List of Figures

List of Tables

List of Equations

CHAPTER 1
INTRODUCTION

1.1 Background Study

1.1.1 Hydrogen Demand

Hydrogen is the simplest molecule known to man. It is considered an energy carrier which can be produced from various sources;

- Fossil Fuel
  Hydrogen can be produced from natural gas by gas reforming or coal gasification.

- Electricity
  Hydrogen can be produced by splitting the water molecule into hydrogen and oxygen by electrolysis.

- Renewable Sources
  Hydrogen can be produced by gasification or pyrolysis of biomass.

Fig. 1 below shows the percentage of the production of hydrogen in the industrial scale. It shows that the majority of industries, 73%, produce hydrogen from natural gas, 24% produce hydrogen from oil and only 3% of industries produce hydrogen by electrolysis [1].

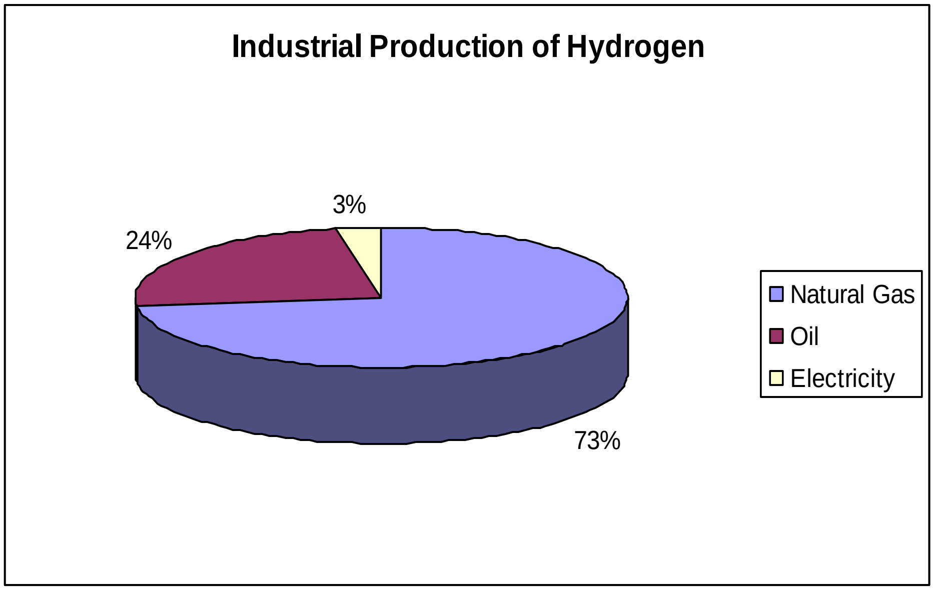

Figure 1: Industrial Production of Hydrogen [1]

In 2003, the global hydrogen demand was 40Mton/yr (±10%) [1]. Fig. 2 below shows that 49% of the global hydrogen demand is of petroleum refineries, which is estimated to be 19.6 Mton/yr [1]. In 2008, the Egyptian local hydrogen demand for the petroleum refineries is estimated to be between 94,500ton/yr and 160,500ton/yr [2].

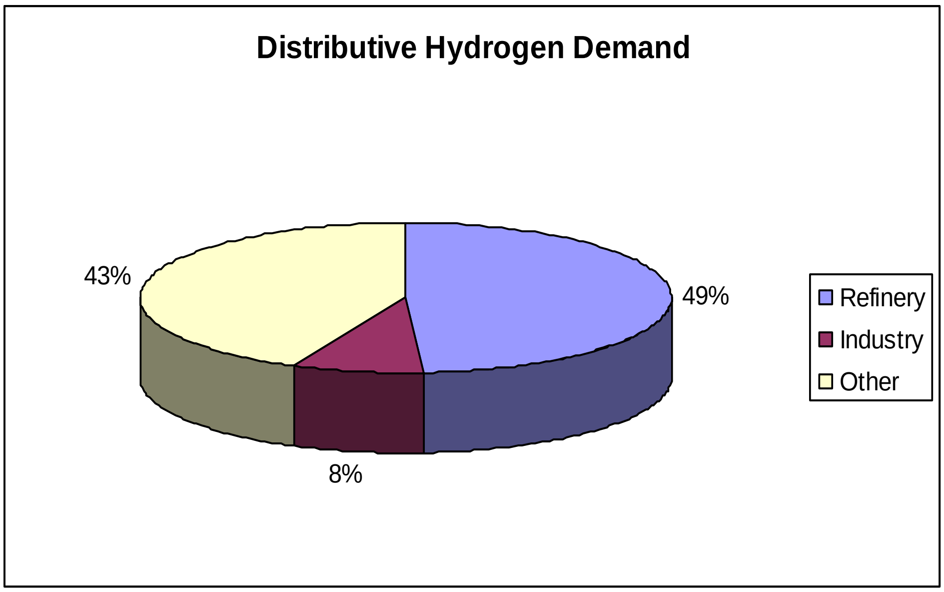

Figure 2: Distributive Hydrogen Demand [1]

