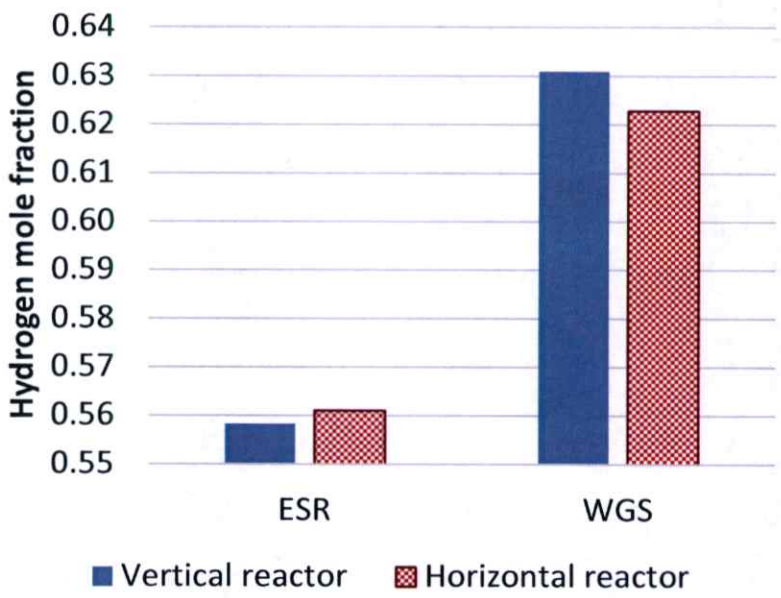


Figure 3.3 Hydrogen (product) mole fraction comparison between Vertical & Horizontal reactors

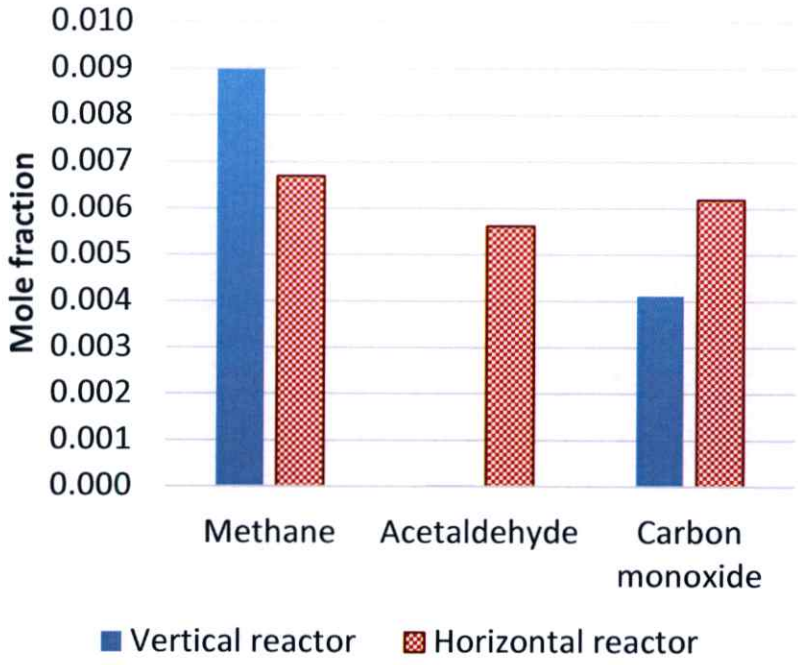


Figure 3.4 Other product comparison between Vertical & Horizontal reactors

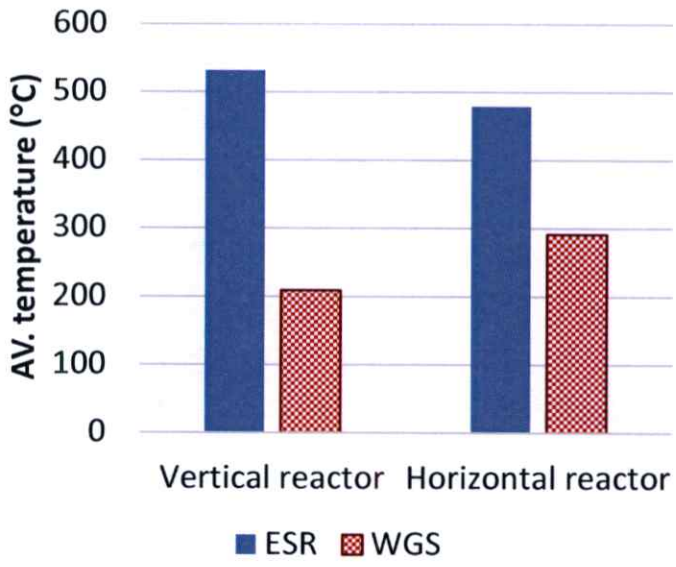
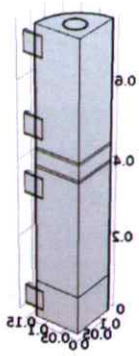


Figure 3.5 Average temperature of ESR & WGS reactions comparison between Vertical & Horizontal reactors



	Vertical reactor	Horizontal reactor	Unit
Diameter	240.644	481.288	mm
Height	750	400	mm
Volume	0.0341	0.0728	m^3
	34.11	72.77	L

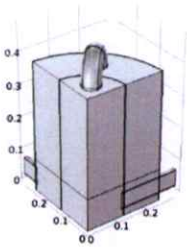


Figure 3.6 Dimensional comparison between Vertical & Horizontal reactors (Jiwanurak 2014)

After obtaining the most appropriate design concepts of the hydrogen production reactor, the simulation program was then performed to determine the most appropriate dimension of the vertical reactor which can produce the highest yield of hydrogen product and also matching with the laboratory facilities that we have i.e. an 48 mm ID/ 53 mm OD-Inconel stainless steel tubes which are currently adopted for raw material for the steam reforming reactors. Figures 3.7 – 3.11 show the simulation data and details of the most appropriate hydrogen production form ethanol steam reforming (which matches with our laboratory facility).

Figure 3.7-3.8 show the simulation results of hydrogen production in the area of ESR reaction to find the most appropriate length of the reactors. In Figure 3.7, the graph presents mole fraction of hydrogen products which obtained from varied length of ESR reactors. The results show that longer reactor length can provide greater value of hydrogen mole fraction.

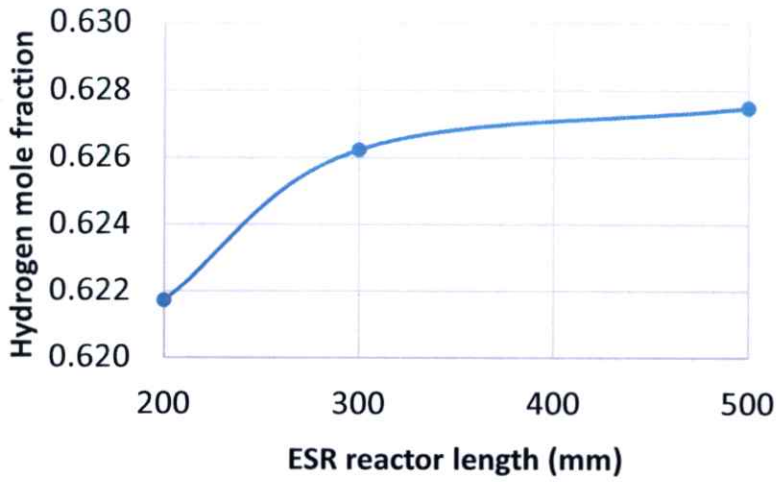


Figure 3.7 Mole fraction of hydrogen products at varied length of ESR reactor

Figure 3.8 demonstrates the mole fraction of methane, acetaldehyde, and carbon monoxide which obtained from varying length of ESR reactors.

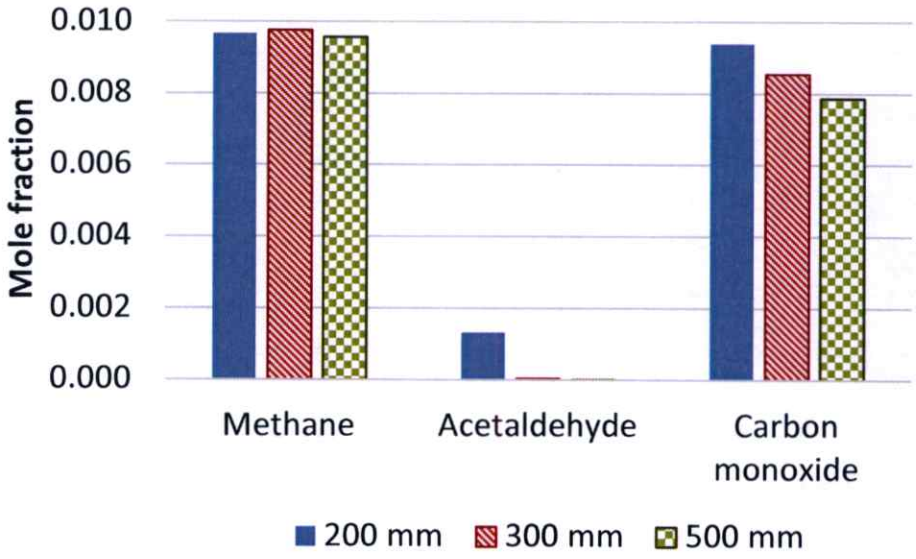


Figure 3.8 Mole fraction of ESR reaction products (besides hydrogen) at varied length of ESR reactor

From Figures 3.8-3.9, the results show that longer ESR reactors can provide higher yield of hydrogen mole fraction. Anyway, the graph in Figure 3.7 presents that the hydrogen mole fraction is drastically increased when increasing the reactor length from 200 to 300 mm, then become saturated when increasing from 300 to 500 mm. From these events, the highest yield of hydrogen could be obtained when 500 mm length of the reactor is designed. However, since the hydrogen yield of ESR at 500 mm is higher just only ~ 0.0015% compare to that with the length of 300 mm. Therefore, the reactor's length of 300 mm is selected (for all 4 reactor tubes) so that the unit is more compact.

The simulation result of the WGS reaction is shown in figures 3.9-3.10. In Figure 3.9, the mole fraction of hydrogen products obtained from various lengths of the WGS reactors are shown. The results also show that longer reactor length can provide higher number of hydrogen product mole fraction similar to the results of the ESR.

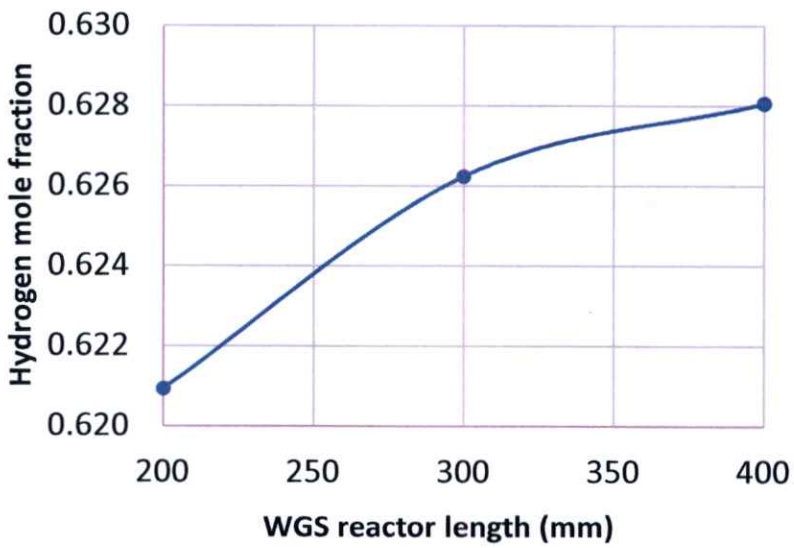


Figure 3.9 Mole fraction of hydrogen products at varied length of WGS reactor

Figure 3.10 presents mole fractions of carbon monoxide and carbon dioxide which are other products of WGS reactions. The graph shows that the longer reactor length can provide greater value of carbon dioxide, but lesser amount of carbon monoxide which is reasonable for the characteristic of WGS reaction.

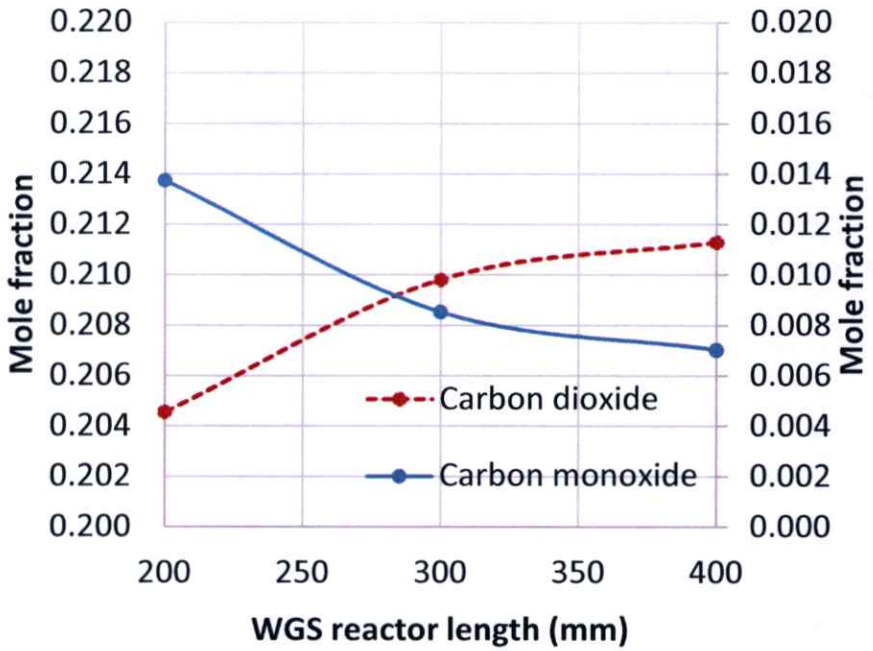


Figure 3.10 Mole fraction of CO and CO_2 at varied length of WGS reactor

From the results in Figures 3.9 – 3.10, the highest yield of hydrogen and lowest yield of carbon monoxide could be obtained when 500 mm long of the reactor is designed. However similar to the case of ESR, the length of 300 mm is selected for the unit to be compact, while the hydrogen yield and remaining carbon monoxide and carbon dioxide are only <0.002%-lower and <0.002%-higher respectively compare to the length of 500 mm.

Moreover, further simulation results are also achieved such as insulation thickness of the furnace, Air gap area (the area between ESR and WGS), and ethanol molar flow rate. All final simulation results are presented in Table 3.1.

Table 3.1 Parameters of hydrogen production from ESR and WGS reactor obtained from COMSOL simulation program

Parameter	Value	Unit
Chamber inner diameter	235	mm
Chamber outer diameter	241	mm
Reactor inner diameter	47.5	mm
Reactor outer diameter	53.5	mm
ESR reactor length	300	mm
WGS reactor length	301	mm
Insulation thickness	100	mm
Air gap height	50	mm
Ethanol molar flow rate	0.0035	mole/s

(Jiwanurak 2014)

3.2 Manufacturing Design of Hydrogen Production Unit

In this study, a computer aided design (CAD) program is used for 3D sketch design and manufacturing drawing of the reformer, sub-unit components, and also measurement-devices layout.

The hydrogen production unit can be separated into 6 main sub-units which are 1) reformer unit, 2) combustion gases supply unit, 3) raw material feeding unit, 4) utility-gases unit, 5) cooling system unit, and 6) product measurement unit.

3.2.1 Reformer

The reformer is designed based on the chemical reaction-simulation results and heat transfer principle. The reformer unit can be separated into two main parts which are porous media furnace, and reforming reactors.

3.2.1.1 Porous media furnace

The furnace is based on the fuel combustion which uses LPG as a fuel. This furnace is a kind of porous media burner which is packed with the 20 ppi – 20x20x20 mm^3 – Silicon carbide (SiC) ceramic foam. The combustion chamber of the furnace has an inner diameter of 290 mm and 295 mm high.

The air input has 3 stages which are 1^{st} air stage inlet feeding air at the bottom of the furnace. It has the highest mixing rate of all stages because the air is mixed with LPG directly at the bottom of the furnace.

The 2^{nd} air stage inlet is located at 210 mm from the bottom. Its design concept is for being a secondary air supply. The mixture is expected to have a slow mixing rate and burned completely at the middle area of combustion chamber.

The 3^{rd} air stage inlet is located at the bottom side area of the furnace, then flow through a ceramic air-distributor plate and meet a premixed mixture at 175 mm from bottom of the furnace. This is expected that the 3^{rd} air would be distributed through an air-distributor plate, and then mixed with a rich condition premixed fuel at the early bottom area of combustion chamber. By slow mixing rate of mixture; this would lead the combustion to occur at around middle and top areas of the chamber.

Porous media furnace diagram and air-stages locations are shown in Figures 3.11 and 3.12, respectively.

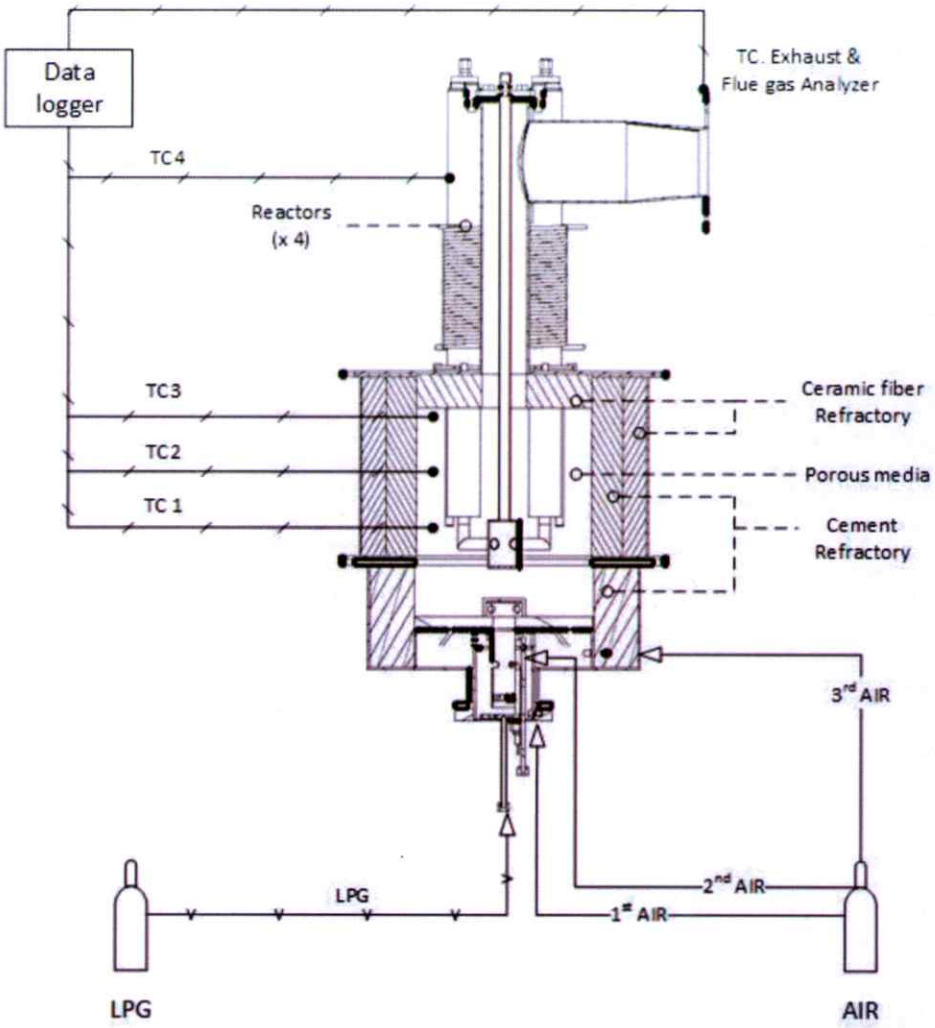


Figure 3.11 Porous media furnace diagram

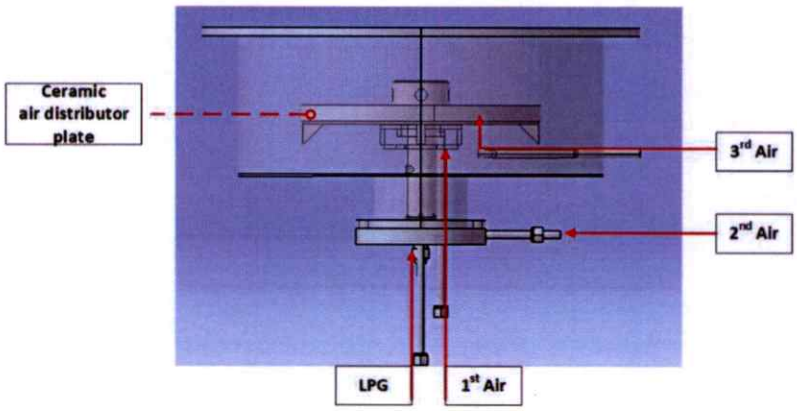


Figure 3.12 Air-stages locations on the furnace

3.2.1.2 Reforming reactors

The reforming reactor is an appliance used in the hydrogen production process. In the process, ethanol is converted to hydrogen by ethanol steam reforming (ESR) and water gas shift (WGS) processes. In the ESR process, the reactions are shown in Reactions (3.1), and (3.2).