1.1.2 Petroleum Refinery

Petroleum is a mixture of organic liquids containing crude oil and natural gas. Petroleum occurs deep in the ground either on land or in the sea. The composition and color of crude oil differ from an oilfield to another ranging from pale yellow low viscosity liquids to heavy black consistencies. Crude oil is not valuable in its crude form, so it is distilled into more valuable fuels, lubricating oils, waxes and asphalt.

In a petroleum refinery, a series of processes occur to produce chemical and physical changes to the crude oil to convert it into more valuable products such as petrol, diesel, lubricating oils, fuel oils and bitumen.

Crude oil comes from the well containing a mixture of hydrocarbon compounds and small quantities of contaminants such as oxygen, sulfur, nitrogen, water and salts. In the refinery, most of these contaminants are removed and the crude oil is broken down into more valuable products and may be blended into more useful products.

1.1.3 Hydrogen Usage in Petroleum Refineries

Hydrogen is used in hydrotreating and hydrocracking processes in the petroleum refineries. Hydrotreating process is the process of removing sulfur and nitrogen contaminants in the crude oil. Hydrogen reacts with sulfur forming hydrogen sulfide (H_2S) and reacts with nitrogen compounds forming ammonia (NH_4). Hydrocracking process is the process of breaking down heavy hydrocarbon fractions into more valuable lighter hydrocarbons in the presence of hydrogen [3].

1.1.4 Processes to Produce Hydrogen

Hydrogen can be produced by several processes; Electrolysis is an electro-chemical process splitting water molecule into oxygen and hydrogen molecules using electricity. Efficiency of the electrolysis process is high yet it is considered the most costly process due to the large cost of electricity used [3].

The process of coal gasification produces hydrogen along with by-products of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4). A water-gas shift reaction can convert the carbon monoxide into more hydrogen and carbon dioxide. The coal gasification is considered more expensive than natural gas reforming because of the higher demand of oxygen in the gasifier [3].

The natural gas reforming is the most widely used process for the production of hydrogen industrially. Methane of the natural gas reacts with steam at high temperature producing carbon monoxide and hydrogen at a temperature range between 700^{o}C and 1100^{o}C. A water-gas shift reaction is also used to convert the carbon monoxide into more hydrogen and carbon dioxide [3].

1.1.5 Biomass as a Sustainable Source

Plants use photosynthesis process to convert carbon dioxide and water into sugars, these sugars are stored in the plants in different forms. The cellulose, a very complex sugar polymer produced in some plants, can be gasified and converted into bio-fuels.

As shown in table 1, although rice husk and rice straw are not the highest produced agricultural waste in Egypt, they are considered the major polluting factor in Egypt. Both rice husk and rice straw are burned causing emissions of greenhouse gases such as carbon monoxide and carbon dioxide into the atmosphere causing what is called “black cloud” over some major cities in Egypt [2, 4].

Utilization of rice husk and rice straw as a feedstock for the production of hydrogen would solve their disposal problems in Egypt as well as generating useful energy.

Table 1: Agriculture Residues in Egypt [4]

Kind	**Total Waste (Mton/yr)**
Cotton-Stalks	0.96
Fruits	1.74
Rice Straw	3.34
Rice Husk	1.50
Sugar Cane	5.17
Sugar Beet	0.40
Maize	3.81
Cobs	1.20
Sorghum	0.96
Wheat	7.64
Barley	0.47
Legumes	0.32
Vegetables	2.56
Date Palms	0.91

Unlike fossil fuel, using biomass to produce hydrogen would not introduce new carbon in the ecosystem leading to a net zero carbon dioxide emission. Fig. 3 explains that carbon dioxide emissions from hydrogen production are used by the plants which are the feedstock for the hydrogen production.

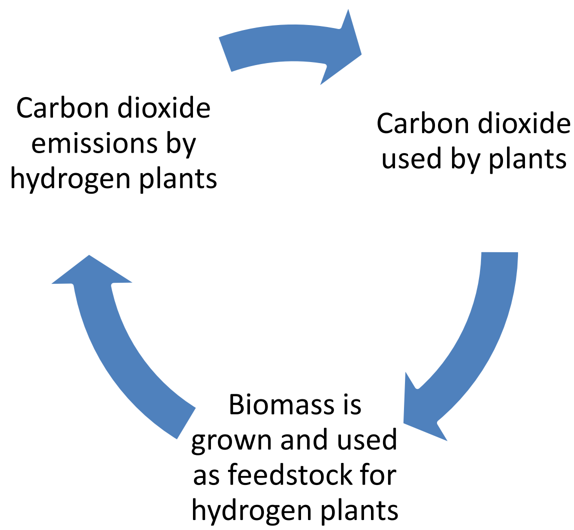

Figure 3: Net Zero Carbon Dioxide Emission

In 2007, the global rice husk and rice waste production was estimated to be 600 Mt/yr divided into 100 Mt/yr of rice husk and 500 Mt/yr of rice straw [4]. 90% of the rice waste production is generated in the developing countries [4].

1.1.6 Gasification of Biomass

Gasification of biomass is one of the processes to convert biomass into hydrogen. Gasification products are hydrogen, carbon dioxide, carbon monoxide, methane and un-burnt carbon [5].

The gasification process necessitates a gasifying agent to provide oxygen. The gasifying agents are air, oxygen, steam and carbon dioxide [5]. Carbon dioxide is self-produced agent as it is being produced during the early oxidation process. Air is the most commonly used agent as it is always available at no cost. Air as an agent has a major disadvantage because of the nitrogen content. Oxygen as an agent in the gasification of biomass gives the produced gas an advantage of having higher heating value but will have a major drawback of the high cost of pure oxygen. Using steam as an agent has a main advantage of the increase of hydrogen content in the product gas. Steam gasification is highly endothermic reaction so it needs a temperature at least 800^{o}C in case no catalyst is used. The heat required for the reaction to take place can be transferred by indirect heating or by partial combustion of fuel in the reactor [5].

The production of hydrogen is increased with the increase of the gasifying agent temperature up to 1,300^{o}C [5, 10].

1.2 Problem Statement

The design of a biomass based hydrogen plant for an existing refinery as the existing hydrogen plants mainly use natural gas and coal gasification which has major issues;

1) The fluctuation and instability of prices of natural gas.
2) The depletion of source of fossil fuel.
3) The emission of greenhouse gases such as carbon dioxide and carbon monoxide.

Hence, this project aims to design a cleaner production of hydrogen to be used in an existing petroleum refinery using rice husk and rice straw biomass as a feedstock.

The hydrogen production process selected is via biomass gasification. Due to the extensive and exhaustive range of operating conditions feasible, the study is performed using a computational and simulation approach. Furthermore, this approach is less expensive relative to the experimental work

1.3 Objectives

This study focuses on designing a flowsheet for a biomass-based hydrogen plant for an existing petroleum refinery using computational and simulation approach. The objectives of this study are;

1) To collect the hydrogen demand data for an existing refinery in Egypt.
2) To select a feedstock and collect information on its availability.
3) To collect the reaction kinetics data on the gasification process for the selected biomass.
4) To synthesize the flowsheet that consists of the treatment of the biomass up to the production of hydrogen based on the demand of the refinery.
5) To simulate the flowsheet using a simulation tool.
6) To predict the hydrogen production with respect to different operating conditions.

1.4 Scope of Study

1.4.1 Timeframe

We propose the design for the biomass-based hydrogen plant for an existing petroleum refinery to be completed in one year timeframe that consists of two tasks;

- Research and Literature Review

  This task is to be completed by the end of the first semester in which literature research are be done on hydrogen demands, feedstock availability and sustainability and previous papers on similar projects where reaction kinetics for the selected biomass are collected and screened.

- Flowsheet Development

  This task is to be completed by the end of the second semester and is focused on the flowsheet design and the simulation of the hydrogen plant using MATLAB and PETRONAS owned process simulator software, iCON.

1.4.2 Place of Study

All information is gathered are with respect to Egypt including hydrogen demand of existing petroleum refineries and the availability of biomass.

CHAPTER 2
LITERATURE REVIEW

2.1 Hydrogen Demand by Refineries in Egypt

Egypt has a total of nine petroleum refineries, one is considered an integrated (complex) refinery and eight are non-integrated refineries [2].

The production/consumption of hydrogen for the eight non-integrated is estimated to be between 105 and 183 t/day [2].

The production/consumption of hydrogen for the integrated refinery is estimated to be between 210 and 350 t/day [2].

Hence, the total hydrogen production/consumption of Egyptian petroleum refineries is estimated to be between 315 and 533 t/day [2].