ESR: $C_2H_5OH + H_2O \Leftrightarrow CH_4 + CO_2 + 2H_2$ *($\Delta H°_{298}$ = 51.3 kJ/mol)* (3.1)

$CH_4 + H_2O \Leftrightarrow CO + 3H_2$ *($\Delta H°_{298}$ = 206.2 kJ/mol)* (3.2)

WGS: $CO + H_2O \Leftrightarrow CO_2 + H_2$ *($\Delta H°_{298}$ = -41.2 kJ/mol)* (3.3)

Overall: $C_2H_5OH + 3H_2O \Leftrightarrow 2CO_2 + 6H_2$ *($\Delta H°_{298}$ = 216.3 kJ/mol)* (3.4)

For the ESR products, CO reacts with H_2O in the water gas shift reaction as shown in Reaction (3.3). Therefore, the theoretical overall reaction in the reformer unit is shown in Reaction (3.4) which is based on an endothermic reaction.

A 3-D model of the reactors is shown in Figure 3.13. Each reactor can be separated into 3 zones by longitudinal distance which are: ESR, Cooling, and WGS zones respectively from bottom to top of each reactor.

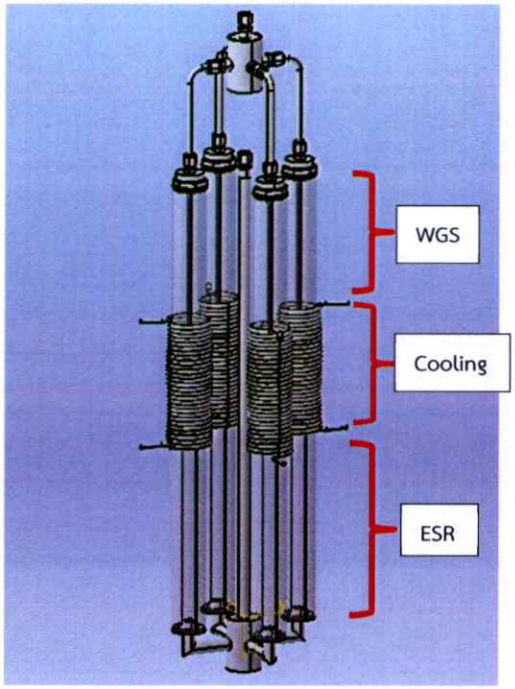


Figure 3.13 3D model of hydrogen production reactors

The ESR zone is located inside the combustion chamber of the furnace (see Figure 3.11) to obtain a heat from LPG combustion inside porous matrix for fulfilling the required temperature of ESR reaction at around 700-900°C.

The middle area of each reactor is called Cooling zone. The zone is an area where the ESR-reaction temperature is cooled down to be around 300-400°C. The purpose of this zone is to arrange the temperature of the reaction inside each reactor to be suitable for a required temperature of a WGS reaction. The design of the cooling area is based on heat exchanger design principle, by a ¼" Ø- copper tube is spiraled around each reactor at 275 mm to 480 mm from the bottom of a reactor, then water is fed inside each tube to be a heat transfer substance.

At the upper area after cooling zone, the hydrogen production temperature is expected to be around 300-400 °C which is a required temperature for WGS reaction, therefore the area is so-called WGS zone. The zone is the area which waste CO from ESR reacts with excess amount of H_2O as mentioned above. Physically, the WGS-zone reactors are wrapped by a ceramic fiber and insulation foil tape for the prevention of heat loss from the system to an environment.

3.2.2 Combustion-gases unit

Combustion-gases unit is a unit which control and supply gases for the porous media combustion. The gases are LPG and 3 stages of air as already introduced in the 3.2.1.1. For controlling of gas flow rate, EL-FLOW Base mass flow controllers (with rated accuracy ±1%FS), and Dwyer air rotameters (with accuracy of ±2%) are used to be gas control devices; Figure 3.14 presents system diagram of this unit. Laboratory's confidential measurement-unit

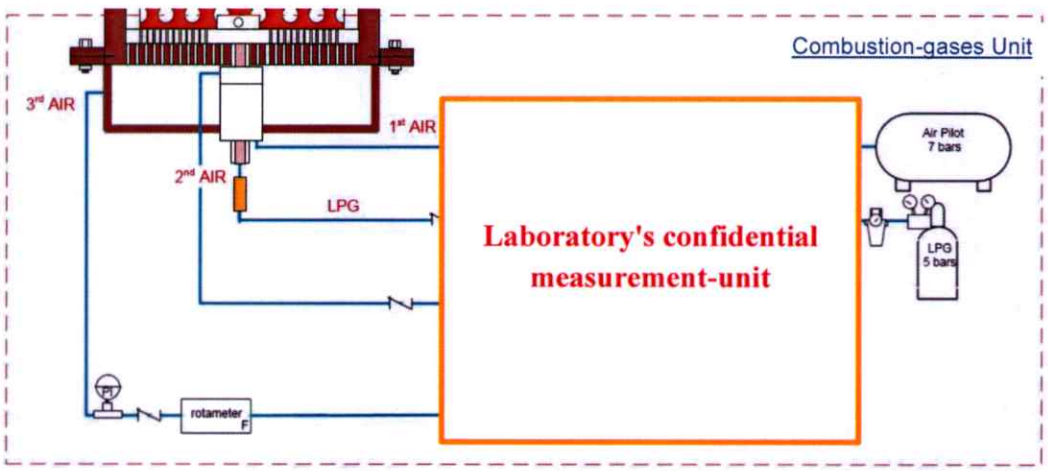


Figure 3.14 Combustion-gases unit system diagram

3.2.3 Raw material feeding unit

Ethanol mixed with water is a raw material for production of hydrogen in this research. An electromagnetic pump is used to feed the mixture raw material in to the reactors. KOFLOC-RX1200 rotameter for ethanol (with accuracy of ±2%FS) is located at the downstream of this unit to control a volume flow rate of the raw material input for the hydrogen production unit. The system diagram of the raw material feeding unit is shown in Figure 3.15. After this unit, the mixture was vaporized at the preheating furnace component called boiler before entering a reforming reactor.

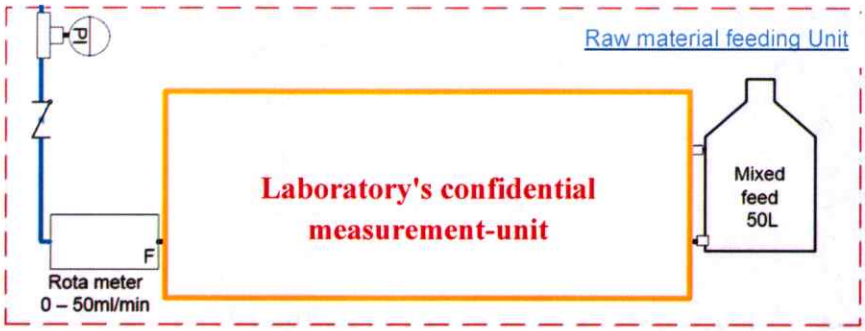


Figure 3.15 Raw material feeding unit system diagram

3.2.4 Utility gases Unit

Gases in this unit- which are hydrogen, zero air, and nitrogen- are utilized in the catalyst reduction, regeneration of coked catalyst, and unit flooding processes, respectively. The catalyst reduction and regeneration of coked catalyst is shown in Reaction (3.5)-(3.6). Figure 3.16 demonstrates the utility gases system diagram.

Catalyst reduction $$NiO_2 + 2H_2 \rightarrow Ni + 2H_2O \quad (3.5)$$

Regeneration of Coked catalyst $$C + O_2 + 3.76N_2 \rightarrow CO_2 + 3.76N_2 \quad (3.6)$$

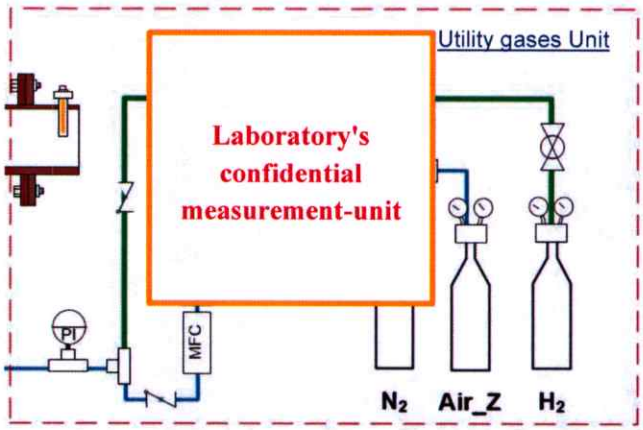


Figure 3.16 Utility gases unit system diagram

3.2.5 Cooling system Unit

As already introduced about the cooling zone in 3.2.1.2, Figure 3.17 shows a system diagram of the cooling system unit. Electric water pump is used for cooling the water feeding, then the KOFLOC water rotameter (with accuracy of ±6 %FS) is used for volume flow rate control of the water. After rotameter, the water is fed inside of each spiraled copper tube from the bottom side and come out at the top, see Figure 3.18.

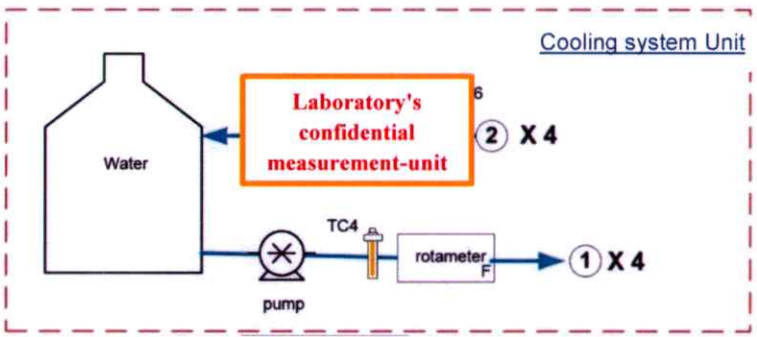


Figure 3.17 Cooling system unit system diagram

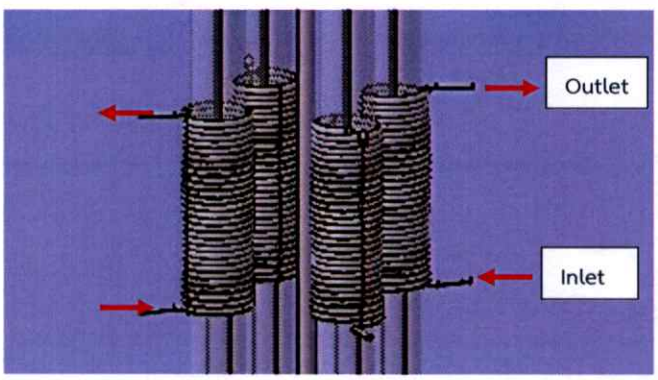


Figure 3.18 Flow direction of cooling water

50x45x5 cm3 radiator with cooling fan is utilized as a heat exchanger of this unit. Hot water, which come out from top end of the spiraled tube, is

continued to the radiator before flowing back to a water tank. Heat loss at the radiator can be calculated by a differential temperature before and after.

3.2.5 Products measuring Unit

This unit has the main purpose for measuring and analyzing compounds that can be vaporized without decomposition in total products of hydrogen production. EL-FLOW Base mass flow meter (with rated accuracy ±1%FS) is located at the downstream of the production unit to measure overall products volume flow rate. Then a gas chromatography (GC) is used in analytical chemistry for separating and analyzing compounds of all products, Figure 3.19 presents the products measuring unit diagram.

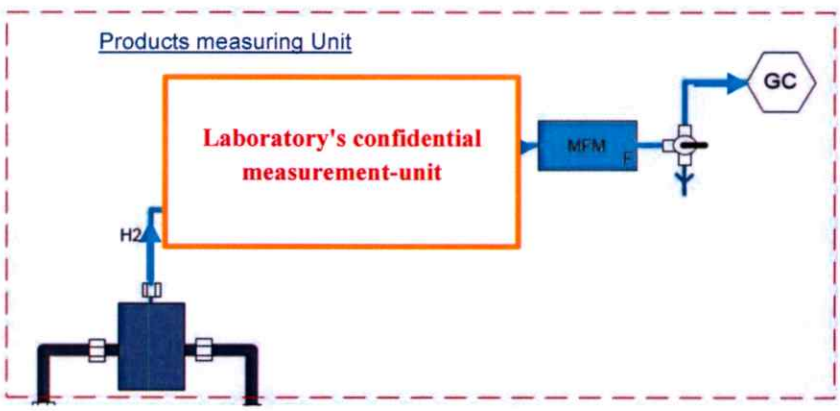


Figure 3.19 Products measuring unit system diagram

These sub-units—which are combustion-gases, raw material feeding, utility-gases, cooling system, and products measuring units— are connected with hydrogen production reformer by tubing fittings. The hydrogen production from ethanol steam reforming unit system diagram is presented in Figure 3.20.

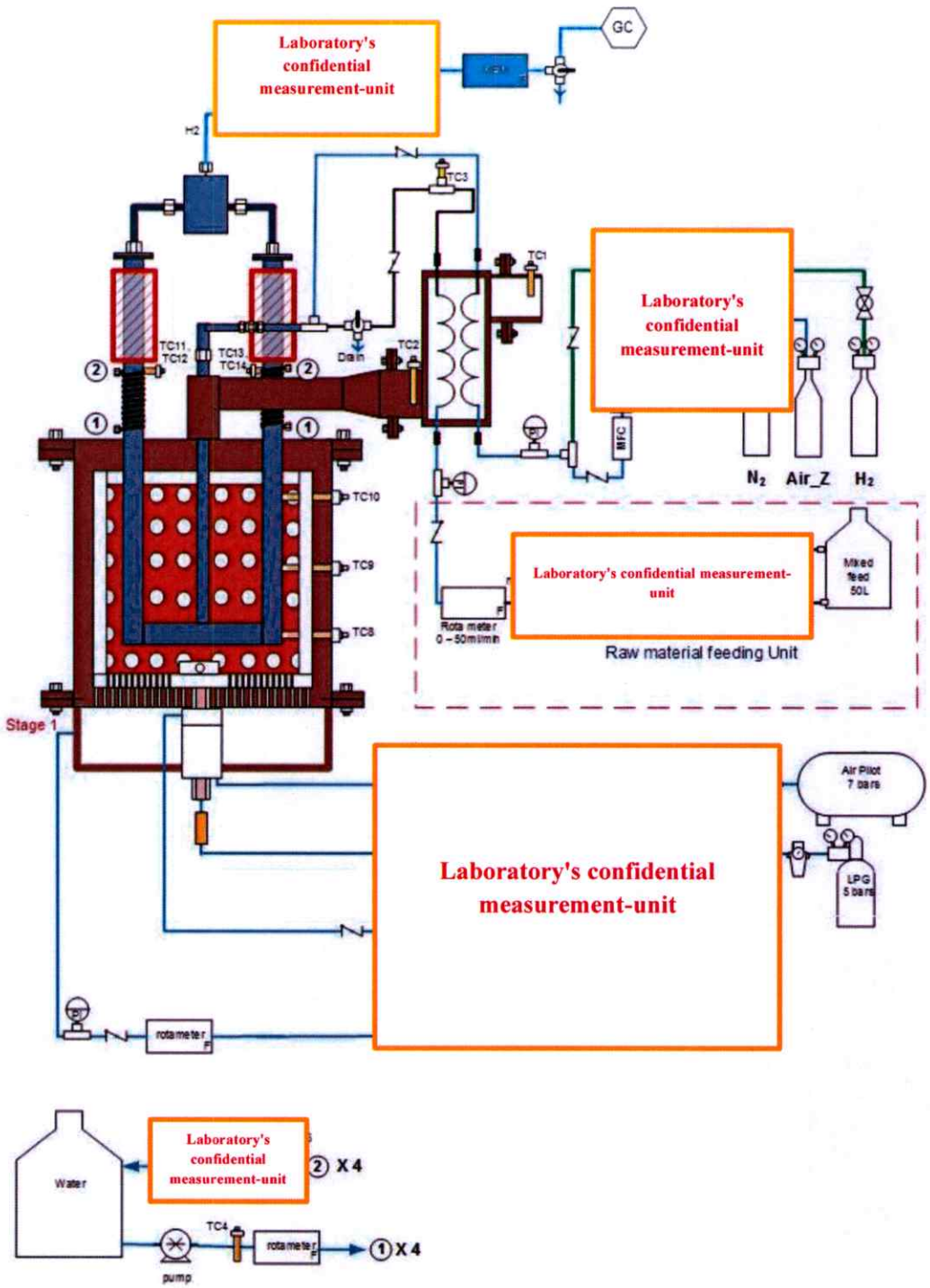


Figure 3.20 Hydrogen production from ethanol steam reforming unit system diagram (Thanathon Sesuk 2015)

3.3 Experimental Conditions of Hydrogen Production from Ethanol Unit

3.3.1 Experimental condition of porous media furnace

The 3 stages of air, and a stage of LPG are supplied at 5 bar for combustion which is performed in several operating conditions based on heat rate and limited exhaust emission of the furnace as shown in Table 3.3.

The heating rate from the furnace is a rate of temperature in the unit of °C/min. It is required to be less than 5 °C/min because of physically crack-ability of the catalyst matters. There are 4 positions of K-type thermocouples which are located at 297, 380, 462, and 927 mm height from bottom of the furnace (see Figure 3.11) for temperature monitoring along the vertical direction of the furnace.

For the emissions control CO, and NO_x are not to exceed 690, and 200 ppm, respectively (Ministry of Natural Resources and Environment of Thailand, 2006). The exhaust gas was measured by using a flue-gas analyzer (Testo 350-XL) which has an accuracy of the sensor as follows: ±0.3% O_2 for O_2 sensor, and ±5% of reading for other species. By measuring period the flue gas was at every 15 minutes in the start-up period, and every 30 minutes when the temperature is at steady state.

Table 3.2 Experimental condition

Time	Event	Air States				Fuel	A/F ratio
		1st state	2nd state	3rd state	Total Air	LPG	
(hour)		(SLPM)	(SLPM)	(SLPM)	(SLPM)	(SLPM)	(kg/kg)
0–2.5	1st	84.9	0.0	0	84.85	1.10	46.1
2.5–4.25	2nd	95.5	0.0	0	95.46	2.02	28.3
4.25–5.75	3rd	95.5	0.0	45	140.46	2.94	28.6
5.75–7.25	4th	95.5	0.0	70	165.46	3.49	28.4

Table 3.3 Emission results

Time	Event	Flue Gases (% Vol.)				
		O_2	CO	CO_2	NO	NO_2
(hour)		(%)	(ppm)	(%)	(ppm)	(ppm)
0–2.5	1st	20.42	54	-	0	0.00
2.5–4.25	2nd	7.71	235	8.73	81	11.20
4.25–5.75	3rd	7.53	558	8.85	92	4.00
5.75–7.25	4th	7.78	29	8.68	89	1.10

Table 3.4 Heating rate of the furnace

Time	Event	Heating rate		
		H.R.8	H.R.9	H.R.10
(hour)		(°C/min)	(°C/min)	(°C/min)
0 – 2.5	1st	2	0.4	0.6
2.5 – 4.25	2nd	3.6	2.3	1.8
4.25 – 5.75	3rd	5.7	4.9	3.5
5.75 – 7.25	4th	0.1	2.9	1.8

3.3.2 Operating condition of hydrogen production reactions

Hydrogen production reactions – which are ESR, and WGS – are performed on Ni based catalyst, by liquid ethanol mixed water is used as a reactant.

The catalysts are divided for particular purposes into two types which are catalysts for the ESR, and WGS reaction.

Lab scale experiments of catalysts testing and design were performed by (other co-worker). Varied operating temperature and composition percentages of Ni-based catalysts were tested on the condition of ESR reaction. At 800°C, the catalyst can provides the highest yield of hydrogen.

For WGS reaction, the experiment was performed at varied temperatures and compositions percentage of catalysts. As a result, at 350°C operating condition can provide the highest hydrogen yield.