2.2 Quantity of Rice Husk and Rice Straw in Egypt

Rice cultivation in Egypt produces rice husk and rice straw as wastes. From the period of the 1960s till 1990, the rice waste was estimated to be constant at 2.3 Mton/yr. The production of rice increased leading to the increase of production of waste to 5.8 Mton/yr in 2004. In 2007, the rice waste production decreased to 3.5 Mton/yr [4].

In 2009, the total production of rice wastes slightly increased to 3.6 Mton/yr divided into 3 Mton/yr of rice straw and 0.6 Mton/yr of rice husk [6].

2.3 Rice Husk and Rice Straw Analysis

Table 2: Egyptian Rice Straw Elemental Composition [4]

Composition	C	H	O
Percentage	46.6%	6.2%	46.5%

Table 3: Egyptian Rice Husk Elemental Composition [4]

Composition	C	H	O
Percentage	49.9%	7.0%	41.3%

2.4 Hydrogen from Biomass

Hydrogen production from biomass can be achieved by several processes [4, 7];

- Thermo-chemical gasification coupled with water-gas shift.
- Direct solar gasification
- Miscellaneous novel gasification
- Fast pyrolysis followed by reforming of carbohydrate fraction of bio-oil.
- Biomass-derived syn-gas conversion.
- Microbial conversion of biomass.

2.5 Biomass Reaction Model

Assumptions [5]:

- The gasification product is CO, CO_2, H_2, CH_4, N_2, H_2O and un-burnt carbon.
- All reactions are at thermodynamic equilibrium.
- All reactions continue adiabatically.
- Oxidation is a fast reaction and goes to completion.
- Moisture content is neglected and the product depend only on x and y which are the hydrogen and the oxygen atoms in the biomass respectively.

In the gasifier, a series of reactions take place to produce the different products [5];

$C + O_2 = CO_2$		Equation 1: Oxydation reaction
$C + CO_2 \leftrightarrow 2CO$	$\Delta H = -221$ KJ/mol	Equation 2: Boudouard Reaction
$C + H_2O \leftrightarrow CO + H_2$	$\Delta H = 131$ KJ/mol	Equation 3: Steam Gasification
$CH_4 + H2O \leftrightarrow CO + 3H_2$	$\Delta H = 206$ KJ/mol	Equation 4: Methanation Reaction
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H = -41$ KJ/mol	Equation 5: Water Gas-Shift

The above equations can be combined to and overall general gasification equation [5];

$$CH_xO_y + z\,(O_2 + 3.76\,N_2) + k\,H_2O \leftrightarrow a\,CO_2 + b\,CO + c\,H_2 + d\,CH_4 + e\,N_2 + f\,H_2O + g\,C$$

Equation 6: General Gasification Equation

2.6 Reaction Kinetics

Table 4 below shows the specific heat capacities of the different components and the equilibrium constants of equations 2-5;

Table 4: Specific Heat Capacities and Equilibrium Constants [8]

T	C_{pCO2}	C_{pCO}	C_{pH2}	C_{pCH4}	C_{pC}	K_1	K_2	K_3
600	1.075	1.087	14.55	3.256	0.85	$1.870*10^{-6}$	$5.058*10^{-5}$	$9.235*10^{1}$
800	1.168	1.139	14.71	3.923	0.85	$1.090*10^{-2}$	$4.406*10^{-2}$	$1.339*10^{0}$
1000	1.234	1.185	14.98	4.475	0.85	$1900*10^{0}$	$2.617*10^{0}$	$9.632*10^{-2}$
1300	1.298	1.234	15.54	4.708	0.85	$9.740*10^{2}$	$3.659*10^{2}$	$4.003*10^{-2}$

Where K_1 is the rate constant of boudouard reaction.
K_2 is the rate constant of steam gasification reaction.
K_3 is the rate constant of methanation reaction.

2.7 Gasification Flowsheet Development

The flowsheet development for the gasification of biomass consists of three main sections [9];

- Gasifier Selection
  The selection of a certain technology is based on the availability of the feedstock, operating conditions needed to yield maximum desired product and the physical characteristics of the feed.

- Gas Treatment Processes
  The raw gas coming from the gasifier needs to be cleaned from particulates and ashes before being used in any treatment process.

- Gas Purification
  Gas purification is the purification of the product gas to be prepared for end-use processes.

2.8 Gasifier Selection

There are four major types of gasifiers [10];

- Fixed Bed Gasifier

  Fixed bed reactor is classified as updraft or downdraft gasifier. The updraft gasifier is the simplest type of gasification reactors. The updraft gasifier is considered a counter flow reactor where the biomass is introduced at the top of the reactor and the air and steam are introduced at the bottom of the reactor. The maximum temperature of the gasifier is typically 1,300^oC. CO_2 and H_2O are partially reduced to form CO and H_2 in a temperature range between 800-1,300^oC.

  The downdraft gasifier is considered a co-current reactor where the biomass and the air and steam are introduced at the top of the reactor and move downwards through the reactor. The temperature ranges for gasification is typically around 800-1,300^oC.

  Both updraft and downdraft gasifiers have feed constraint that the feed has to be uniformly sized to minimize channeling in the reactor.

- Bubbling Fluid Gasifier

  In the bubbling fluid reactor, a gas stream passes upwards through a bed of granular particles, usually sand, in which the gas velocity is high enough that the solid particles are widely separated and circulates freely throughout the bed. The biomass is introduced at the top of the gasifier through a feed chute.
  The operating temperature starts at 540^oC and gradually increases to 870^oC.

- Circulating Fluid Bed Gasifier

  The circulating fluid bed reactor is similar to the bubbling fluid reactor but only the solids of the fluidized bed are collected, separated from the gas and sent back to the bed causing a solid circulation loop. Also the velocity of the gas is much higher than this of the bubbling fluid reactor.

- Entrained Flow Gasifier

  Entrained flow reactor is mainly developed for the gasification of coal. It operates at relatively high temperature at a range of 1,300-1,400^{o}C.

CHAPTER 3
METHODOLOGY

3.1 Flow Chart

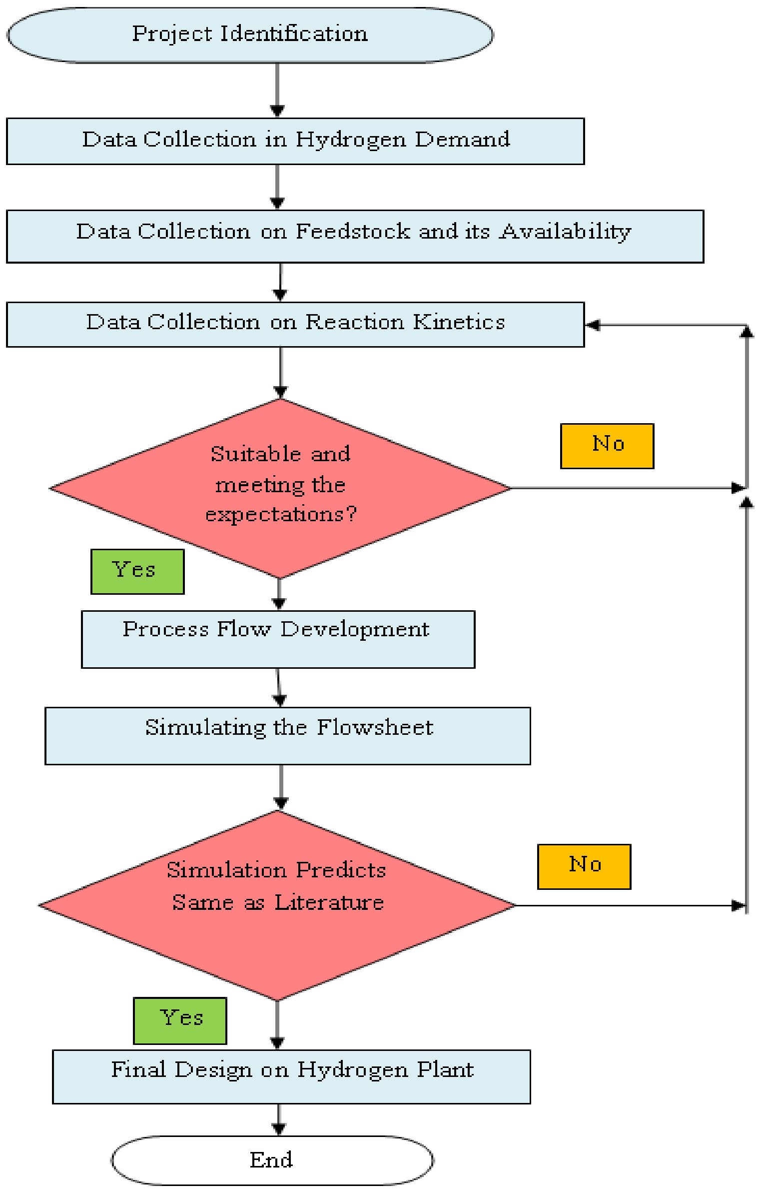

Figure 4: FlowChar of Methodology

3.2 Analysis Technique

This project consists of data gathering on the Egyptian petroleum refineries' hydrogen demand and the selection and availability of biomass feedstock. After deciding the biomass feedstock, the molecular formula of the biomass is determined along with its molecular weight. Also gasification reactions data are gathered with its reaction kinetics.