After all, the lab scale results are used as baselines in the pilot-scale production of hydrogen from ethanol steam reforming. The operating condition for a production of 20 liters/minute hydrogen is as follows: S/C ratio of reactant = 2.5 (Theoretical) with volume flow rate of 20 mL/min (Appendix A); at 800°C, and 350°C for ESR, and WGS reactions respectively.

CHAPTER 4

EXPERIMENTAL RESULTS

These results are obtained from a pilot-scale hydrogen production from ethanol steam reforming unit at the National Metal and Material Technology Center (MTEC). The experimental apparatus and conditions have been introduced in previous chapter.

The results are measured from two main sub-unit components which are the experimental results of porous media furnace, and the reforming reactor.

4.1 Experimental results of Porous media furnace

The porous media furnace is required to generate heat around 700-900°C. To fulfill the required temperature of ESR reaction, the temperature should be evenly distributed within the specified region to maintain the optimum condition for the catalytic reaction. The input and output data is going to be used in the processes of energy conversion and unit energy assessment in the next chapter.

4.1.1 Input data

For the porous media furnace, LPG and air were supplied to the combustion. Five events of operating conditions were applied based on the optimum condition from previous experiments to obtain the required heat rates and low emissions.

The furnace was operated in lean combustion conditions. Air-Fuel ratio was set around 46 at the early state due to the overall furnace temperature was still low, then decreased to be about 28 to obtain a complete combustion of LPG which was monitored by using a flue gas analyzer. The A/F ratio used for the porous media-LPG combustion in this hydrogen production unit is presented in Figure 4.1.

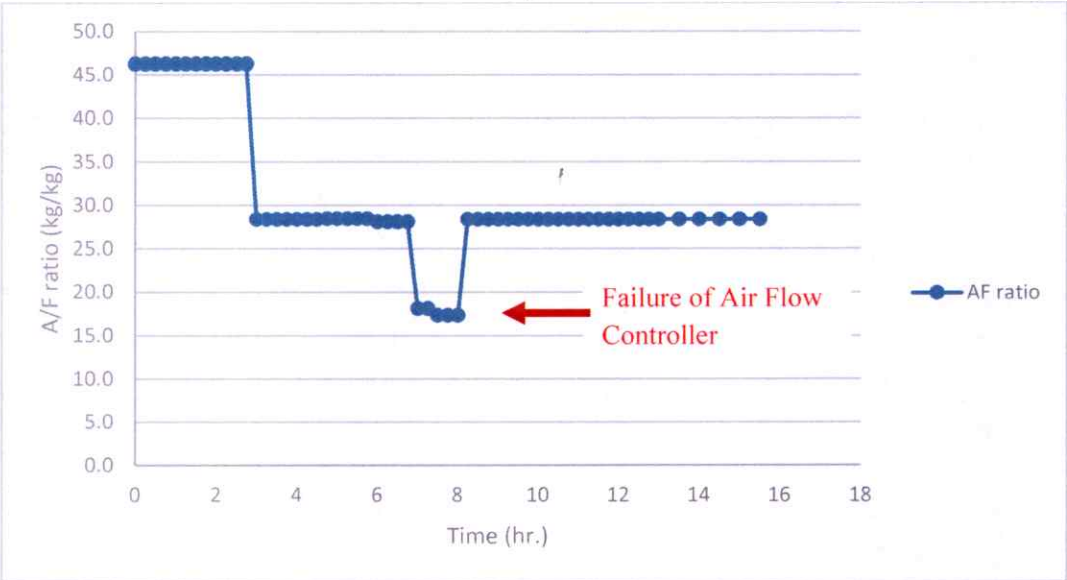


Figure 4.1 A/F ratio for the porous media-LPG combustion in hydrogen production unit

Table 4.1 shows the fuel and air conditions of the furnace from furnace startup up to the hydrogen production periods.

Table 4.1 Fuel and Air input condition

Time	Event	Air States				Fuel	A/F ratio
		1st state	2nd state	3rd state	Total	LPG	
(hour)		(SLPM)	(SLPM)	(SLPM)	(SLPM)	(SLPM)	(kg/kg)
0-3	1st	87.6	0.0	0	87.6	1.13	46.1
3 - 4.75	2nd	98.6	0.0	0	95.46	2.08	28.4
4.75 – 5.75	3rd	98.6	0.0	45	143.59	3.03	28.4
5.75 – 8.25	4th	98.6	0.0	70	168.59	3.59	28.1
8.25 – 15.5	5th	98.6	47.6	15	161.15	3.40	28.4

4.1.2 Output data

The output data are collected from operations of the porous media furnace. The results include 1) furnace temperature distribution, 2) heat rates along the vertical axis of the furnace, and 3) exhaust gas components which should not exceed 690, and 200 ppm for CO, and NO_x, respectively.

Figure 4.2 shows a temperature distribution inside the porous media furnace. The temperatures were expected to be about 700-900°C, then they were measured at three positions along the height of the furnace by using K-type thermocouples (see Figure 3.13).

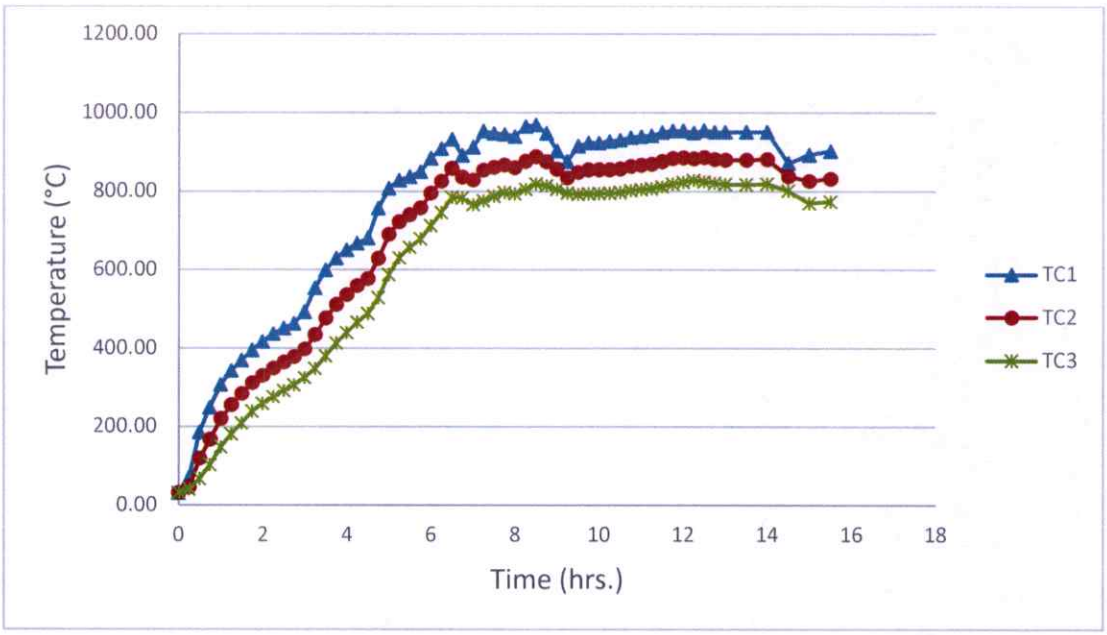


Figure 4.2 Porous media-LPG furnace temperature distribution

The heating rates are measured at the same positions as the furnace temperatures. They are expected not to exceed 5°C/min to avoid cracking of the catalyst. The heating rates along the entire height of the furnace is plotted in Figure 4.3.

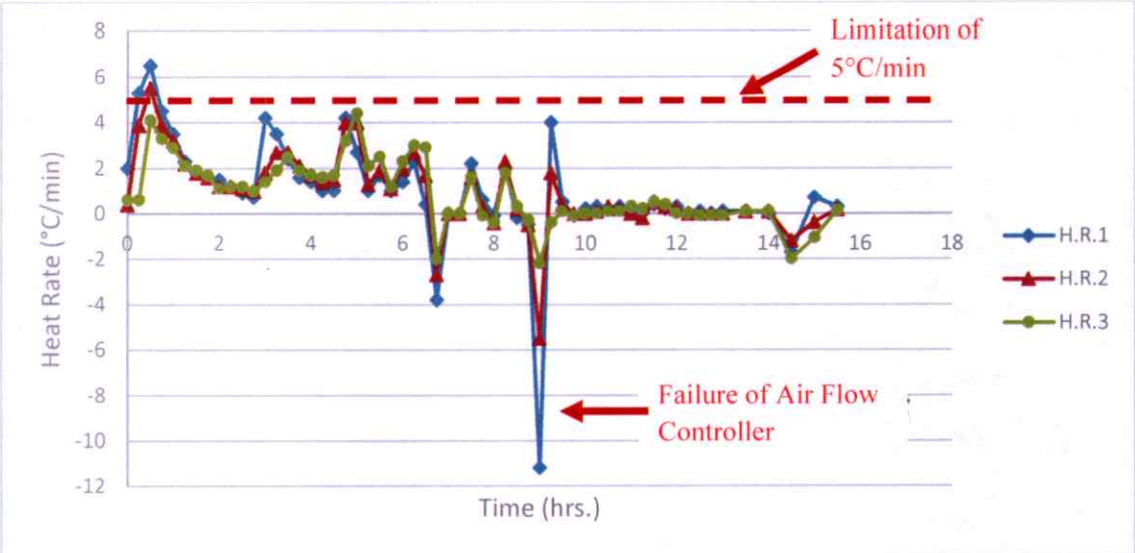


Figure 4.3 Heating rates at three positions along the entire height of the furnace

Figure 4.4 shows the results of CO composition in the exhaust gas which are analyzed using a flue-gas analyzer (Testo 350-XL). Actually, CO composition was expected not to exceed 690 ppm as indicated in previous experiment. In that case, the furnace were only heated up until reaching the required temperature for ESR reaction without any catalyst packing. However, for this hydrogen production experiment, the catalyst absorbed heat from the furnace, therefore the overall temperature was a little bit lower than in the previous testing. Because of too low temperature of the furnace for air-fuel adjustment, therefore the furnace provided a high amount of CO emission immediately after the A/F ratio was adjusted, but suddenly when the furnace temperature was high enough (about 15 minutes or a period of measurement) CO emission was decreased to the expected values.

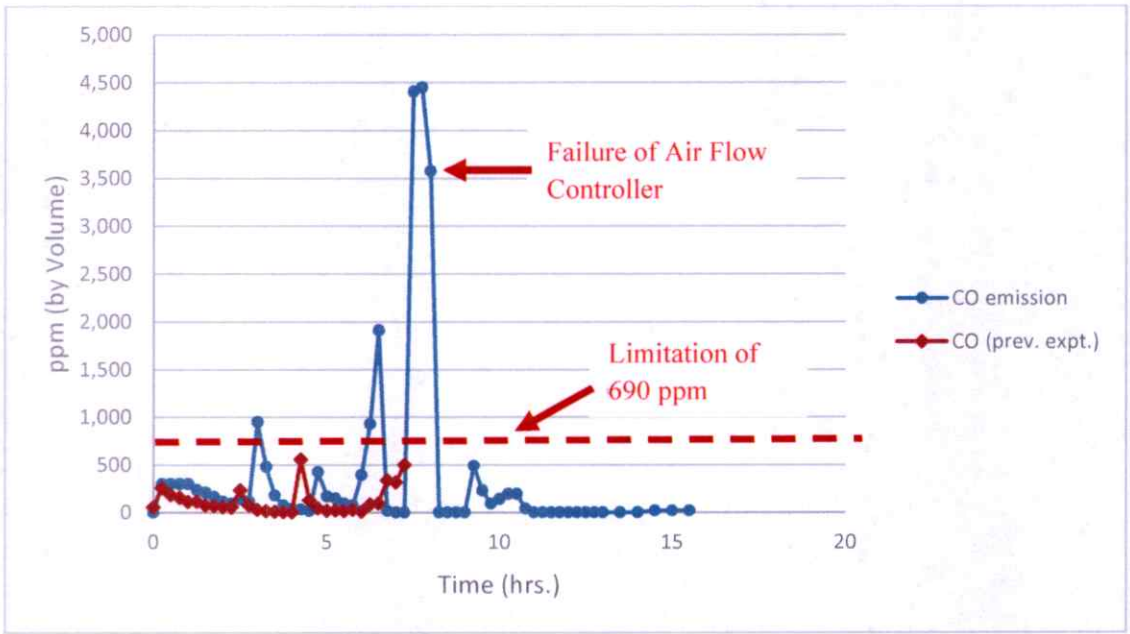


Figure 4.4 CO emissions from H_2 production furnace and the result from the previous experiment

The results of NO_x emission is shown in Figure 4.5. NO_x component in the exhaust gas is limited to below 200 ppm as set by the national environmental policy.

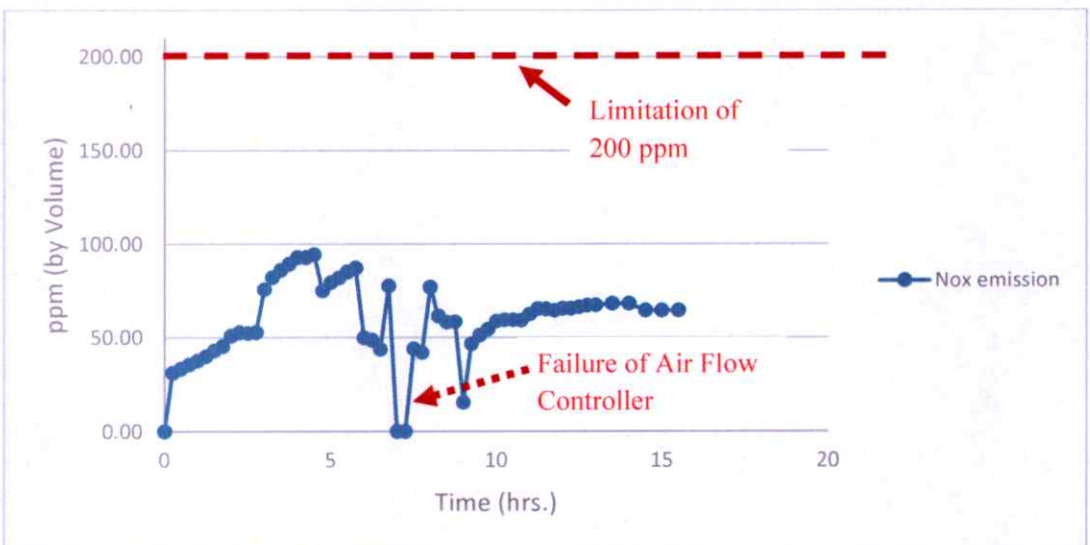


Figure 4.5 Heat rates at three position along entire height of the furnace

4.2 Experimental results of the Reforming reactor

The reforming reactor is packed with Ni-based catalysts which are separated into two zones i.e. ESR and WGS. Ethanol mixed with water at the S/C ratio of 2.5 was used as a reactant. To obtain hydrogen of 20 L/minute, the liquid reactant needs to be fed at 0.02 L/minute (Appendix A). The input and output data are used in the process of energy conversion and unit energy assessment in the next chapter. All data were recorded at 15 and 15.5 hours, then the unit was shut down.

4.2.1 Input data

For the hydrogen production, liquid ethanol mixed with water were supplied as a reactant of the reaction. From the mass balance equation, 0.02 liter/minute of liquid reactant is needed to produce 20 liters/minute of hydrogen gas, (for the 100% conversion of the catalytic reaction). The reactant flow rate was controlled by using KOFLOC-RX1200 ethanol rotameter. As a result, the reactant flow rate is not steady only at the early state because of a fluctuated pressure inside the reactors at the first time feeding. Figure 4.6 shows the reactant flow rate at 15 and 15.5 hours.

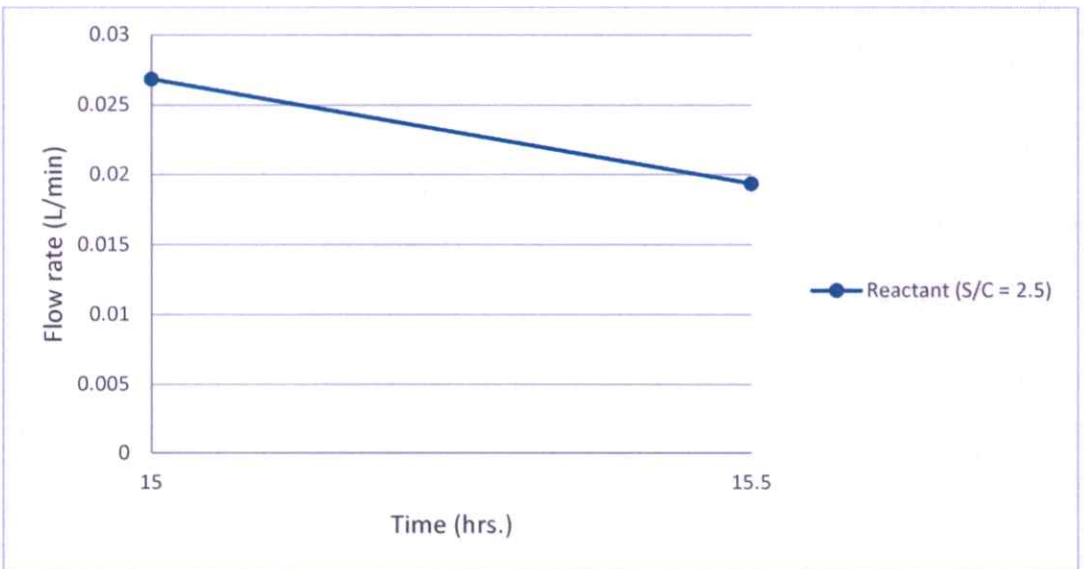


Figure 4.6 Reactant (Ethanol + Water) flow rate at S/C ratio = 2.5

4.1.1 Output data

The output data is collected from ESR and WGS reactions. A mass flow meter was used to measure the total product flow rates. In the next step, a gas chromatography (GC) was utilized in the product components analytical process. Finally, hydrogen and others products flow rate can be obtained by multiplication of total mass flow rate (L/min), and product components (% by Volume). Figure 4.7 presents the hydrogen product flow rate at two periods of measurement. As a result, the obtained hydrogen product is higher than expectation of 20 liters/minute. The reactant is a little bit higher than calculated values from the reason mentioned earlier.

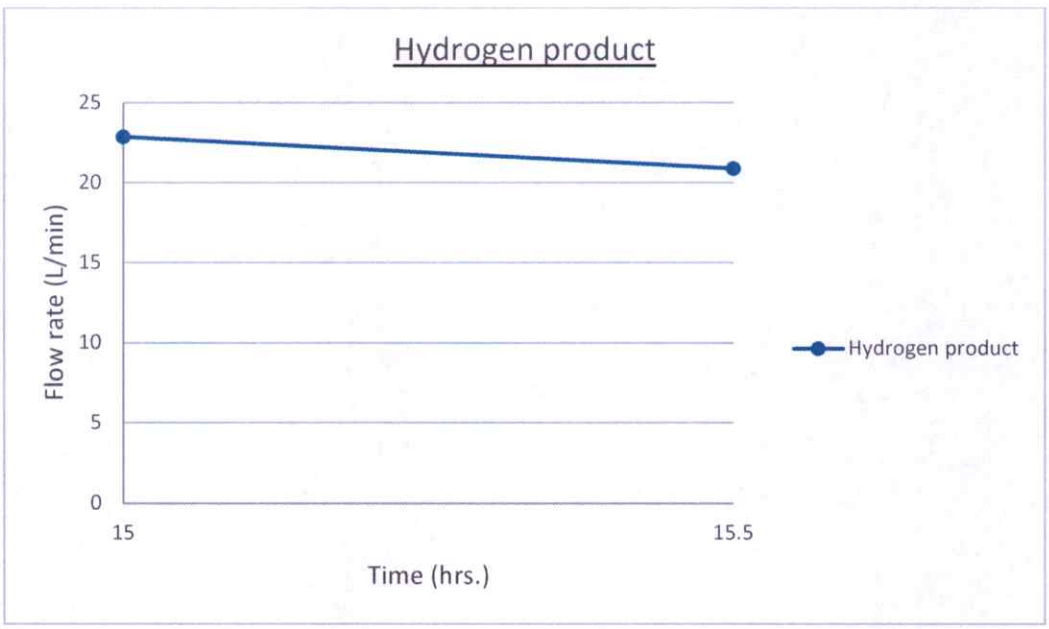


Figure 4.7 Hydrogen product flow rate

The product compositions analyzed by GC after 15 and 15.5 hours are shown in Figures 4.8 and 4.9, respectively.