From the data gathered above, a block diagram is developed showing the main units of the hydrogen plant. Afterwards, a detailed flowsheet simulation using iCON simulation program is developed showing the mole concentrations of different components of the product gas with respect to different temperatures.

3.2 Gantt Chart

A Gantt chart is prepared in order to organize the timeline of the project throughout the semester. Table 5 below shows the Gantt chart including the main processes and the key milestones of the project this semester.

Table 5: Gantt Chart for FYP II

No.	Detail/ Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14	18
1	Data Collection on Reaction Kinetics	■	■	■							**Mid-semester break**						
2	Submission of Progress Report I				●												
3	MATLAB work for the determining of general equation				■	■	■	■	■	■							
4	Submission of Progress Report II								●								
5	Flowsheet Developement											■					
6	iCON work for the simulation of the flowsheet												■	■	■		
7	Poster Exhibition													●			
8	Submission of Dissertation (Soft Bound)															●	
9	Oral Presentation																●
10	Submission of Dissertation (Hard Bound)											After Oral Presentation by 7 days					

3.3 Tools Required

MATLAB programming tool is required to balance the general gasification equation to be used in the simulation of the flowsheet.

PETRONAS owned process simulator software, iCON is used in the simulation of the flowsheet.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Biomass Molecular Formula

4.1.1 Assumptions [5]

- Biomass is represented by the formula CH_xO_y, where x and y are the H/C ratio and the O/C ratio respectively.
- The moisture content of the biomass is being neglected.

4.1.2 Rice Husk

From the elemental composition in Chapter 2, rice husk composition shown in Table 3 is as follows;

Table 3: Rice Husk Elemental Composition

Composition	C	H	O
Percentage	49.9%	7.0%	41.3%
Atomic Mass	12	1	16

The number of carbon, hydrogen and oxygen atoms in the molecule is determined by dividing the percentage of each atom by its atomic mass. The number of atoms is shown in Table 6 below;

Table 6: Number of Atoms in Rice Husk

	C	H	O
Number of Atoms	4.16	7	2.83

From the number of atoms in Table 6, the H/C ratio and the O/C ratio can be determined for the rice husk;

H/C ratio = 1.68

O/C ratio = 0.68

Hence, rice husk empirical formula is $CH_{1.68}O_{0.68}$

4.1.3 Rice Straw

From the elemental composition in Chapter 2, rice straw composition shown in Table 2 is as follows;

Table 2: Elemental Composition of Rice Straw

Composition	C	H	O
Percentage	46.6%	6.2%	46.5%
Atomic Mass	12	1	16

The number of carbon, hydrogen and oxygen atoms in the molecule is determined by dividing the percentage of each atom by its atomic mass. The number of atoms is shown in Table 7 below;

Table 7: Number of Atoms in Rice Straw

	C	H	O
Number of Atoms	3.88	6.2	2.91

From the number of atoms shown in Table 7, The H/C ratio and the O/C ratio can be determined for rice straw;

H/C ratio = 1.60

O/C ratio = 0.75

Hence, rice straw empirical formula is $CH_{1.60}O_{0.75}$

4.2 Solving for the General Equation

As stated in chapter 2, Equation 6, the general gasification equation is;

$CH_xO_y + z (O_2 + 3.76 N_2) + k H_2O \leftrightarrow a CO_2 + b CO + c H_2 + d CH_4 + e N_2 + f H_2O + g C$

Equation 6: General Gasification Equation

From the previous calculation, we determined the rice husk and rice straw compositions so the general equation for rice husk and rice straw will be;

General Gasification Equation for Rice Husk

$CH_{1.68}O_{0.68} + z (O_2 + 3.76 N_2) + k H_2O \leftrightarrow a CO_2 + b CO + c H_2 + d CH_4 + e N_2 + f H_2O + g C$

(Equation 7)

General Gasification Equation for Rice Straw

$CH_{1.60}O_{0.75} + z (O_2 + 3.76 N_2) + k H_2O \leftrightarrow a CO_2 + b CO + c H_2 + d CH_4 + e N_2 + f H_2O + g C$

(Equation 8)

To solve for balanced stoichiometric equations, atom balance and energy balance equations are solved.