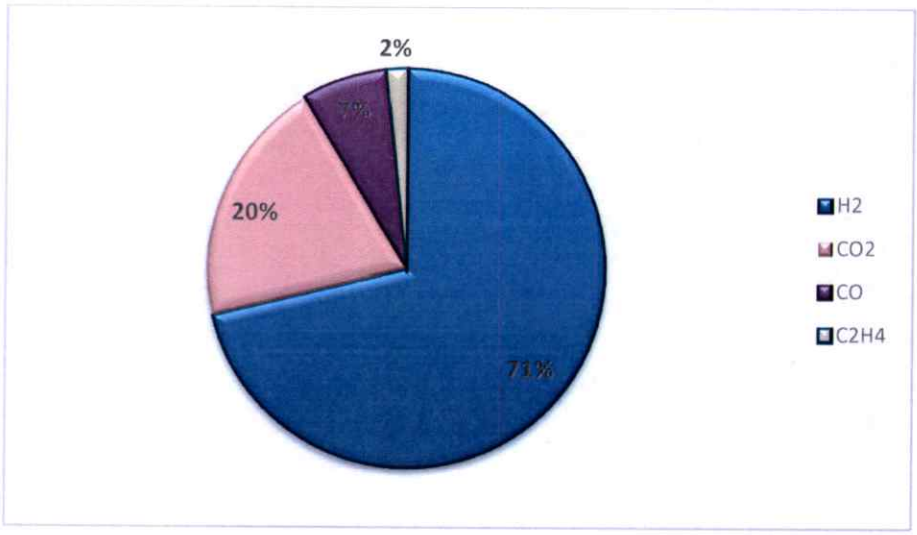


Figure 4.8 Product compositions after 15 hours.

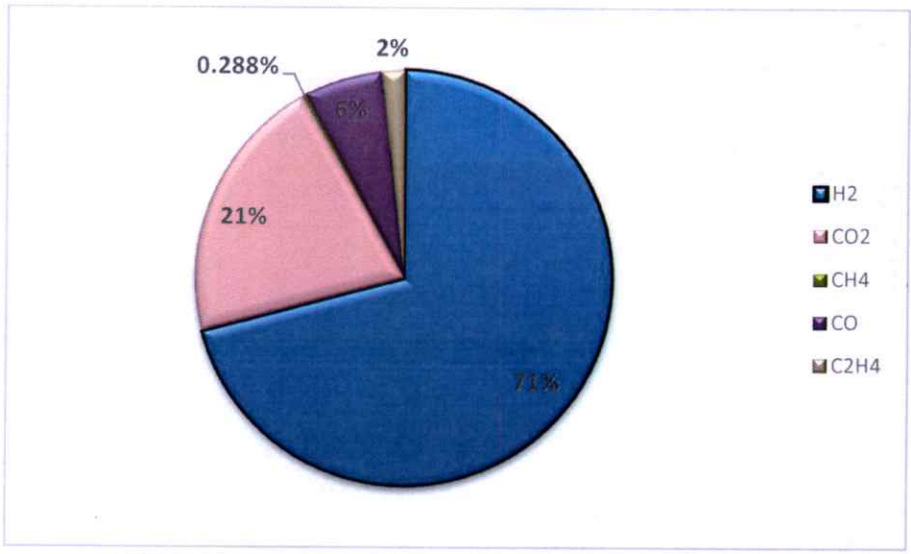


Figure 4.9 Product compositions after 15.5 hours.

After all, the experimental results will be used for calculation in the next chapter for: the energy conversion of sub-system, deviation from energy loss, and assessment of hydrogen production from ethanol steam reforming unit by comparing between theoretical and practical energy consumption.

CHAPTER 5

ENERGY CALCULATIONS AND DISCUSSION

Experimental results from the pilot-scale hydrogen production are used for calculation of an energy conversion of the unit. Theoretical energy consumption for production of 20 liters/minute hydrogen from ethanol steam reforming using a LPG combustion as a heat source is determined by an energy balance equation. A purpose of the calculations is to define an efficiency of the existing unit in order to produce hydrogen gas of 20 liter/minute, and also the energy efficiency of sub units. They are 1) reforming reactor, and 2) porous-media furnace.

5.1 Energy Consumption for the Hydrogen production unit

Theoretical and practical calculations of energy consumption to produce 20 liters/minute hydrogen are calculated by energy balance equation, under an assumption that the systems occur under a constant pressure.

5.1.1 Theoretical calculation

Theoretical energy consumption of the hydrogen production from ethanol steam reforming unit is calculated to determine a total amount of energy which is just enough to fulfill the theoretical requirement of 20 liters/minute hydrogen production. The calculation is divided into two parts i.e. reforming reactor, and porous media-LPG furnace.

5.1.1.1 Reforming reactor

The theoretical energy consumption of the reforming reactor is calculated based on stoichiometric equation of 2.5-S/C ratio reactant to produce 20 liter/minute of hydrogen. The chemical equation is shown in Reaction 5.1.

$$C_2H_5OH + 5H_2O \rightarrow 6H_2 + 2CO_2 + 2H_2O \qquad (5.1)$$

To produce 20 liters/minute at the standard temperature and pressure (STP), the reactant need to be supplied at 0.02 liter/minute at STP (Appendix A1). Equation 5.2 shows an energy balance equation of the reforming reactor, with $(\Delta \dot{E}_{Reforming})_{Theoretical}$ denoting the required energy for theoretical hydrogen production. $\Sigma \dot{E}_{Product}$ and $\Sigma \dot{E}_{Reactant}$ denote the respective total energies of products and reactants.

$$(\Delta \dot{E}_{Reforming})_{Theoretical} = (\Sigma \dot{E}_{Product} - \Sigma \dot{E}_{Reactant})_{Theoretical} \quad (5.2)$$

As a result, the hydrogen production from ethanol steam reforming requires 0.81 kW of energy input rate to produce the decided amount of hydrogen (Appendix A1).

5.1.1.2 Porous media-LPG furnace

The theoretical energy consumption of the porous media-LPG furnace is calculated to find an amount of LPG input rate enough to fulfill the energy requirement of 0.81 kW from the hydrogen reforming reactor. Table 5.1 shows properties of LPG (Petroleum Thailand Co., Ltd). The stoichiometric equation of LPG combustion is presented in Reaction 5.3.

Table 5.1 Properties of LPG (Petroleum Thailand Co., Ltd).

Properties of	Quantity	Unit
Proportional of Propane (C_3H_8) : Butane (C_4H_{10})	40 : 60	% by volume
Low heating value	45.8	MJ/kg
Density of gas 2.011 kg/m3	2.011	kg/m3

Volume of 1 kg Gas (at 1 bar) at 0°C	508	liter
Flame temperature	1925	°C
Ignition temperature with air	510	°C
Air fuel ratio (stoichiometry)	15.6	kg_{air}/kg_{fuel}

$$(0.4C_3H_8 + 0.6C_4H_{10}) + (5.9O_2 + 5.9(3.76)N_2) \rightarrow 3.6CO_2 + 4.6H_2O + 5.9(3.76)N_2 \quad (5.3)$$

Equation 5.4 shows an energy balance equation which state that 0.02 g/sec LPG provides enough energy rate to fulfill the requirement of 0.81 kW from the reforming reactor when the combustion is complete (Appendix A1).

$$\Sigma \dot{E}_{Requirement} = (\Sigma \dot{E}_{Furnace})_{Stoichiometric.} = (\Sigma \dot{E}_{Exhaust} - \Sigma \dot{E}_{LPG})_{Stoichiometric.} \quad (5.4)$$

$\Sigma \dot{E}_{Requirement}$ is the total energy requirement to fulfill the theoretical hydrogen reforming reaction. $(\Sigma \dot{E}_{Furnace})_{Stoichiometric.}$ is an amount of energy which should be supplied from the furnace. $\Sigma \dot{E}_{Exhaust}$ and $\Sigma \dot{E}_{LPG}$ are stoichiometric total energies released from an exhaust gas, and energies supplied from LPG, respectively of the furnace.

Finally, the theoretical energy-consumption equation of the hydrogen production unit can be presented in Equation 5.5, which is denoted by $(\Sigma \dot{E}_{Consumption})_{Theoretical}$.

$$(\Sigma \dot{E}_{Consumption})_{Theoretical} = (\Sigma \dot{E}_{Reactant} + \Sigma \dot{E}_{LPG})_{Theoretical} \quad (5.5)$$

From the calculation, 3.98 kW total energy input rate is required for a production of 20 liter/minute hydrogen gas at STP in theory (Appendix A1). Fractions of energy input to produce 20L hydrogen are 99% from reactant (ethanol mixed with water), and 1% from supplied LPG.

5.1.2 Practical calculation

The practical energy consumption of hydrogen production from ethanol steam reforming unit is calculated to find the total energy used for production of 20 liter/minute hydrogen using a pilot-scale unit. Figure 5.1 demonstrates an energy pathway diagram of the hydrogen production unit.

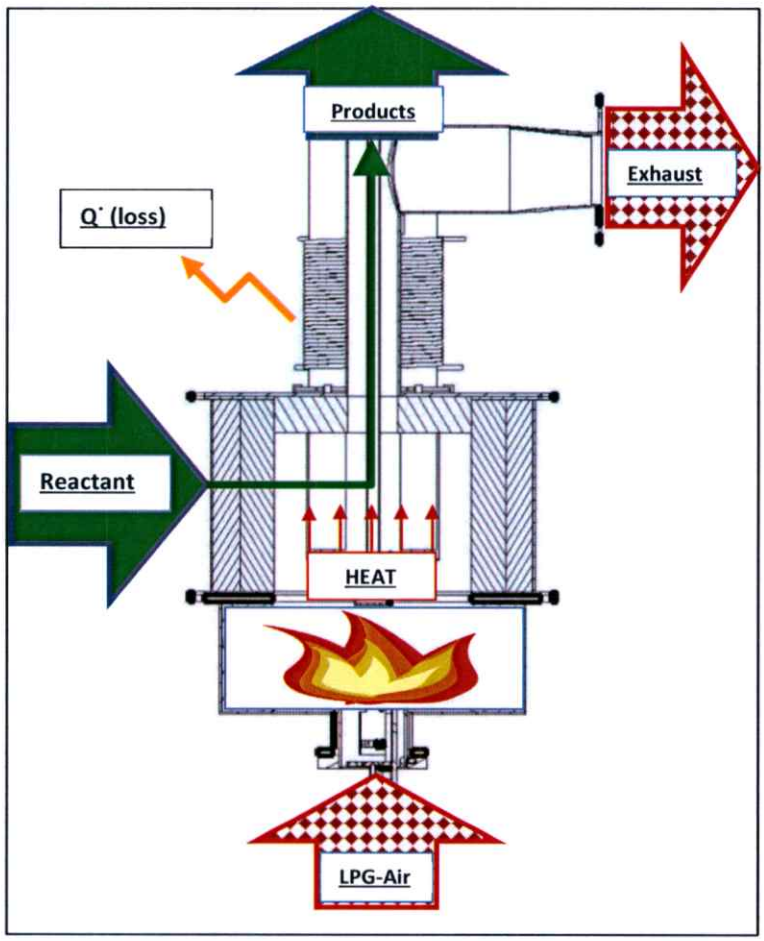


Figure 5.1 Energy pathways diagram of the pilot-scale hydrogen production unit

The operating data and results which introduced earlier in the previous chapter are divided into 2 parts for calculation i.e. reforming reactor, and porous media-LPG furnace as shown in Table 5.2.

Table 5.2 Collected data from a pilot-scale unit to produce 20 liters/minute hydrogen

1) Reforming reactor		
1.1) Input1 (Reactant); S/C =2.5		
$\dot{V}_{(reactant)}$=	0.027	(liters/min)
Ethanol =	39.50	(% Volume)
Water =	60.50	(% Volume)
$T_{Reactant}$ =	25	°C
1.2) Output1 (Products)		
$\dot{V}_{(total\ product)}$ =	29	(L/min)
H_2 =	71.22	(% Volume)
H_2 =	**20.45**	**(L/min)**
CO =	6.91	(% Volume)
CO_2 =	20.13	(% Volume)
C_2H_4 =	1.73	(% Volume)
$T_{Product}$ =	25	°C
2) Porous media-LPG furnace		
2.1) Input2 (Air/Fuel)		
Air =	161.15	(liters/min)
LPG =	3.4	(liters/min)

$T_{Air/Fuel}$ =	25	°C
2.2) Output2 (Exhaust)		
O_2 =	7.67	(% Volume)
CO =	20	(ppm Volume)
CO_2 =	8.76	(% Volume)
$T_{Exhaust}$ =	170	°C

5.1.2.1 Reforming reactor

The actual energy consumption of the reforming reactor is calculated based on total energy of the reaction using data in Table 5.2. Equation 5.6 shows an energy balance equation of the pilot-scale reforming reactor

$$(\Delta \dot{E}_{Reforming})_{Actual} = (\Sigma \dot{E}_{Product} - \Sigma \dot{E}_{Reactant})_{Actual} \qquad (5.6)$$

where $(\Delta \dot{E}_{Reforming})_{Actual}$ is the actual energy consumption of the reforming reactor. $(\Sigma \dot{E}_{Product})_{Actual}$ and $(\Sigma \dot{E}_{Reactant})_{Actual}$ are the actual total energies of products and reactants, respectively. As a result, the reforming reactor requires 0.93 kW of energy input rate for production of 20 liters/minute hydrogen (Appendix A2).

5.1.2.2 Porous media-LPG furnace

The actual energy consumption of the porous media-LPG furnace was calculated to find an energy rate to fulfill a requirement of the hydrogen production unit. 3.4 liters/minute of LPG was supplied to fulfill the required temperature at about 700-900°C. Energy rate released from the furnace can be calculated based on the law of energy conservation. Heat energy of the exhaust gas is calculated from exhaust gas compositions, at exhaust temperature of 170°C. Nitrogen

oxide (NO_X) is neglected from its very small amount. Equation 5.7 presents an actual energy balance equation of the porous media-LPG furnace

$$(\Delta \dot{E}_{furnace})_{Actual} = (\Sigma \dot{E}_{Exhaust} - \Sigma \dot{E}_{LPG})_{Actual} \qquad (5.7)$$

where $(\Delta \dot{E}_{furnace})_{Actual}$ denotes the actual energy consumption of the porous media-LPG furnace. $(\Sigma \dot{E}_{Exhaust})_{Actual}$ and $(\Sigma \dot{E}_{LPG})_{Actual}$ are the actual total energies of exhaust gases and LPG, respectively. The calculation result states that 4.16 kW heat is released from a combustion of the actual used LPG (Appendix A2).

Finally, the actual energy consumption to produce 20 liters/minute hydrogen is obtained from the reforming reactor, and porous media-LPG furnace. Equation 5.8 presents the total energy consumption of the practical hydrogen production unit, which is denoted by $(\Sigma \dot{E}_{Consumption})_{Actual}$.

$$(\Sigma \dot{E}_{Consumption})_{Actual} = (\Sigma \dot{E}_{Reactant} + \Sigma \dot{E}_{LPG})_{Actual} \qquad (5.8)$$

As a result from the calculation, 5.39 kW total energy input rate was practically supplied for production of 20 liters/minute hydrogen at STP (Appendix A2). Fractions of the actual energy input to produce 20L hydrogen are 95% from reactant (ethanol mixed with water), and 5% from supplied LPG (Appendix A0).

From energy consumption calculations of the hydrogen production from ethanol steam reforming using a porous media-LPG furnace as a heat source unit, the total energy consumption to produce 20 liters/minute hydrogen is 5.55 kW in practice, while 3.98 kW is required in theory. Therefore, energy loss of the whole unit can be defined to be 1.57 kW (as a differential value between the practical and theoretical energy consumption rates). Equation 5.9 presents an efficiency of the hydrogen production

from ethanol steam reforming unit, using a porous media-LPG furnace as a heat source, to produce 20 liters/minute hydrogen gas at STP, which is denoted by η_{Unit}.

$$\eta_{Unit}(\%) = \frac{(\Sigma \dot{E}_{Consumption})_{Theoretical}}{(\Sigma \dot{E}_{Consumption})_{Actual}} \times 100 \qquad (5.9)$$

As a result, efficiency of the unit is 73.88% (Appendix A0). The energy loss of 26.12% due mainly to 1) incomplete conversion of a catalytic reactions, 2) radiated heat loss from the furnace where the metal part was directly exposed to the environment, and 3) energy loss at the furnace stack. Figure 5.2 a presents total energy fraction of the hydrogen production from ethanol steam reforming using porous media-LPG furnace as a heat source.

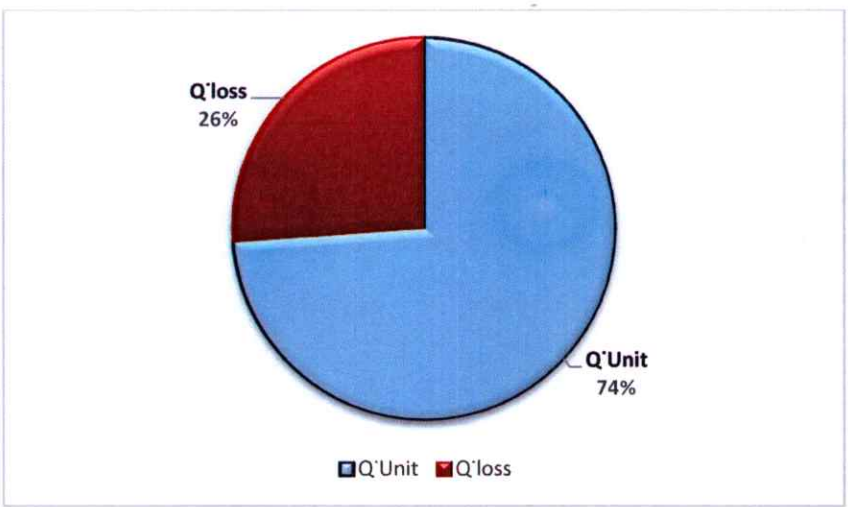


Figure 5.2 Energy fractions of a total energy used for the unit, and an energy loss

An energy conversion of the sub-units which are 1) reforming reactor, and 2) porous media-LPG furnace, product yield, and the furnace-energy assessment will be determined, respectively.

5.2 Energy conversion of Sub Units.

To calculate sub-units energy conversion of the hydrogen production unit which are 1) reforming reactor, and 2) porous media-LPG furnace, a yield of the hydrogen product, and furnace efficiency assessment need to be calculated, respectively.

5.2.1 Reforming reactor

From Table 5.2, 0.027 liter/minute reactant is supplied to produce about 20 liters/minute hydrogen, in practice. On the other hand, theoretically, 0.027 liters/minute reactant can produce 26.65 liters/minute hydrogen (Appendix A3), by based on mass balance equation shown in Equation 5.10.

$$\sum \dot{m}_{Product} = \sum \dot{m}_{Reactant} \tag{5.10}$$

Reaction 5.11 shows a stoichiometric equation of a hydrogen production from ethanol steam reforming which is used to calculate a mass fraction of hydrogen in the theoretical total product.

$$C_2H_5OH + 5H_2O \rightarrow 6H_2 + 2CO_2 + 2H_2O \tag{5.11}$$

Therefore, the yield of the reforming reaction can be defined by Equation 5.12,

$$Yield_{H_2}(\%) = \frac{(\dot{\forall}_{H_2})_{Actual}(L/\min)}{(\dot{\forall}_{H_2})_{Theoretical}(L/\min)} \times 100 \tag{5.12}$$

where $Yield_{H_2}$ is yield of a hydrogen product. $(\dot{\forall}_{H_2})_{Actual}$ and $(\dot{\forall}_{H_2})_{Theoretical}$ are an actual volume flow rate and theoretical volume flow rate of a hydrogen product,

respectively. As a result, the yield of a hydrogen product from the pilot-scale ethanol steam reforming unit is 78.08% (Appendix A0).

5.2.2 Porous media-LPG furnace

An efficiency assessment of the porous media-LPG furnace can be considered for two scenarios which are 1) combustion efficiency, and 2) thermal efficiency. The combustion efficiency is the ratio of heat actually developed in a combustion process to the heat that would be released if the combustion were complete. While, thermal efficiency is the ratio of useful heat actually consumed in a process of reforming reaction to the heat that actually developed in a combustion process.

5.2.2.1 Thermal efficiency

Practically, the operation of the porous media-LPG furnace released heat of 4.00 kW (see **5.1.2.2**), while an energy of 1.04 kW was consumed for a reforming reaction to produce 20 liters/minute hydrogen (mentioned in **5.1.2.1**).

Therefore, a thermal efficiency of the porous media-LPG furnace can be defined by the ratio of actual heat consumed in the process of reforming reaction to actual heat developed in the combustion, as presented in Equation 5.13, $\eta_{Thernal}$ denotes the furnace thermal efficiency.

$$\eta_{Thernal}(\%) = \frac{(\Delta \dot{E}_{\text{Re}\,formin\,g})_{Actual}(kW)}{(\Delta \dot{E}_{Furnace})_{Actual}(kW)} \times 100 \qquad (5.13)$$

As a result, a thermal efficiency of the porous media-LPG furnace which was used as a heat source of the hydrogen production unit was 22.44% (Appendix A0). The energy loss due mainly to 1) heat loss at a surface of the reactor where the metal part was directly exposed to the environment, 2) a large amount of energy loss at the furnace stack, and 3) loss of sensible heat of the reforming products,

since the products need to be cooled down for a product-measurement process. Figure 5.3 shows an energy fractions on the porous media-LPG furnace, based on thermal efficiency.

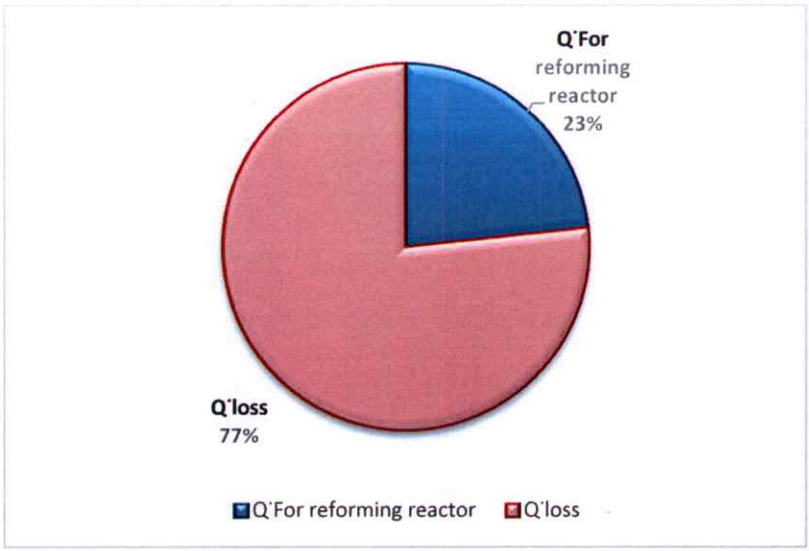


Figure 5.3 Energy fractions on the porous media-LPG furnace

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS

6.1 Conclusions

To make hydrogen gas renewable, and also cost effective, it requires a method having high efficiency with a renewable feedstock. In Thailand, ethanol is more suitable feedstock to supply to a hydrogen production than natural gas since ethanol is a renewable energy resource and it can be produced by fermentation of agricultural waste products. Moreover, it strengthens the nation's energy stability and stabilizes the price of agricultural crops for farmers.

A hydrogen production from ethanol steam reforming unit, using porous media-LPG furnace as a heat source, has been developed at the National Metal and Material Technology Center (MTEC). The scope includes design, and develop a pilot scale prototype of a hydrogen production from ethanol unit.

A thermal assessment of the unit is determined based on an energy balance equation and experimental data from a pilot-scale operation. To produce 20 liters/minute hydrogen, 5.55 kW total energy input was consumed, in practice. While in theory, only 3.98 kW energy is required. Therefore, the efficiency of the unit is 73.88%, as a ratio of theoretical energy-requirement to the actual total-energy consumption. The energy loss of 26.12% was due mainly to 1) incomplete conversion of a catalytic reactions, 2) radiated heat loss from the furnace where the metal part was directly exposed to the environment, and 3) energy loss at the furnace stack, and 4) loss of sensible heat of the reforming products, since the products need to be cooled down for a product-measurement process.

The efficiency of 73.88% is equal to an efficiency of a mature technology in the production of hydrogen from steam methane reforming which is about 70-80% (T-Raissi 2004). Therefore, the hydrogen production from ethanol steam reforming, using

porous media-LPG furnace as a heat source, can be considered as a feasible hydrogen production technology.

6.2 Suggestions

For an efficiency improvement of the unit in the future, an energy assessment should be further considered on subunits of the system which are 1) reforming reactor, and 2) porous media-LPG furnace.

For the reforming reactor, the percent yield of hydrogen can be determined as an efficiency of the catalytic reaction. From a yield calculation, the percent yield is obtained at 78.08%. Therefore, an improvement of the catalytic reaction should be taken into account.

For the porous media-LPG furnace, an efficiency assessment can be considered by thermal efficiency of the furnace.

From an energy calculation the thermal efficiencies of the furnace is 23.31%. Most energy loss was due mainly to: 1) heat loss at a surface of the furnace where the metal part was directly exposed to the environment, 2) a large amount of energy loss at the furnace stack, 3) loss of sensible heat of the reforming products. To reduce the heat loss, more heat insulator, and more exhaust gas heat-recirculation system should be added to reduce a radiated heat loss at a furnace surface, and energy of at the furnace stack, respectively.

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APPENDIX A

ENERGY CALCULATION

Appendix: A0

Assessment of Hydrogen Production from Ethanol Steam Reforming

1) Fractions of Energy consumption - Theoretical

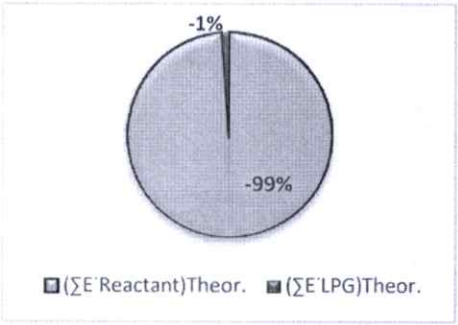
$$(\Sigma \dot{E}_{Consumption})_{Theoretical} = (\Sigma \dot{E}_{Reactant} + \Sigma \dot{E}_{LPG})_{Theoretical}$$

$(\Sigma \dot{E}_{Reactant})_{Theor.}$ = -3.93 (kW)

$(\Sigma \dot{E}_{LPG})_{Theor.}$ = -4.53E-02 (kW)

Therefore;

$(\Sigma \dot{E}_{Consump.})_{Theor.}$ = -3.98E+00 (kW)



2) Fractions of Energy consumption - Actual

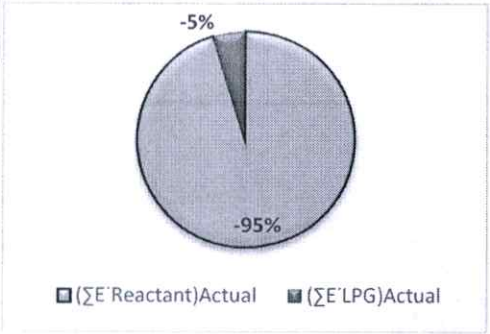
$$(\Sigma \dot{E}_{Consumption})_{Actual} = (\Sigma \dot{E}_{Reactant} + \Sigma \dot{E}_{LPG})_{Actual}$$

$(\Sigma \dot{E}_{Reactant})_{Actual}$ = -5.13E+00 (kW)

$(\Sigma \dot{E}_{LPG})_{Actual}$ = -2.56E-01 (kW)

Therefore;

$(\Sigma \dot{E}_{Consump.})_{Actual}$ = -5.39E+00 (kW)



3) Efficiency of the Unit

$$\eta_{Unit}(\%) = \frac{(\Sigma \dot{E}_{Consumption})_{Theoretical}}{(\Sigma \dot{E}_{Consumption})_{Actual}} \times 100$$

$(\Sigma \dot{E}_{Consump.})_{Theor.}$ = -3.98E+00 (kW)

$(\Sigma \dot{E}_{Consump.})_{Actual}$ = -5.39E+00 (kW)

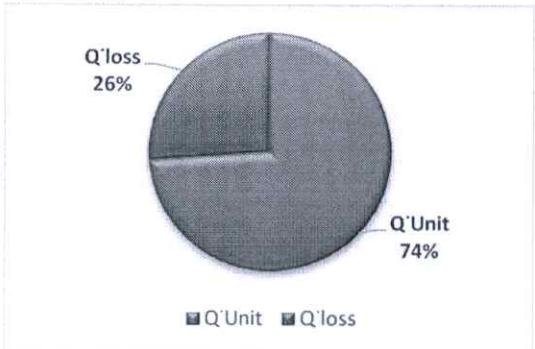
Then;

η_{Unit} = **73.88** (%)

Therefore;

$\dot{Q}_{Unit}$ = 73.88 (%)

$\dot{Q}_{loss}$ = 26.12 (%)



4) Hydrogen percent yield

$$Yield_{H_2}(\%) = \frac{(\dot{\forall}_{H_2})_{Actual}(L/\min)}{(\dot{\forall}_{H_2})_{Theoretical}(L/\min)} \times 100$$

$(\dot{V}_{H2})_{Actual}$ = 20.65 (L/min)

$(\dot{V}_{H2})_{Theor.}$ = 26.45 (L/min)

Therefore;

$Yield_{H2}$ = 78.08 (%)

---

6) Actual Thermal Efficiency of the Porous media-LPG furnace

$$\eta_{Thermal}(\%) = \frac{(\Delta \dot{E}_{Reforming})_{Actual}(kW)}{(\Delta \dot{E}_{Furnace})_{Actual}(kW)} \times 100$$

$(\Delta \dot{E}_{Reforming})_{Actual}$ = 9.33E-01 (kW)

$(\Delta \dot{E}_{Furnace})_{Actual}$ = 4.16E+00 (kW)

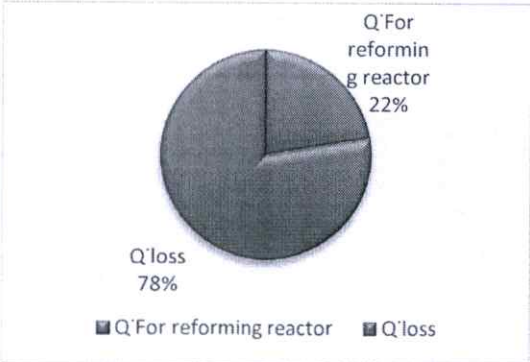
Then;

$\eta_{Thermal}$ = **22.44** (%)

Therefore;

$\dot{Q}_{For\ reforming\ reactor}$ = 22.44 (%)

$\dot{Q}_{loss}$ = 77.56 (%)



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7) Theoretical Thermal Efficiency of the Porous media-LPG furnace

$$\eta_{Thermal}(\%) = \frac{(\Delta \dot{E}_{Reforming})_{Theoretical}(kW)}{(\Delta \dot{E}_{Furnace})_{Theoretical}(kW)} \times 100$$

$(\Delta \dot{E}_{Reforming})_{Theor.}$ = 1.05E+00 (kW)

$(\Delta \dot{E}_{Furnace})_{Theor.}$ = 4.50E+00 (kW)

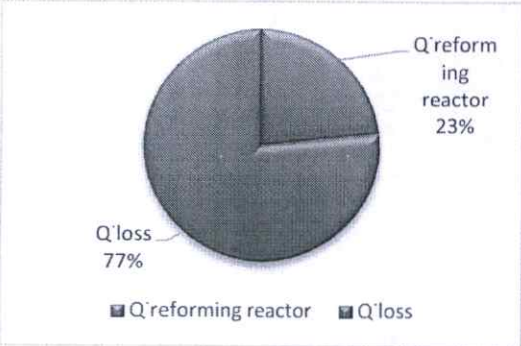
Then;

$\eta_{Thermal}$ = **23.35** (%)

Therefore;

$\dot{Q}_{reforming\ reactor}$ = 23.35 (%)

$\dot{Q}_{loss}$ = 76.65 (%)



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8) Energy accumulation in the porous media-LPG furnace during the startup period

*Using Ceramic foam material as a heat transfer media

$$\Sigma \dot{H}_{In(Time\_step)} - \Sigma \dot{H}_{Out(Time\_step)} = \Sigma \dot{H}_{Accumulation(Time\_step)}$$

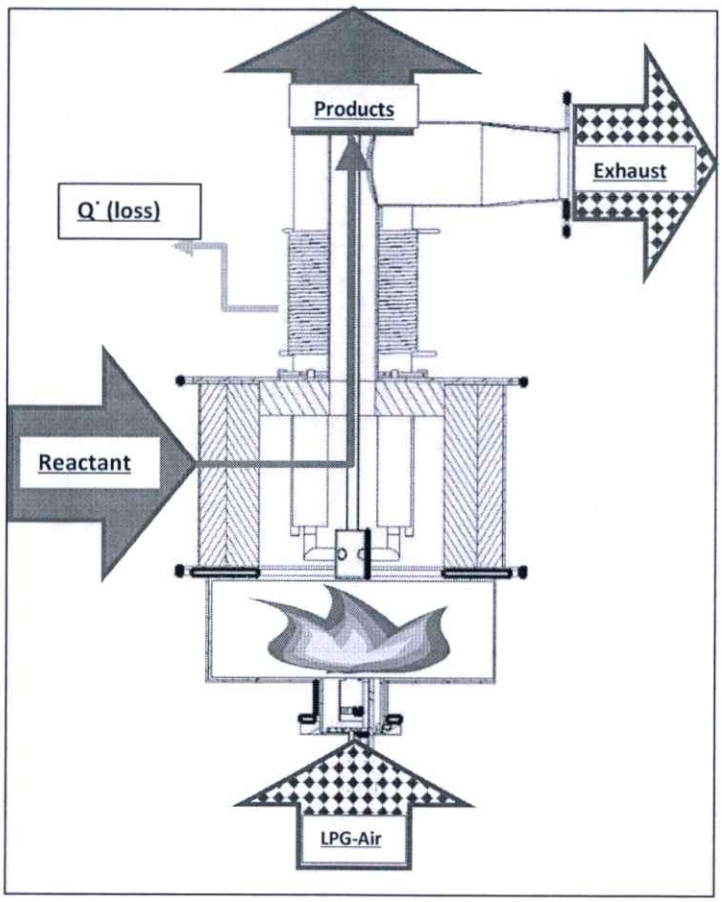
$\Sigma H'_{In(Time\_step)}$	=	-5.47E+03 (kJ)
$\Sigma H'_{Out(Time\_step)}$	=	-9.63E+04 (kJ)
$\Sigma H'_{Accumulation}$	=	9.08E+04 (kJ)

*For more calculation details, please see in Excel file (.xlsx) in a CD attached with this book

Appendix: A1

Theoretical Energy calculation of Hydrogen Production Unit

*To find an theoretical energy-consumption for H_2 production using LPG as a heat source



Energy balance equation of the Unit, in theory;

$$\sum \dot{E}_{(In)} = \sum \dot{E}_{(Out)}$$

$$\left[\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right) + \dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(In1)} + \left[\dot{m}_{LPG}\left(\frac{\Delta h^{\circ}_{f(C_3H_8)}}{MW_{C_3H_8}} + \frac{\Delta h^{\circ}_{f(C_4H_{10})}}{MW_{C_4H_{10}}}\right) + \dot{m}_{AIR}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}} + \frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)\right]_{(In2)}$$

$$= \left[\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right) + \dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right)\right]_{(Out2-Product)}$$

$$+ \left[\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)} + \Delta h_{si(CO_2)})}{MW_{CO_2}}\right) + \dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)} + \Delta h_{si(H_2O)})}{MW_{H_2O}}\right) + \dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)} + \Delta h_{si(N_2)})}{MW_{N_2}}\right)\right]_{(Out1-exhaust)}$$

1) Hydrogen reforming Reactions

From;

$$C_2H_5OH + 5H_2O \rightarrow 6H_2 + 2CO_2 + 2H_2O$$

Mass balance equation of ethanol steam reforming

(1)C2H5OH+ (5)H2O → (6)H2 + (2)CO2 + (2)H2O

Mass	46	90	12.000	88.000	36.000	(A. mass)
ρ @ 25°C	783	1000	0.083	1.812	1000.000	(kg/m3)
Volume	0.059	0.09	144.596	48.576	0.036	(Volume)
Target	**0.008**	**0.012**	**20.000**	**6.719**	**0.005**	**(L/min)**
Target (m')	6.363	12.449	1.660	12.172	4.979	(g/min)
V' total =	**0.02**	**(L/min)**		=	26.724	**(L/min)**
%Volume	39.5	60.5				

Then;

Input1: (Reaction-Reactants)

V'(total)= 2.06E-02 (L/min)
Ethanol = 39.50 (% Volume)
Water = 60.50 (% Volume)

Output1: (Reaction-Products)

H2 = 20.000 (L/min)
CO2 = 6.719 (L/min)
H2O = 0.005 (L/min)

ρ(H2) = 0.08299 kg/m^3 at 25°C
ρ(CO2) = 1.8116 kg/m^3 at 25°C
ρ(H2O) = 1000 kg/m^3 at 25°C

Energy balance equation

1.1) Input1 - (Ethanol + Water)

$$\left[\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right) + \dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(In2)}$$

1.1.1) Ethanol

From; $V'_{Ethanol}$ = 0.008125883 **(L/mim)**
$\rho_{Ethanol}$ = 783 (kg/m^3)

Therefore; $m'_{Ethanol}$ = 6.362566667 (g/min)

$m'_{Ethanol}$ = 6.36E-03 (kg/min)

$m'_{Ethanol}$ = 1.06E-04 (kg/sec)

C_2H_5OH = 1 (mole)

C_2H_5OH ;

$\Delta h°_{f(C2H5OH)}$ =	-277.69	(kJ/mol)
$MW_{(C2H5OH)}$ =	46	(g/mol)
$MW_{(C2H5OH)}$ =	0.046	(kg/mol)

Therefore;

$$\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)=$$

E'_{C2H5OH} = -0.6401526 (kW) ;(liquid)

1.1.2) Water

From; V'_{Water} = 0.0124485 **(L/mim)**

ρ_{Water} = 1000 (kg/m^3)

Therefore; m'_{Water} = 12.4485 (g/min)

m'_{Water} = 1.24E-02 (kg/min)

m'_{Water} = 2.07E-04 (kg/sec)

H_2O = 5 (mole)

H_2O ;

$\Delta h°_{f(H2O)}$ =	-285.83	(kJ/mol)
$MW_{(H2O)}$ =	18	(g/mol)
$MW_{(H2O)}$ =	0.018	(kg/mol)

Therefore;

$$\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)=$$

E'_{H2O} = -3.2945877 (kW) ;(liquid)

Therefore; **$\Sigma E'_{Reactants}$ = -3.93 (kW)**

1.2) Output1 - Products (H_2 + CO_2)

$$\left[\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right)+\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right)+\dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(Out2-Product)}$$

From;

$$\sum \dot{m}_{Product} = \sum \dot{m}_{Reactant}$$

$\sum \dot{m}_{Products}$ = **3.14E-04** **(kg/sec)**

H_2	=	6.0	(mol/mol)
CO_2	=	2.0	(molmol)
H2O	=	2.0	(mol/mol)

$MW_{(H2)}$ =	2.016	(g/mol)
$MW_{(H2)}$ =	0.002016	(kg/mol)
$MW_{(CO2)}$ =	44.01	(g/mol)
$MW_{(CO2)}$ =	0.04401	(kg/mol)
$MW_{(H2O)}$ =	18.016	(g/mol)
$MW_{(H2O)}$ =	0.018016	(kg/mol)

And; Mass fraction of H2, CO_2, and H_{20} in the Product compositions are

Mass Fraction H_2 =	0.09
Mass Fraction CO_2=	0.65
Mass Fraction H_2O=	0.26

Therefore;

$\dot{m}_{Product,H2}$ =	**2.79E-05**	**(kg/sec)**	=	2.01E+01	(L/min)
$\dot{m}_{Product,CO2}$ =	**2.03E-04**	**(kg/sec)**	=	6.71E+00	(L/min)
$\dot{m}_{Product,H2O}$ =	**8.30E-05**	**(kg/sec)**	=	4.98E-03	(L/min)

1.2.1) H_2

$$\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right) = ?$$

From; $\Delta h^{\circ}_{f(H2)}$ = 0 (kJ/mol)

So;

$\dot{E}_{H2}$ = **0** **(kW)**

1.2.2) CO_2

$$\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(CO2)}$ = -393.52 (kJ/mol)

So;

$\dot{E}_{CO2}$ = **-1.81** **(kW)**

1.2.3) H_2O

$$\dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(H2O)}$ = -285.83 (kJ/mol)

So;

$\dot{E}_{H2O}$ = **-1.3164025** **(kW)**

$\Sigma \dot{E}_{Products}$ = **-3.13** **(kW)**

Finally; $\Sigma \dot{E}_{Reaction}$ = **0.81** **(kW)**

The reaction need energy = 0.81 (kW)
to producing of 20 L/min hydrogen

---

2) Heat Source of the Reaction - LPG combustion

From the stoichiometric equation of LPG combustion

2.1) LPG Combustion

(Input) **(Output)**

$$(0.4C_3H_8 + 0.6C_4H_{10}) + (5.9O_2 + 5.9(3.76)N_2) \rightarrow 3.6CO_2 + 4.6H_2O + 5.9(3.76)N_2$$