4.2.1 Atom Balance

Carbon

$1 = a + b + d + g$ (Equation 9)

Oxygen

$y + 2z + k = 2a + b + f$ (Equation 10)

Hydrogen

$x + 2k = 2c + 4d + 2f$ (Equation 11)

Nitrogen

$3.76z = e$ (Equation 12)

4.2.1 Energy Balance

$$\Delta H_R (T) = \Delta H_R (T_R) + \sum n_i \int_{TR}^{T} C_{pi}\, dT \qquad [13]$$

Since the process is adiabatic

$$0 = \Delta H_R (T_R) + \sum n_i \int_{TR}^{T} C_{pi}\, dT \qquad \text{(Equation 13)}$$

Equations 9-13 are solved simultaneously using MATLAB FSOLVE function to solve for a, b, c, d, e, f, g, k and z

Appendix 1 shows the MATLAB M-file containing the calculations and the function.

The results from the MATLAB FSOLVE function are shown in Table 8 and 9 below;

Table 8: Values for Rice Husk Equation

a	b	c	d	e	f	g	z	k
0.3859	0.2313	0.8095	0.0334	0.5389	1.1102	0.3494	0.1433	1.1466

Table 9: Values for Rice Straw Equation

a	b	c	d	e	f	g	z	k
0.4142	0.2295	0.8034	0.0099	0.5353	1.1157	0.3463	0.1424	1.1389

Therefore, the balanced general gasification equations for rice husk and rice straw can be estimated to be;

Rice Husk Balanced Equation

$CH_{1.68}O_{0.68} + 0.14 (O_2 + 3.76 N_2) + 1.15 H_2O \leftrightarrow 0.39 CO_2 + 0.23 CO + 0.81 H_2 + 0.03 CH_4 + 0.54 N_2 + 1.11 H_2O + 0.35 C$ (Equation 14)

Rice Straw Balanced Equation

$$CH_{1.60}O_{0.75} + 0.14\ (O_2 + 3.76\ N_2) + 1.14\ H_2O \leftrightarrow 0.41\ CO_2 + 0.23\ CO + 0.80\ H_2 + 0.01\ CH_4 + 0.54\ N_2 + 1.12\ H_2O + 0.35\ C \quad \text{(Equation 15)}$$

4.3 Process Synthesis and Development

4.3.1 Block Diagram

Based on the guidelines stated in chapter 2, section 2.7, a block diagram is designed as shown in Fig. 4

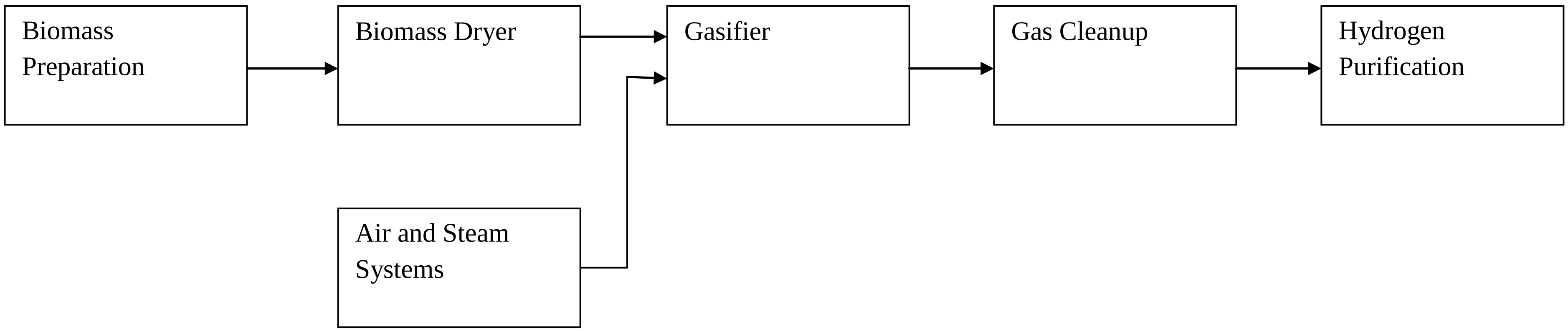

Figure 5: Block Diagram

4.3.2 Process Description

- Biomass Preparation Unit

  The purpose of this unit is to prepare the feedstock of biomass at a uniform size to be ready for gasification.

  The main equipments of this unit;

  - Truck

    The trucks will be used to transport the rice husk and rice straw from their field where they were grown to the hydrogen plant near the petroleum refinery.

  - Magnet

    The magnet is used to purify the rice husk and the rice straw from any metal content that can be found in the feedstock.

  - Grinder

    The grinder is used to grind the feedstock into a specified identical length.

  - Feed Hopper

    A feed hopper is used to collect the grinded feedstock to be transferred to the Biomass Dryer Unit.