Combust 1 mol/sec of LPG ($0.4C_3H_8$ + $0.6C_4H_{10}$) / provide Heat = **?** (kW)
(In case of complete combustion)

2.1) Input2 - (LPG + AIR)

2.1.1) LPG

$$\dot{m}_{LPG}\left(\frac{(\Delta h^{\circ}_{f(C_3H_8)} \times 0.4)}{MW_{C_3H_8}} + \frac{(\Delta h^{\circ}_{f(C_4H_{10})} \times 0.6)}{MW_{C_4H_{10}}}\right) = ?$$

C_3H_8 = 0.40 (mol/mol)
C_4H_{10} = 0.60 (mol/mol)

C_3H_8 ;

$\Delta h^{\circ}_{f(C3H8)}$ = -103.85 (kJ/mol)
$MW_{(C3H8)}$ = 44.097 (g/mol)

	$MW_{(C3H8)}$ =	0.044097	(kg/mol)
C_4H_{10} ;	$\Delta h°_{f(C4H10)}$ =	-126.15	(kJ/mol)
	$MW_{(C4H10)}$ =	58.124	(g/mol)
	$MW_{(C4H10)}$ =	0.058124	(kg/mol)

	For	1	(mol/sec); of LPG
1 mol LPG;	$m'_{(C3H8)}$ =	0.026	(kg/sec)
	$m'_{(C4H10)}$ =	0.035	(kg/sec)
	$m'_{(LPG)}$ =	0.061	(kg/sec)

Therefore;

$$\dot{m}_{(C_3H_8)}\left(\frac{\Delta h^{\circ}_{f(C_3H_8)}}{MW_{C_3H_8}}\right)+\dot{m}_{(C_4H_{10})}\left(\frac{\Delta h^{\circ}_{f(C_4H_{10})}}{MW_{C_4H_{10}}}\right)=$$

E'_{LPG} = -138 (kW)

2.1.2) AIR

$$\dot{m}_{O_2}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)=?$$

O_2 =	5.90	(mol/mol)
N_2 =	22.20	(mol/mol)

O_2 ;	$\Delta h°_{f(O2)}$ =	0.000	(kJ/mol)
	$MW_{(O2)}$ =	31.999	(g/mol)
	$MW_{(O2)}$ =	0.032	(kg/mol)
N_2 ;	$\Delta h°_{f(N2)}$ =	0.000	(kJ/mol)
	$MW_{(N2)}$ =	28.013	(g/mol)
	$MW_{(N2)}$ =	0.028	(kg/mol)

	For	1	(mol/sec); of LPG
Air (O_2/N_2)	$m'_{(O2)}$ =	0.189	(kg/sec)
	$m'_{(N2)}$ =	0.622	(kg/sec)
	$m'_{(AIR)}$ =	0.811	(kg/sec)

Due to;

$\Delta h°_{f(O2)}$ =	0	(kJ/mol)
$\Delta h°_{f(N2)}$ =	0	(kJ/mol)

Therefore;

$$\dot{m}_{O_2}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)=$$

$\dot{E}_{AIR}$ = **0** **(kW)**

Finally; $\Sigma E_{(input)}$ = **-138** **(kW)**

2.2) Output1 - Exhaust(CO2 + H2O + N2)

$$\left[\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)+\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)+\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)\right]_{(Out1-exhaust)}$$

CO_2	=	3.6	(mol/mol)
H_2O	=	4.6	(mol/mol)
N_2	=	(5.9)*(79/21)	(mol/mol)
	=	22.1952381	(mol/mol)

$MW_{(CO2)}$	=	44.01	(g/mol)
$MW_{(CO2)}$	=	0.04401	(kg/mol)
$MW_{(H2O)}$	=	18.015	(g/mol)
$MW_{(H2O)}$	=	0.018015	(kg/mol)
$MW_{(N2)}$	=	28.013	(g/mol)
$MW_{(N2)}$	=	0.028013	(kg/mol)

		For	1.00	(mol/sec); of LPG
Exhaust (H_2OCO_2/N_2)		$m'_{(CO2)}$ =	0.16	(kg/sec)
		$m'_{(H2O)}$ =	0.08	(kg/sec)
		$m'_{(N2)}$ =	0.62	(kg/sec)
		$m'_{(Exhaust)}$ =	0.86	(kg/sec)

2.2.1) CO_2

$$\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)=?$$

Due to;	$\Delta h^{\circ}_{f(CO2)}$ =	-393.52	(kJ/mol)	
	$\Delta h_{si(CO2)}$ =	6.17	(kJ/mol)	at 170°c

So;

$\dot{E}_{CO2}$ = **-1394.47** **(kW)**

2.2.2) H_2O

$$\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)=?$$

Due to; $\Delta h^{\circ}_{f(H2O)}$ = -285.83 (kJ/mol)
$\Delta h_{si(H2O)}$ = 5.05 (kJ/mol) at 170°c

So;

$\dot{E}_{CO2}$ = **-1291.57 (kW)**

2.2.3) N_2

$$\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)=?$$

Due to; $\Delta h^{\circ}_{f(N2)}$ = 0 (kJ/mol)
$\Delta h_{si(N2)}$ = 4.28 (kJ/mol) at 170°c

So;

$\dot{E}_{N2}$ = **95.07 (kW)**

Therefore; **$\Sigma E_{(output)}$ = -2590.97 (kW)**

Finally; **$\Sigma E_{(combustion)} = \Sigma E_{(output)} - \Sigma E_{(input)}$ = -2452.97 (kW)**

So that; **1 mol/sec of LPG can provides Heat =** -2452.97 **(kW)**
From ; production of 20 L/min hydrogen reaction require Heat = 0.81 (kW)
Therefore; To produce 20L/min of hydrogen, the reaction requires LPG combustion to fullfill the endothermic reaction by using of LPG = **3.29E-04** (mol/sec)

3.1) Actual Input - (LPG + AIR)

3.1.1) LPG

$$\dot{m}_{LPG}\left(\frac{(\Delta h^{\circ}_{f(C_3H_8)}\times 0.4)}{MW_{C_3H_8}}+\frac{(\Delta h^{\circ}_{f(C_4H_{10})}\times 0.6)}{MW_{C_4H_{10}}}\right)=?$$

C_3H_8 = 0.40 (mol/mol)
C_4H_{10} = 0.60 (mol/mol)

C_3H_8 ;	$\Delta h°_{f(C3H8)}$ =	-103.85	(kJ/mol)
	$MW_{(C3H8)}$ =	44.097	(g/mol)
	$MW_{(C3H8)}$ =	0.044097	(kg/mol)
C_4H_{10} ;	$\Delta h°_{f(C4H10)}$ =	-126.15	(kJ/mol)
	$MW_{(C4H10)}$ =	58.124	(g/mol)
	$MW_{(C4H10)}$ =	0.058124	(kg/mol)

	For	3.29E-04	(mol/sec); of LPG
1 mol LPG;	$m'_{(C3H8)}$ =	8.693E-06	(kg/sec)
	$m'_{(C4H10)}$ =	1.146E-05	(kg/sec)
	$m'_{(LPG)}$ =	2.02E-05	(kg/sec)

Therefore;

$$\dot{m}_{(C_3H_8)}\left(\frac{\Delta h°_{f(C_3H_8)}}{MW_{C_3H_8}}\right)+\dot{m}_{(C_4H_{10})}\left(\frac{\Delta h°_{f(C_4H_{10})}}{MW_{C_4H_{10}}}\right)=$$

E'_{LPG} = -4.53E-02 (kW)

3.1.2) AIR

$$\dot{m}_{O_2}\left(\frac{\Delta h°_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h°_{f(N_2)}}{MW_{N_2}}\right)=?$$

O_2 =	5.90	(mol/mol)
N_2 =	22.20	(mol/mol)

O_2 ;	$\Delta h°_{f(O2)}$ =	0.000	(kJ/mol)
	$MW_{(O2)}$ =	31.999	(g/mol)
	$MW_{(O2)}$ =	0.032	(kg/mol)
N_2 ;	$\Delta h°_{f(N2)}$ =	0.000	(kJ/mol)
	$MW_{(N2)}$ =	28.013	(g/mol)
	$MW_{(N2)}$ =	0.028	(kg/mol)

	For	3.29E-04	(mol/sec); of LPG
Air (O_2/N_2)	$m'_{(O2)}$ =	6.203E-05	(kg/sec)
	$m'_{(N2)}$ =	2.043E-04	(kg/sec)
	$m'_{(AIR)}$ =	2.663E-04	(kg/sec)

Due to;

$\Delta h°_{f(O2)}$ =	0	(kJ/mol)
$\Delta h°_{f(N2)}$ =	0	(kJ/mol)

Therefore;

$$\dot{m}_{O_2}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)=$$

$\dot{E}_{AIR}$ = **0.00E+00** **(kW)**

Finally; $\Sigma E_{(input)}$ = **-4.53E-02** **(kW)**

After all; The energy for 20 L/min hydrogen production is accomplish.
By; Total required energy for production of 20 L/min hydrogen is including with:
1) Ethanol + Steam (as the reactants), and 2) LPG + Air (for heat source input)
Total energy consumption = **-3.98E+00** **(kW)**

Appendix: A2
Practical Energy calculation of Hydrogen Production Unit

*To find an actual energy consumption for hydrogen production using LPG as a heat source

Collected data from experiment

Input1 (Comustion-AF)

LPG = 3.4 (L/mim)
Air = 161.15 (L/mim)

Output1 (Combustion-Exhaust gas)

M'(total)=	**?**	**(L/min)**	*(will be defined by mass balance eq.)
O2 =	7.67	(% Volume)	
CO =	20	(ppm)	
CO2 =	8.76	(% Volume)	
NO =	64	(ppm)	neglected in calculation
NO2 =	0.6	(ppm)	because it is very less amount.

Input2 (Reaction-Reactants)

V'(total)=	0.027	**(L/min)**	
Ethanol =	39.50	(% Volume)	S/C = 2.5
Water =	60.50	(% Volume)	Ethanol: Water = 1: 5 mol

Output2 (Reaction-Products)

H2 =	71.2216	(% Volume)
CO =	6.919306	(% Volume)
CO2 =	20.12747	(% Volume)
C2H4 =	1.73162	(% Volume)

$V'_{(product)}$ = 29 (L/min) 20.654264
*Assume that remained H specie was become WATER (H2O)

Energy balance equation of the Unit, in theory

$$\sum \dot{E}_{(In)} = \sum \dot{E}_{(Out)}$$

$$\left[\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)+\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(In1)}+\left[\dot{m}_{LPG}\left(\frac{\Delta h^{\circ}_{f(C_3H_8)}}{MW_{C_3H_8}}+\frac{\Delta h^{\circ}_{f(C_4H_{10})}}{MW_{C_4H_{10}}}\right)+\dot{m}_{AIR}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}+\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)\right]_{(In2)}$$

$$=\left[\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right)+\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right)+\dot{m}_{CO}\left(\frac{\Delta h^{\circ}_{f(CO)}}{MW_{CO}}\right)+\dot{m}_{C_2H_4}\left(\frac{\Delta h^{\circ}_{f(C_2H_4)}}{MW_{C_2H_4}}\right)+\dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(Out1-Products)}$$

$$+\left[\dot{m}_{O_2}\left(\frac{(\Delta h^{\circ}_{f(O_2)}+\Delta h_{si(O_2)})}{MW_{O_2}}\right)+\dot{m}_{CO}\left(\frac{(\Delta h^{\circ}_{f(CO)}+\Delta h_{si(CO)})}{MW_{CO}}\right)+\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)\right.$$

$$\left.+\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)+\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)\right]_{(Out2-Exhaust)}$$

1) Hydrogen reforming Reactions

1.1) Input1 - (Ethanol + Water)

$$\left[\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)+\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(In1)}$$

1.1.1) Ethanol

From;	$V'_{Ethanol}$	=	1.06E-02	**(L/mim)**
	$\rho_{Ethanol}$	=	783	(kg/m^3)
Therefore;	$m'_{Ethanol}$	=	8.30E+00	(g/min)
	$m'_{Ethanol}$	=	8.30E-03	(kg/min)
	$m'_{Ethanol}$	=	1.38E-04	(kg/sec)

C_2H_5OH ;

$\Delta h°_{f(C2H5OH)}$	=	-277.69	(kJ/mol)
$MW_{(C2H5OH)}$	=	46	(g/mol)
$MW_{(C2H5OH)}$	=	0.046	(kg/mol)

Therefore;

$$\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)=$$

$\dot{E}_{C2H5OH}$ = **-0.834877** **(kW)** ;(liquid)

1.1.2) Water

From;	V'_{Water}	=	1.62E-02	**(L/mim)**
	ρ_{Water}	=	1000	(kg/m^3)
Therefore;	m'_{Water}	=	16.2351457	(g/min)
	m'_{Water}	=	1.62E-02	(kg/min)

m'_{Water} = 2.71E-04 (kg/sec)

H_2O ;

$\Delta h°_{f(H2O)}$ =	-285.83	(kJ/mol)
$MW_{(H2O)}$ =	18	(g/mol)
$MW_{(H2O)}$ =	0.018	(kg/mol)

Therefore;

$$\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right) =$$

E'_{H2O} = -4.296752 (kW) ;(liquid)

Therefore; **$\Sigma E'_{Reactants}$ = -5.131629 (kW)**

1.2) Output1 - Products (H_2 + CO_2+ CO+ C_2H_4+ H_2O)

$$= \left[\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right) + \dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right) + \dot{m}_{CO}\left(\frac{\Delta h^{\circ}_{f(CO)}}{MW_{CO}}\right) + \dot{m}_{C_2H_4}\left(\frac{\Delta h^{\circ}_{f(C_2H_4)}}{MW_{C_2H_4}}\right) + \dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(Out)-Products}$$

From;

V' (H2) =	3.44E-04	(m^3/sec)	at 25°C	
V' (H2) =	**20.65**	**(L/min)**	at 25°C	*Target product
V' (CO) =	3.34E-05	(m^3/sec)	at 25°C	
V' (CO_2) =	9.73E-05	(m^3/sec)	at 25°C	
V' (C_2H_4) =	8.37E-06	(m^3/sec)	at 25°C	

From;

MW_{H2} =	**2.02**	**(g/mol)**
MW_{CO} =	**28.01**	**(g/mol)**
MW_{CO2} =	**44.01**	**(g/mol)**
MW_{C2H4} =	**28.05**	**(g/mol)**
MW_{H2O} =	**18.02**	**(g/mol)**

at T =	25 °C	=	**298.15**	**(K)**
and P =	1 atm	=	**101.325**	**(kPa)**

$$n = \frac{\text{mass}}{\text{molar mass}}$$

substituting & rearranging

$$P = \frac{\text{mass}}{\text{molar mass}} \times \frac{RT}{V}$$

mass / V = d (the density in g / L)
substituting & rearranging

$$\text{molar mass} = \frac{dRT}{P}$$

R_U = **8.31447 (kJ/kmol*K)**

ρ(d)= $$\rho(d) = \frac{P \times (molar\_mass)}{R_U T}$$ **(kg/m^3)**

ρ_{H2} =	**0.0824 (kg/m^3)**	at25°C
ρ_{CO} =	**1.1449 (kg/m^3)**	at25°C
ρ_{CO2} =	**1.7989 (kg/m^3)**	at25°C
ρ_{C2H4} =	**1.1467 (kg/m^3)**	at25°C

m' (H_2) = 2.84E-05 (kg/sec)
m' (CO) = 3.83E-05 (kg/sec)
m' (CO_2) = 1.75E-04 (kg/sec)
m' (C_2H_4) = 9.60E-06 (kg/sec)
m' (H_2O) = 1.58E-04 (kg/sec) *Remained m' from mass balance eq.

1.2.1) H_2

$$\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(CO2)}$ = 0 (kJ/mol)

So;

$\dot{E}_{H2}$ = **0 (kW)**

1.2.2) CO

$$\dot{m}_{CO}\left(\frac{\Delta h^{\circ}_{f(CO)}}{MW_{CO}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(CO2)}$ = -110.53 (kJ/mol)

So;

$\dot{E}_{CO2}$ = **-0.15 (kW)**

1.2.3) CO_2

$$\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right) = ?$$

Due to; $\Delta h°_{f(CO2)}$ = -393.52 (kJ/mol)

So;

$\dot{E}_{CO2}$ = **-1.56 (kW)**

1.2.4) C_2H_4

$$\dot{m}_{C_2H_4}\left(\frac{\Delta h^{\circ}_{f(C_2H_4)}}{MW_{C_2H_4}}\right) = ?$$

Due to; $\Delta h°_{f(C2H4)}$ = 52.28 (kJ/mol)

So;

$\dot{E}_{C2H4}$ = **0.02 (kW)**

1.2.5) H_2O *Remained m' from mass balance eq.

$$\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right) = ?$$

Due to; $\Delta h°_{f(H2O)}$ = -285.83 (kJ/mol)

So;

$\dot{E}_{H2O}$ = **-2.5011 (kW)**

$\Sigma E'_{Products}$ = -4.20 (kW)

Finally; **$\Sigma E'_{Reactions}$ = 0.93 (kW)**

The reaction need energy 0.93 (kW)
to produce of 20 L/min hydrogen

---

2) Heat Source of the Reaction - LPG combustion

2.1) Input1 - (LPG + AIR)

2.1.1) LPG

$$\dot{m}_{LPG}\left(\frac{(\Delta h^{\circ}_{f(C_3H_8)}\times 0.4)}{MW_{C_3H_8}} + \frac{(\Delta h^{\circ}_{f(C_4H_{10})}\times 0.6)}{MW_{C_4H_{10}}}\right) = ?$$

From; V'_{LPG} = 3.4 **(L/mim)**

- ρ_{LPG} = 2.011 (kg/m^3)

Therefore; m'_{LPG} = 6.8374 (g/min)

m'_{LPG} = 6.84E-03 (kg/min)

m'_{LPG} = 1.14E-04 (kg/sec)

Table 2 Properties of LPG (Petroleum Thailand Co., Ltd)

Properties of LPG (Commercial Butane).

Properties of	Quantity	Unit
Chemical formula (Propane:Butane)	C_3H_8:C_4H_{10}	–
Proportional of gas mixture Propane:Butane	40:60	% by mol
Low heating value	45.8	MJ/kg
Density of gas	2.011	kg/m^3
Volume of 1 kg Gas (at 1 bar) at 0 °C	508	liter
Wobbe index	20.79	kwh
Flame temperature	1925	oC
Ignition temperature with air	510	oC
Air fuel ratio (stoichiometry)	15.6	kg_{air}/kg_f

C_3H_8 = 0.40 (mol/mol)

C_4H_{10} = 0.60 (mol/mol)

C_3H_8 ;

$\Delta h°_{f(C3H8)}$ =	-103.85	(kJ/mol)
$MW_{(C3H8)}$ =	44.097	(g/mol)
$MW_{(C3H8)}$ =	0.044097	(kg/mol)

C_4H_{10} ;

$\Delta h°_{f(C4H10)}$ =	-126.15	(kJ/mol)
$MW_{(C4H10)}$ =	58.124	(g/mol)
$MW_{(C4H10)}$ =	0.058124	(kg/mol)

Therefore;

$$\dot{m}_{LPG}\left(\frac{(\Delta h^{\circ}_{f(C_3H_8)}\times 0.4)}{MW_{C_3H_8}}+\frac{(\Delta h^{\circ}_{f(C_4H_{10})}\times 0.6)}{MW_{C_4H_{10}}}\right)=$$

$\dot{E}_{LPG}$ = -0.255745 (kW)

2.1.2) AIR

$$\dot{m}_{AIR}\left(\frac{(\Delta h^{\circ}_{f(O_2)}\times 5.9)}{MW_{O_2}}+\frac{(\Delta h^{\circ}_{f(N_2)}\times 5.9\times 3.76)}{MW_{N_2}}\right)=?$$

From;

V'_{AIR} = 161.15 **(L/mim)**

ρ_{AIR} = 1.18 (kg/m^3) at 25°C

Therefore;

m'_{AIR} = 190.157 (g/min)

m'_{AIR} = 1.90E-01 (kg/min)

m'_{AIR} = 3.17E-03 (kg/sec)

Due to;

$\Delta h°_{f(O2)}$ =	0	(kJ/mol)
$\Delta h°_{f(N2)}$ =	0	(kJ/mol)

Therefore;

$$\dot{m}_{AIR}\left(\frac{(\Delta h^{\circ}_{f(O_2)}\times 5.9)}{MW_{O_2}}+\frac{(\Delta h^{\circ}_{f(N_2)}\times 5.9\times 3.76)}{MW_{N_2}}\right)=$$

$\dot{E}_{AIR}$ = **0** **(kW)**

Therefore; $\Sigma \dot{E}_{Heat\ input}$ = **-0.26** **(kW)**

2.2) Output1 - Exhaust(O_2+CO+CO_2 + H_2O + N_2)

$$\left[\dot{m}_{O_2}\left(\frac{(\Delta h^{\circ}_{f(O_2)}+\Delta h_{si(O_2)})}{MW_{O_2}}\right)+\dot{m}_{CO}\left(\frac{(\Delta h^{\circ}_{f(CO)}+\Delta h_{si(CO)})}{MW_{CO}}\right)+\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)\right.$$

$$\left.+\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)+\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)\right]_{(Out2-Exhaust)}$$

From;

$$\sum \dot{m}_{Exhaust}=\sum \dot{m}_{Fuel\_Supply}$$

$\Sigma \dot{m}_{Exhaust}$ = **3.28E-03** **(kg/sec)**

***Assumptions**

1) For $\dot{m}$ of N_2 - obtained from assumed that all remained Nytrogen-species are only become N_2 ($\dot{m}$ of Nox is neglected b/c it is very small value.)
2) For $\dot{m}$ of HC- species - assumed no HC remained
3) For $\dot{m}$ of H_20 (water) -- assumed that all remained Hydrogen(H)-species become H_2O

$MW_{(O2)}$ =	31.999	(g/mol)
$MW_{(O2)}$ =	0.031999	(kg/mol)
$MW_{(CO)}$ =	28.011	(g/mol)
$MW_{(CO)}$ =	0.028011	(kg/mol)
$MW_{(CO2)}$ =	44.01	(g/mol)
$MW_{(CO2)}$ =	0.04401	(kg/mol)
$MW_{(N2)}$ =	28.013	(g/mol)
$MW_{(N2)}$ =	0.028013	(kg/mol)
$MW_{(H2O)}$ =	18.015	(g/mol)
$MW_{(H2O)}$ =	0.018015	(kg/mol)

And; Mass fraction of Exhaust components are

Mass Fraction O_2 =	0.11
Mass Fraction CO=	0.01
Mass Fraction CO_2 =	0.08

Mass Fraction N_2 =	0.74
Mass Fraction H_2O=	0.05

Therefore;

$\dot{m}_{Exhaust,O2}$ =	**3.63E-04**	**(kg/sec)**
$\dot{m}_{Exhaust,CO}$ =	**4.45E-05**	**(kg/sec)**
$\dot{m}_{Exhaust,CO2}$ =	**2.67E-04**	**(kg/sec)**
$\dot{m}_{Exhaust,N2}$ =	**2.43E-03**	**(kg/sec)**
$\dot{m}_{Exhaust,H2O}$ =	**1.76E-04**	**(kg/sec)**

2.1) O_2

$$\dot{m}_{O_2}\left(\frac{(\Delta h^{\circ}_{f(O_2)} + \Delta h_{si(O_2)})}{MW_{O_2}}\right) = ?$$

Due to;

$\Delta h^{\circ}_{f(O2)}$ = 0 (kJ/mol)

$\Delta h_{si(O2)}$ = 4.48 (kJ/mol) at 170°C

So;

$\dot{E}_{O2}$ = **0.05** **(kW)**

2.2) CO

$$\dot{m}_{CO}\left(\frac{(\Delta h^{\circ}_{f(CO)} + \Delta h_{si(CO)})}{MW_{CO}}\right) = ?$$

Due to;

$\Delta h^{\circ}_{f(CO)}$ = -110.53 (kJ/mol)

$\Delta h_{si(CO)}$ = 4.32 (kJ/mol) at 170°C

So;

$\dot{E}_{CO}$ = **-0.17** **(kW)**

2.3) CO_2

$$\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)} + \Delta h_{si(CO_2)})}{MW_{CO_2}}\right) = ?$$

Due to;

$\Delta h^{\circ}_{f(CO2)}$ = -393.52 (kJ/mol)

$\Delta h_{si(CO2)}$ = 6.17 (kJ/mol) at 170°C

So;

$\dot{E}_{CO_2}$ = **-2.35** **(kW)**

2.6) N_2

$$\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)=?$$

Due to; $\Delta h^{\circ}_{f(N2)}$ = 0 (kJ/mol)

$\Delta h_{si(N2)}$ = 4.28 (kJ/mol) at 170°C

So;

$\dot{E}_{N2}$ = **0.37 (kW)**

2.7) H_2O

$$\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)=?$$

Due to; $\Delta h^{\circ}_{f(H2O)}$ = -241.82 (kJ/mol)

$\Delta h_{si(H2O)}$ = 5.05 (kJ/mol) at 170°C

So;

$\dot{E}_{H2O}$ = **-2.32 (kW)**

Therefore; $\Sigma E'_{Exhaust}$ = **-4.41 (kW)**

Finally; $\Sigma E'_{Furnace}$ = **-4.16 (kW)**

*Actual

The combustion releases energy = -4.16 (kW)
to the reforming reactor
while, the reactor requires only = 0.93 (kW)

Therefore, Energyloss of the unit is = 3.22

After all; The energy for 20 L/min hydrogen production is accomplish.
By; Total required energies for producing of 20 L/min hydrogen is including with
1) Ethanol + Steam (as the reactants), and 2) LPG + Air (for heat source input)
Total energy consumption = **-5.39E+00 (kW)**

Appendix: A3
Subunits Energy calculation

* To find an amount of Theoretical H_2 product which should be obtained when feeding with actual amount of reactant

1) Reforming reactor

V'(total)=	0.027 **(L/min)**		
Ethanol =	39.50 (% Volume)	}	S/C = 2.5
Water =	60.50 (% Volume)		Ethanol:Water = 1: 5 mol

1.1) Input1 - (Ethanol + Water)

$$\left[\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)+\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(In2)}$$

1.1.1) Ethanol

From;	$V'_{Ethanol}$	=	0.0106	**(L/mim)**
	$\rho_{Ethanol}$	=	783	(kg/m^3)
Therefore;	$m'_{Ethanol}$	=	8.297963342	(g/min)
	$m'_{Ethanol}$	=	8.30E-03	(kg/min)
	$m'_{Ethanol}$	=	1.38E-04	(kg/sec)
	C_2H_5OH	=	1	(mole)

C_2H_5OH ;

$\Delta h°_{f(C2H5OH)}$	=	-277.69	(kJ/mol)
$MW_{(C2H5OH)}$	=	46	(g/mol)
$MW_{(C2H5OH)}$	=	0.046	(kg/mol)

Therefore;

$$\dot{m}_{Ethanol}\left(\frac{\Delta h^{\circ}_{f(C_2H_5OH)}}{MW_{C_2H_5OH}}\right)=$$

$\dot{E}_{C2H5OH}$ = **-0.83487733** **(kW)** (liquid)

1.1.2) Water

From;	V'_{Water}	=	0.016	**(L/mim)**
	ρ_{Water}	=	1000	(kg/m^3)
Therefore;	m'_{Water}	=	16.23514567	(g/min)
	m'_{Water}	=	1.62E-02	(kg/min)
	m'_{Water}	=	2.71E-04	(kg/sec)

H_2O = 5 (mole)

H_2O :

$\Delta h°_{f(H2O)}$ =	-285.83	(kJ/mol)
$MW_{(H2O)}$ =	18	(g/mol)
$MW_{(H2O)}$ =	0.018	(kg/mol)

Therefore;

$$\dot{m}_{Water}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right) =$$

E'H2O = -4.29675156 (kW) (liquid)

Therefore; **$\sum E'_{Reactants}$ = -5.13162889 (kW)**

1.2) Output1 - Products ($H_2 + CO_2 + H_2O$)

$$\left[\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right)+\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right)+\dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right)\right]_{(Out2-\Pr oduct)}$$

From;

$$\sum \dot{m}_{\Pr oduct} = \sum \dot{m}_{\mathrm{Re}\,ac\,\tan t}$$

$\sum m'_{Products}$ = 4.09E-04 (kg/sec)

H_2 =	6.0	(mol/mol)
CO_2 =	2.0	(molmol)
H2O =	2.0	(mol/mol)

$MW_{(H2)}$ =	2.016	(g/mol)
$MW_{(H2)}$ =	0.002016	(kg/mol)
$MW_{(CO2)}$ =	44.01	(g/mol)
$MW_{(CO2)}$ =	0.04401	(kg/mol)
$MW_{(H2O)}$ =	18.016	(g/mol)
$MW_{(H2O)}$ =	0.018016	(kg/mol)

And; Mass fraction of CO_2, H_2O, and N_2 in the Exhaust components are

Mass Fraction H_2 =	0.09
Mass Fraction CO_2=	0.65
Mass Fraction CO_2=	0.26

Therefore;

$\dot{m}_{Product,H2}$ =	3.63E-05	(kg/sec)
$\dot{m}_{Product,CO2}$ =	2.64E-04	(kg/sec)
$\dot{m}_{Product,H2O}$ =	1.08E-04	(kg/sec)

ρ_{H2} = 0.0824 (kg/m^3) at25°C

and;

$\dot{V}_{Product,H2}$ =	26.45	(L/min)

*Theoretical amount of product that would be obtained when feeding actual reactant flow rate

2.1) H_2

$$\dot{m}_{H_2}\left(\frac{\Delta h^{\circ}_{f(H_2)}}{MW_{H_2}}\right) = ?$$

From; $\Delta h^{\circ}_{f(H2)}$ = 0 (kJ/mol)

So;

$\dot{E}_{H2}$ = **0** **(kW)**

2.2) CO_2

$$\dot{m}_{CO_2}\left(\frac{\Delta h^{\circ}_{f(CO_2)}}{MW_{CO_2}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(CO2)}$ = -393.52 (kJ/mol)

So;

$\dot{E}_{CO2}$ = **-2.36** **(kW)**

2.3) H_2O

$$\dot{m}_{H_2O}\left(\frac{\Delta h^{\circ}_{f(H_2O)}}{MW_{H_2O}}\right) = ?$$

Due to; $\Delta h^{\circ}_{f(H2O)}$ = -285.83 (kJ/mol)

So;

$\dot{E}_{H2O}$ = **-1.71683231** **(kW)**

$\Sigma \dot{E}'_{Products}$ =	-4.08	(kW)

Finally;

$\Delta \dot{E}'_{Reactions}$ =	1.05	(kW)

The reaction need energy = 1.05 (kW)
to producing of 20 L/min hydrogen

*To Find a released energy from the theoretical lean-LPG combustion when using actual Air-Fuel inlet from the experiment

2) Porous media-LPG furnace

LPG = 3.4 (L/mim)
Air = 161.15 (L/mim)
AF ratio = 28.4

$$AF(ratio) = \frac{n((MW_{O_2}) + (3.76) \times (MW_{N_2}))}{(0.4 \times MW_{C_3H_8}) + (0.6 \times MW_{C_4H_{10}})}$$

n = 10.860

(0.4)C3H8 + (0.6)C4H10 + (10.86)O2 + (10.86*3.76)N2
⟶ (A)CO2 + (B)H2O + (C)N2 + (D)O2

(A) = 3.6
(B) = 4.6
(C) = 40.8
(D) = 9.9

Therefore; The theoretical LPG combustion equation when using a inlet amout that obtained from actual experiment

$$(0.4C_3H_8 + 0.6C_4H_{10}) + 10.86(O_2 + (3.76)N_2) \rightarrow 3.6CO_2 + 4.6H_2O + 10.86(3.76)N_2 + 9.9O_2$$

Practical Energy evaluation of Hydrogen production from ethanol

Data from the experiment

Input1 (Comustion-AF)

LPG = 3.4 (L/mim)
Air = 161.15 (L/mim)

From the theoretical equation of the lean-LPG combustion

(Input) **(Output)**

$$(0.4C_3H_8 + 0.6C_4H_{10}) + 10.86(O_2 + (3.76)N_2) \rightarrow 3.6CO_2 + 4.6H_2O + 10.86(3.76)N_2 + 9.9O_2$$

2.1) Input1 - (LPG + AIR)

2.1.1) LPG

$$\dot{m}_{LPG}\left(\frac{(\Delta h^{\circ}_{f(C_3H_8)} \times 0.4)}{MW_{C_3H_8}} + \frac{(\Delta h^{\circ}_{f(C_4H_{10})} \times 0.6)}{MW_{C_4H_{10}}}\right) = ?$$

From; V'_{LPG} = 3.4 **(L/mim)**

ρ_{LPG} = 2.011 (kg/m^3)

Therefore; m'_{LPG} = 6.8374 (g/min)

m'_{LPG} = 6.84E-03 (kg/min)

m'_{LPG} = 1.14E-04 (kg/sec)

C_3H_8 = 0.40 (mol/mol)

C_4H_{10} = 0.60 (mol/mol)

C_3H_8 ;

$\Delta h°_{f(C3H8)}$ =	-103.85	(kJ/mol)
$MW_{(C3H8)}$ =	44.097	(g/mol)
$MW_{(C3H8)}$ =	0.044097	(kg/mol)

C_4H_{10} ;

$\Delta h°_{f(C4H10)}$ =	-126.15	(kJ/mol)
$MW_{(C4H10)}$ =	58.124	(g/mol)
$MW_{(C4H10)}$ =	0.058124	(kg/mol)

Therefore;

$$\dot{m}_{(C_3H_8)}\left(\frac{\Delta h^{\circ}_{f(C_3H_8)}}{MW_{C_3H_8}}\right)+\dot{m}_{(C_4H_{10})}\left(\frac{\Delta h^{\circ}_{f(C_4H_{10})}}{MW_{C_4H_{10}}}\right)=$$

E'_{LPG} = -0.25574499 (kW)

1.2) AIR

$$\dot{m}_{O_2}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)=?$$

From; V'_{AIR} = 161.15 **(L/mim)**

ρ_{AIR} = 1.18 (kg/m^3) at 25°C

Therefore; m'_{AIR} = 190.157 (g/min)

m'_{AIR} = 1.90E-01 (kg/min)

m'_{AIR} = 3.17E-03 (kg/sec)

O_2 ;

$\Delta h°_{f(O2)}$ =	0.000	(kJ/mol)
$MW_{(O2)}$ =	31.999	(g/mol)
$MW_{(O2)}$ =	0.032	(kg/mol)

N_2 ;

$\Delta h°_{f(N2)}$ =	0.000	(kJ/mol)
$MW_{(N2)}$ =	28.013	(g/mol)
$MW_{(N2)}$ =	0.028	(kg/mol)

Due to;

$\Delta h°_{f(O2)}$ =	0	(kJ/mol)

$\Delta h°_{f(N2)}$ =	0	(kJ/mol)

Therefore;

$$\dot{m}_{O_2}\left(\frac{\Delta h^{\circ}_{f(O_2)}}{MW_{O_2}}\right)+\dot{m}_{N_2}\left(\frac{\Delta h^{\circ}_{f(N_2)}}{MW_{N_2}}\right)=$$

$\dot{E}_{AIR}$ = **0** **(kW)**

Finally; $\Sigma E_{(Heat\text{-}input)}$ = **-0.26** **(kW)**

2.2) Output - (Exhaust)

$$(0.4C_3H_8+0.6C_4H_{10})+10.86(O_2+(3.76)N_2)\rightarrow 3.6CO_2+4.6H_2O+10.86(3.76)N_2+9.9O_2$$

2) Output1 - Exhaust(CO2 + H2O + N2 + O2)

From;

$$\sum\dot{m}_{Exhaust}=\sum\dot{m}_{Fuel\_Supply}$$

$\Sigma\dot{m}_{Exhaust}$ = **3.28E-03** **(kg/sec)**

$$\left[\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)+\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)+\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)+\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(O_2)}+\Delta h_{si(O_2)})}{MW_{O_2}}\right)\right]_{(Out\text{-}exht.)}$$

CO_2	=	3.6	(mole)
H_2O	=	4.6	(mole)
N_2	=	40.8	(mole)
O_2	=	9.9	(mole)

$MW_{(CO2)}$	=	44.01	(g/mol)
$MW_{(CO2)}$	=	0.04401	(kg/mol)
$MW_{(H2O)}$	=	18.015	(g/mol)
$MW_{(H2O)}$	=	0.018015	(kg/mol)
$MW_{(N2)}$	=	28.013	(g/mol)
$MW_{(N2)}$	=	0.028013	(kg/mol)
$MW_{(O2)}$	=	31.999	(g/mol)
$MW_{(O2)}$	=	0.031999	(kg/mol)

And; Mass fraction of CO_2, H_2O, and N_2 in the Exhaust components are

Mass Fraction CO_2 =	0.09

Mass Fraction H_2O=	0.05
Mass Fraction N_2 =	0.67
Mass Fraction O_2 =	0.19

Therefore;

$\dot{m}_{Exhaust,CO2}$ =	**3.06E-04**	**(kg/sec)**
$\dot{m}_{Exhaust,H2O}$ =	**1.60E-04**	**(kg/sec)**
$\dot{m}_{Exhaust,N2}$ =	**2.21E-03**	**(kg/sec)**
$\dot{m}_{Exhaust,O2}$ =	**6.12E-04**	**(kg/sec)**

2.2.1) CO_2

$$\dot{m}_{CO_2}\left(\frac{(\Delta h^{\circ}_{f(CO_2)}+\Delta h_{si(CO_2)})}{MW_{CO_2}}\right)=?$$

Due to;

$\Delta h^{\circ}_{f(CO2)}$ =	-393.52	(kJ/mol)	
$\Delta h_{si(CO2)}$ =	6.17	(kJ/mol)	at 170°c

So;

$\dot{E}_{CO2}$ = **-2.69** **(kW)**

2.2.2) H_2O

$$\dot{m}_{H_2O}\left(\frac{(\Delta h^{\circ}_{f(H_2O)}+\Delta h_{si(H_2O)})}{MW_{H_2O}}\right)=?$$

Due to;

$\Delta h^{\circ}_{f(H2O)}$ =	-285.83	(kJ/mol)	
$\Delta h_{si(H2O)}$ =	5.05	(kJ/mol)	at 170°c

So;

$\dot{E}_{CO2}$ = **-2.49** **(kW)**

2.2.3) N_2

$$\dot{m}_{N_2}\left(\frac{(\Delta h^{\circ}_{f(N_2)}+\Delta h_{si(N_2)})}{MW_{N_2}}\right)=?$$

Due to;

$\Delta h^{\circ}_{f(N2)}$ =	0	(kJ/mol)	
$\Delta h_{si(N2)}$ =	4.28	(kJ/mol)	at 170°c

So;

$\dot{E}_{N2}$ = **0.34** **(kW)**

2.2.4) O_2

$$\dot{m}_{O_2}\left(\frac{(\Delta h^{\circ}_{f(O_2)} + \Delta h_{si(O_2)})}{MW_{O_2}}\right) = ?$$

Due to;

$\Delta h^{\circ}_{f(N2)}$ =	0	(kJ/mol)		
$\Delta h_{si(N2)}$ =	4.48	(kJ/mol)	at 170°c	

So;

$\dot{E}_{O2}$ = **0.09** **(kW)**

Therefore; $\Sigma E_{(output)}$ = **-4.76** **(kW)**

Finally; $\Delta E'_{Furnace.}$ = **-4.50** **(kW)**

*Theoretically

Appendix: A4
Sensible Enthalpy of Gases

Cp: (kJ/(kmol*K))

Ideal-gas specific heats of various common gases (As a function of temperature)

$Cp = (a) + (b)T + cT^2 + dT^3$ (kJ/(kmol*K)); T in (K)

	a	b	c	d
N2:	28.9	-1.57E-03	8.08E-06	-2.87E-09
O2:	25.48	1.52E-02	-7.16E-06	1.31E-09
H2:	29.11	-1.92E-03	4.00E-06	-8.70E-10
CO:	28.16	1.68E-03	5.37E-06	-2.22E-09
CO2	22.26	5.98E-02	-3.50E-05	7.47E-09
H2O(g):	32.24	1.92E-03	1.06E-05	-3.60E-09

Therefore, at the condition of

Exhaust- N2, O2, CO, CO2, and H2O(Vapor)

At T =	170	(°C) =	443.15	(K)
S.T =	25	(°C) =	298.15	(K)

	Cp (kJ/(kmol*K))	Δh_{si} (kJ/mol)
N2:	29.54	4.28
O2:	30.92	4.48
CO:	29.76	4.32
CO2	42.54	6.17
H2O(g):	34.85	5.05

Appendix: A5
Theoretical combustion - Mass balance

Assume for 1 mole of LPG

**Nitrogenoxide (NOx) is neglect because it is very less value.
* Assume as remained N species become N2 // and remained Hydrogen species become H2O.

LPG = **3.4 (L/mim)**
Air = **161.15 (L/mim)**
AF ratio = **28.4**

$$AF(ratio) = \frac{n((MW_{O_2}) + (3.76) \times (MW_{N_2}))}{(0.4 \times MW_{C_3H_8}) + (0.6 \times MW_{C_4H_{10}})}$$

n = 10.860

(0.4)C3H8 + (0.6)C4H10 + (10.86)O2 + 10.86*3.76)N2
⟶ (A)O2+ (B)CO + (C)CO2 + (D)N2 + (E)H2O

C:	3.6	=	(B) + (C)	[1]
H:	4.6	=	(E)	[2]
O:	21.72	=	2(A) + B + 2(C) + E	[3]
N:	40.83	=	(D)	[4]

Mole fraction : Volume fraction

assumed! gases are ideal gas >>> mole fraction = Volume fraction

From flue gas analyzer

O2 =	7.67 (% Volume)	0.0767	%Volume
CO =	20 (ppm)	0.00002	%Volume
CO2 =	8.76 (% Volume)	0.0876	%Volume

O2:	0.0767	=	A/(A+B+C+D+E)	[5]
CO:	0.00002	=	B/(A+B+C+D+E)	[6]
CO2:	0.0876	=	C/(A+B+C+D+E)	[7]

If [5] + [6] + [7];
Then;

0.16432 = ((A+B+C+D+E)-(D+E))/(A+B+C+D+E)
Therefore; (D+E)/(A+B+C+D+E) = 0.84 [8]

Substitute [1], [2], and [4] in [8];

(A+B+C) = [(D+E)/0.84]-(D+E)
Therefore; (A) = 5.33 [9]

Substitute [2], [9], and [4] in [3];

From; 21.72 = 2(A) + B + 2(C) + E

Therefore; (B) + 2(C) = 6.45 [10]

If [10] - (minus) [1];
Then;

(C) = 2.85 [11]

Substitute [11] in [1];
Therefore;

B = 0.75 [12]

Finally;

A =	5.33	26.3203
B =	0.75	
C =	2.85	
D =	40.83	
E =	4.60	

In finally, chemical equation of Practical LPG-combustion is obtained

(0.4)C3H8 + (0.6)C4H10 + (10.86)O2 + (10.86*3.76)N2
⟶ (5.33)O2+ (0.75)CO + (2.85)CO2 + (40.83)N2 + (4.6)H2O

APPENDIX B

CONFERENCE PROCEEDING

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Total Energy Requirement for Hydrogen Production Reactor using Various Porous Media Materials

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Abstract. In a hydrogen production reactor, combustion of LPG was used as a heat source for ethanol steam reforming. For such purpose, the operating temperature was required to be around 700-900°C along the entire height of the reactor. Various types of porous media materials were used as a heat transfer media, i.e. 25mm ceramic saddles, random size bio-filter media from MTEC, ceramic foam, and ceramic balls. The objective of this study was to obtain the practical amount of total energy input, to compare with theoretical calculation which can achieve the required temperature of ethanol steam reforming for the hydrogen production. From our experiments, 13.20 kW of energy was needed to fulfill the requirement of the reactor, while only 2.49 kW was expected from theoretical calculation. Most energy loss was due mainly to: 1) heat loss at the top of the reactor where the metal part was directly exposed to the environment, 2) a large amount of energy loss at the furnace stack and, 3) insufficient mixing at the early stage of combustion at the bottom of the furnace as noticed by high CO concentration in flue gas. The porous media material has a significant effect on temperature distribution and energy consumption. The results show that the use of ceramic saddles as porous media consume more energy than the ceramic foam and the bio-filter media mixed with ceramic saddles during the start-up period of the reactor.

Introduction

Global warming has become a serious issue at present as a result of huge amount of carbon dioxide emission. It has been lately confirmed that this due mainly to abnormal growth of population and also human's activities in power generation sector from the use of fossil fuels [1]. Fossil fuels are used approximately 80% of the present world energy demand [2]. Among renewable energy resources, hydrogen (H_2) is considered as an important energy carrier for the future. Unlike fossil fuels, H_2 burns cleanly, without emission of any toxic pollutants. Moreover, great amount of H_2 is also needed by petrochemical industries to be utilized in purification processes such as hydro-desulfurization. Production of hydrogen comprises thermo-chemical, electrochemical, photo-electrochemical, and photo-biological techniques. Among thermo-chemical technologies, steam reforming is the most widely used in the majority of H_2 production industries because of its high efficiency. In Thailand, one of the most promising methods is a steam reforming of bio-ethanol as it has a high potential to be a source of hydrogen and now in a research stage, moreover bio-ethanol feedstock can be produced from agricultural products which are abundant throughout the country. High temperature about 700-1100°C is required for the endothermic reaction of a steam reforming process [3]. In the reformer unit, it is required that the temperature

should be evenly distributed all along the longitudinal height in order to maintain optimum condition for the catalytic reaction.

One of interesting burner technologies suitable for above requirements is the porous media burner as it has ability to absorb uncertainty of thermal loading of the raw gas. By the concept of this technology, the combustion taking place within the cavity of a porous media matrix can be stabilized under relatively more various operating conditions.

Methodology

Porous media burner. For hydrogen production from ethanol steam reforming, furnace design is one of the most important steps as expected to obtain the required temperature of about 700-900°C. The idea of porous media combustion was presented for our experiments. It has the ability to absorb uncertainty of thermal loading of the raw gas, ability to be heat retention and mixing buffer in the combustion process. With this technology, the combustion taking place within the cavity of porous matrix can be stabilized under wider operating conditions. Accordingly, thermal NO_x is relatively lower compared to the conventional free flame combustion due to lower combustion temperature.

J. Charoensuk, A. Lapirattanakul, 2011 [4] pointed out prior to discuss on the performance of the burner on ignition process. The ignition process can be discussed in three steps. 1) During a startup period ignition takes place within the flammability area. 2) After a porous domain is heated up to an auto-ignition temperature of a fuel, the gas mixtures is self-ignited. 3) When the furnace temperature is heated up to the required temperature, mixture under rich condition is fed at the bottom of the furnace; as an expectation of a complete combustion at the top area of a reactor then significant heat from downstream is fed back to upstream region with heat transfer modes of radiation and conduction through the porous matrix.

Energy requirement. For overview consideration of energy requirement for hydrogen production from ethanol steam reforming, all power inputs which are fuel for combustion, hydrocarbon for steam reforming reaction and all electrical devices are considered. The thermal efficiency of the hydrogen production reactor can be determined by a concept of thermodynamics.

Experimental set up

A porous media burner. A porous combustor had been designed and constructed as a heat source for an ethanol steam reforming reactor; the furnace has the inner diameter of 290 mm with 700 mm height of the combustion area. The ceramic air-distributor was located at the bottom area of the furnace; next to the fuel inlet port to induce a secondary air state to the combustor. Electronic valve controls were applied for automatic adjustment of air-fuel ratio, and flashback prevention. The burner has four air-inlet stages; the 1st air pipe or primary air is connected with the fuel line and mixing chamber at the bottom of the furnace. The 2nd pipe or secondary air is connected tangentially below the ceramic air-distributor. The 3rd and 4th air inlets or tertiary air stages are connected tangentially at the locations of 185 mm. and 465 mm. from the ceramic air-distributor plate, respectively.

J. Charoensuk et al. (2011) [4] had suggested that the operation of 110% excess air is the most desirable as far as the emissions and the temperature distribution are concerned. Our study has adopted their idea of excess-air operation by maintaining the air-fuel ratio to be constant throughout the experiments.

In the combustor, various types of porous media materials were chosen as a heat transfer media, which were: 25mm ceramic saddles, random size bio-filter media from MTEC, and 20x20x20 mm^3 ceramic foam, and inert-ceramic balls; subjecting to availability of the local supplier see Fig.1. Physical properties of each porous media material are shown in Table 1.

Fig. 1 Porous media material 1.) 25 mm. ceramic saddles, 2.) Random size bio-filter media from MTEC, 3.) 20x20x20 mm^3 ceramic foams, 4.) 16 mm. ceramic balls and 5.) 25 mm. ceramic balls

Table 1 Physical properties of porous media materials (Ecocera of MTEC)

Porous materials	Porosity (%)	Thermal conductivity (W/m °C)	Dimension (mm)	Shape	Material composition	Surface area (m2/m3)
Ceramic saddle	77	0.9-1.0	25	Saddle	SiO_2 , $Al2O_3$	254
Bio-filter	55	Very low	25-30	Random	SiO_2, K2O, CaO,	1.04E+07
Ceramic foam (10ppi)	87	1.85	20	Dice	SiC	1.15E+06
Ceramic balls 1	34	6.3	16	Sphere	SiO_2, $Al2O_3$	210
Ceramic balls 2	46	6.3	25	Sphere	SiO_2, Al_2O_3	130

Measurement. Axial temperature distribution within the combustion was measured by using of data logger (GRAPHTEC GL800) with an accuracy ±2.5°C connected with 3 mm. diameter, type-K thermocouples. The thermocouples were located at 6 different locations from 135, 225, 315, 405, 495, and 585 mm. of the ceramic air-distribution plate as illustrated in Fig. 2.

When a steady state is obtained (about 9 hours after starting up), the flue-gas compositions were monitored by using a flue-gas analyzer (Testo 350-XL). An accuracy of the sensor is as follows: ±0.3% O_2 for O_2 sensor, and ±5% of reading for other species. The gas data were used to calculate combustion efficiency.

Fuel analysis. Liquefied petroleum gas (LPG) is utilized as a fuel for porous burner. The composition of LPG is listed in Table 2. It has a lower heating value of 45.8 MJ/kg, density of 2.011 kg/m^3. The composition of propane and butane in LPG are 40 and 60 mol%, respectively. The needle valve and rotameter were used to control and measure the LPG flow rate, respectively.

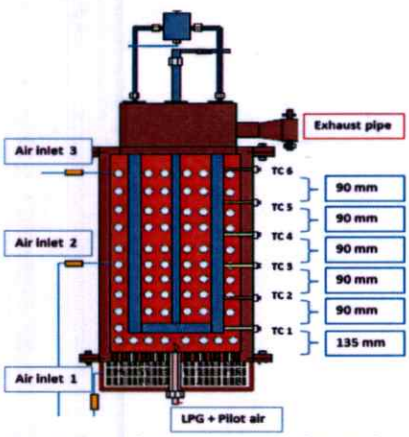

Fig. 2 Experimental set-up of staged porous media burner

Table 2 Properties of LPG (Petroleum Thailand Co., Ltd)

Properties of LPG (Commercial Butane).

Properties of	Quantity	Unit
Chemical formula (Propane:Butane)	C_3H_8:C_4H_{10}	–
Proportional of gas mixture Propane:Butane	40:60	% by mol
Low heating value	45.8	MJ/kg
Density of gas	2.011	kg/m^3
Volume of 1 kg Gas (at 1 bar) at 0 °C	508	liter
Wobbe index	20.79	kwh
Flame temperature	1925	oC
Ignition temperature with air	510	oC
Air fuel ratio (stoichiometry)	15.6	kg_{air}/kg_f

Results and discussion

Effect of porous media materials on temperature profile. Studies were carried out by previous workers on effect of various sizes of spherical ceramics on temperature distributions. J.Charoensuk et al.[4] reported that higher cavity in the porous matrix caused higher temperature throughout the burner distance. The reason of the higher temperature is because of enhancement of mixing rate between fuel and air, as a result from increasing of the bulk flow inside a burner. For our work, four experiments were studied to determine the optimum porous-media composition for hydrogen production furnace. Our experiments were proposed based on porous media material of high cavity in a porous matrix.

1st Experiment. In this experiment, ceramic saddles (25 mm.) with 77% porosity had been chosen to be filling as a reference. A test was carried out at 110% excess air based on literature review [4]. As a result, inhomogeneous cavities in the porous matrix which caused by overlay of the ceramics-saddle shapes caused inhomogeneous air-fuel mixture distribution which led to low overall-temperature in the furnace. Finally, the temperature profile of the furnace dropped drastically along the longitudinal distance since 200 mm. from the air distributor, see Fig.3 (a).

2nd Experiment. Random-round shape bio-filter media from MTEC (≈25 mm.) were thoroughly mixed with the ceramic saddles for reducing the overlay-shape effect; as a purpose of making more homogeneous cavities inside the porous matrix. As a result, the temperature profile of the second experiment was increased from the previous experiment. In addition, radiated heat loss to the furnace stack was notified by a slight drop of the temperature profile at the upper area of the furnace shown in Fig.3 (b).

3rd Experiment. Bio-filter media was mixed with ceramic balls after the good result from 2nd experiment. Ceramic ball material was placing at lower area of the furnace, because of its high strength, to support the load of furnace components. At the upper furnace area, low cavity balls were placed to block a radiated heat loss to the furnace stack. As the result, the lower temperature profile than the previous experiment at all areas along the longitudinal distance of the furnace were obtained. At the lower furnace area, where placing with high cavity ceramic balls, lower temperature profile than the second experiment occurred because the balls have lower cavity in the porous matrix comparing with ceramic saddles. Low thermal conductivity of the bio-filter caused low temperature in the middle of the furnace. The low-cavity ceramic balls placing at the upper area of the furnace were expected to block the radiated heat loss to the furnace stack. Anyhow the ceramic balls of high thermal conductivity, which absorbed high amount of heat from the middle of furnace area, caused higher radiated heat loss to the stack than when using ceramic saddles alone.

4th Experiment. Ceramic foam or well known as cast-iron filter material had been selected to be filling as a porous media because of its high cavity (≈ 87%) in the porous matrix and large pores (10 pores per inch). Due to brittleness of the ceramic foam material, the lower area of the furnace is filled with the ceramic saddle. Bio-filter media had been placed in the upper furnace area as to lower radiated heat loss to the furnace stack by its low thermal conductivity. As a result, the temperature profile from this experiment had reached the requirement of hydrogen production in all areas of the longitudinal distance (700-900°C). The best temperature profile of all experiments is obtained from placing of ceramic foam in the middle area and materials which obtained the good results from previous experiments in the lower and upper zone.

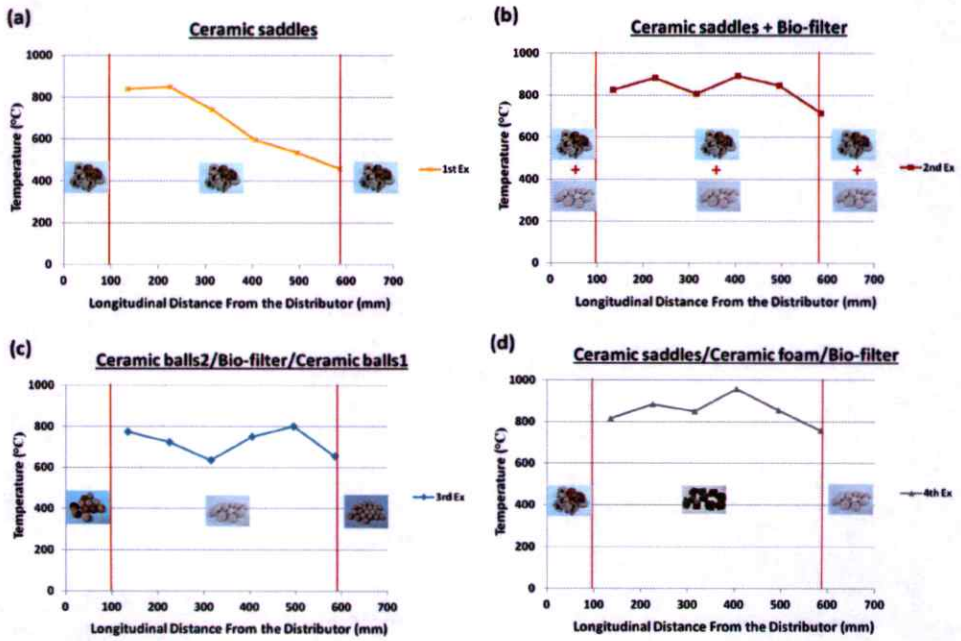

Fig. 3 Experimental results of (a) 1st Experiment, (b) 2nd Experiment, (c) 3rd Experiment, and (d) 4th Experiment

Energy requirements. The total energy requirement for hydrogen production unit is defined by the summation of all energy inputs which were: ethanol reactant for steam reforming reaction, LPG as a heat source of the porous media burner, and all electrical devices. Ethanol and LPG energy consumption rate can be defined by: Eq. 1

$$Energy\ consumption\ rate = V' \times \rho \times LHV\ . \quad (1)$$

Where V' is a volume flow rate of a fluid (kg/m^3), ρ is a gas density (kg/m^3), and LHV is a low heating value (kJ/kg). Energy rate of output (hydrogen product) is also calculated by this equation.

Thermal efficiency of the hydrogen production from ethanol steam reforming reactor can be determined by Eq. 2 in which input or the mass flow rate and lower heating value (LHV) of hydrogen are divided by power inputs.

$$Thermal\ efficiency = \frac{output\ (kW)}{input\ (kW)} \times 100\ (\%)\ . \quad (2)$$

From the calculation, the total rate of energy input and output are equal to 2.49 and 13.20 kW, respectively. The thermal efficiency of hydrogen production system is 18.86%. Most of energy loss was due mainly to: 1) heat loss at the top of the reactor where the metal part was directly exposed to environment, 2) a large amount of energy loss at stack, and 3) insufficient mixing at the early stage of combustion at the bottom of the furnace as noticed by high carbon monoxide (CO) concentration in a flue gas monitored by using a flue-gas analyzer.

Conclusions

The effect of porous media materials on temperature distribution, and total energy requirement for hydrogen production reactor had been investigated. Higher cavity in a porous matrix and high porosity inside a material are the causes of high temperature distribution throughout the burner. Moreover, radiated heat loss to the furnace stack can be lowered by placing the upper area of the furnace with the material of low thermal conductivity. Placing of the ceramic saddles in the lower, ceramic foams in the middle, and bio-filter media in the upper area of the furnace is the most efficient porous-media combination from our experiments.

From the energy calculation, the total rate of energy input and output are equal to 13.20 and 2.49 kW, respectively. The thermal efficiency of the hydrogen production system is 18.86%. Most of energy loss was due mainly to: 1) heat loss at the top of the reactor where the metal part was directly exposed to the atmosphere, 2) a large amount of energy loss at the furnace stack, and 3) an insufficient mixing at the early stage of combustion at the bottom of the furnace as noticed by high carbon monoxide (CO) concentration in the exhaust gas.

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APPENDIX C

HEAT ACCUMULATION DURING A STARTUP PERIOD OF THE POROUS MEDIA-LPG FURNACE

Appendix C

Heat accumulation during a startup period of the porous media-LPG furnace

A porous media-LPG furnace is utilized as a heat source for the hydrogen production from ethanol steam reforming unit. Ceramic foam or well known as cast-iron filter material had been selected to be filling as a porous media because of its high cavity (≈ 87%) in the porous matrix and large pores (10 pores per inch). Due to brittleness of the ceramic foam material, the lower area of the furnace is filled with the ceramic saddle. Bio-filter media had been placed in the upper furnace area as to lower radiated heat loss to the furnace stack by its low thermal conductivity. As a result, the temperature profile from this experiment had reached the requirement of hydrogen production in all areas of the longitudinal distance (700-900°C) (Mek Srilomsak 2015).

A total energy accumulation in the furnace during a startup period of the hydrogen production unit is one of the most interesting issue to be concerned, since the furnace required a long period of time (about 8-10 hours) to be started up until reached the required temperature for a steam reforming reaction at 700-900°C along height of the furnace.

An energy balance equation is used for a calculation of total energy accumulation in the porous media-LPG furnace during a startup period, see Equation aA3.1.

$$\Sigma \dot{H}_{In(Time\_step)} - \Sigma \dot{H}_{Out(Time\_step)} = \Sigma \dot{H}_{Accumulation(Time\_step)} \qquad \text{(A3.1)}$$

$\Sigma \dot{H}_{In(Time\_step)}$ and $\Sigma \dot{H}_{Out(Time\_step)}$ denote total energy inputs and outputs which calculated from LPG supplied and exhaust composition, respectively in the startup period. $\Sigma \dot{H}_{Accumulation(Time\_step)}$ is an energy accumulation inside the porous

media-LPG furnace. Time step of the data recording is 15 minute, by the startup period of the experiment lasted for 8.5 hours.

As a result, the energy accumulation inside the porous media-LPG furnace during an 8.5 hours startup period is 90,832.69 kJ (Appendix A0).

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