- Biomass Dryer Unit

  The purpose of the biomass dryer unit is to dry the biomass feedstock as the equations above assumed the moisture content is neglected.

  The main equipments of this unit;

  - Air Conveyer

    The air conveyer is a type of blower for solid particles that uses air to transfer the solid feedstock from the feed hopper to the dryer [16].

- Dryer

  The dryer is used to dry the rice husk and rice straw from their water content as water content would affect the overall gasification of the biomass.

- Air and Steam Systems Unit

  The Purpose of the air and steam systems is to provide the gasifier with pure gasifying agents which are air and steam at a clean and constant rate.

  The main equipments of this unit;

  - Air
    - Dust Trap

      The dust trap is used to clean the air going into the compressor from the dust existing in the air [16].

    - Air Compressor

      Air compressor is used to supply the air to the process with the desired pressure of 800 bar.

  - Steam

    The feed water from the source usually contains three types of contaminants; biological contaminants, total suspended solids, total dissolved solids.

    - Chlorination Unit

      The Chlorination unit removes the biological contamination from the feed water by adding a dose of chlorine to react with the feed water to produce hydrochloric acid and hypochlorous acid which attacks bacteria and other biological contaminants in the feed water [16].

- Filters

  Filters are used to remove the total suspended solids in the water. The filters are usually sand and gravel filters with different sizes of sand particles to remove various sizes of the suspended solids in the water [16].

- Ion Exchange Unit

  Ion exchange unit is used to remove the total dissolved solids present in the water. Ion exchange is done by a series of anion exchange column followed by a cation exchange column [16].

- Deaerator

  The deaerator unit is used to remove dissolved gases in the water. The dissolved gases such as carbon dioxide and oxygen can line the surfaces in the boiler and cause accelerated corrosion [16].

- Boiler

  The boiler is the unit where the demineralized water is heated up to produce steam at a temperature of 1300^{o}C to be used as a gasifying agent in the gasifier [16].

- Gasifier Unit

  Gasifier unit is the heart of the hydrogen plant. It is the unit where the biomass feedstock is gasified into the various gas products.

  The main equipments of this unit;

  - Fixed Bed Updraft Gasifier

    The fixed bed updraft gasifier is chosen to be used as it is the simplest type of reactor where its temperature range for gasification is between 800^{o}C and 1,300^{o}C [10].

- Gas Cleanup Unit

  Gas Cleanup unit is the unit where the gas is separated from the solid un-burnt carbon to produce a mixture of only gas phase.

  The main equipments of this unit;

  - Hydrocyclone

    Hydrocyclone is used to separate the solid un-burnt carbon from the gas by applying a centrifugal force and depending on the differences of densities where the gas is drawn from the top of the hydrocyclone and the solid is removed from the bottom of the hydrocyclone [16].

  - Cooler

    The gas from the gasifier is at a temperature of 1,300^{o}C so it is cooled down using a series of coolers with a flash drums in between to remove condensed water produced from cooling of gas.

- Hydrogen Purification Unit

  In the hydrogen purification unit, the hydrogen is purified from the other gasification gases such as carbon dioxide, carbon monoxide, methane and steam.

  The main equipments of this unit;

  - Acid Gas Removal Unit

    Acid gas removal unit is used to remove carbon dioxide from the mixture of gas because carbon dioxide would freeze and form dry-ice in the chilling train where the temperature is decreased down to -141^{o}C. The solid carbon dioxide can block the heat exchangers and pipes inside the chilling train [16].

- Dehydration Unit

  The dehydration unit is used to remove the water from the mixture of gas. In very low temperatures in the chilling train, the water freezes which may cause the blockage of the pipes and heat exchangers in the chilling trains [16].

- Chilling train to produce pure hydrogen

  The chilling train uses two types of refrigerants; propane refrigerant and ethylene refrigerant, to cool down the mixture of gases for the easier separation of hydrogen from the methane. Chilling trains can produce hydrogen gas with purity of 99.99+% [16].

4.4 Process Simulation

The simulation of the flowsheet for the hydrogen plant is done using iCON simulation tool. The process flow diagram is drawn for different gasification temperatures to compare the hydrogen concentrations. The balanced chemical general gasification reaction calculated before is entered along with the reaction kinetics [8]

The temperature ranges taken into consideration are 800^{o}C, 1000^{o}C, 1200^{o}C and 1300^{o}C which are the range of gasification temperatures stated in the literature for the fixed bed updraft gasifier [10].

Figure 6 below shows the process flow diagram (PFD) of the hydrogen plant up to the gasification stage where biomass feedstock is converted to a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and un-burnt carbon.

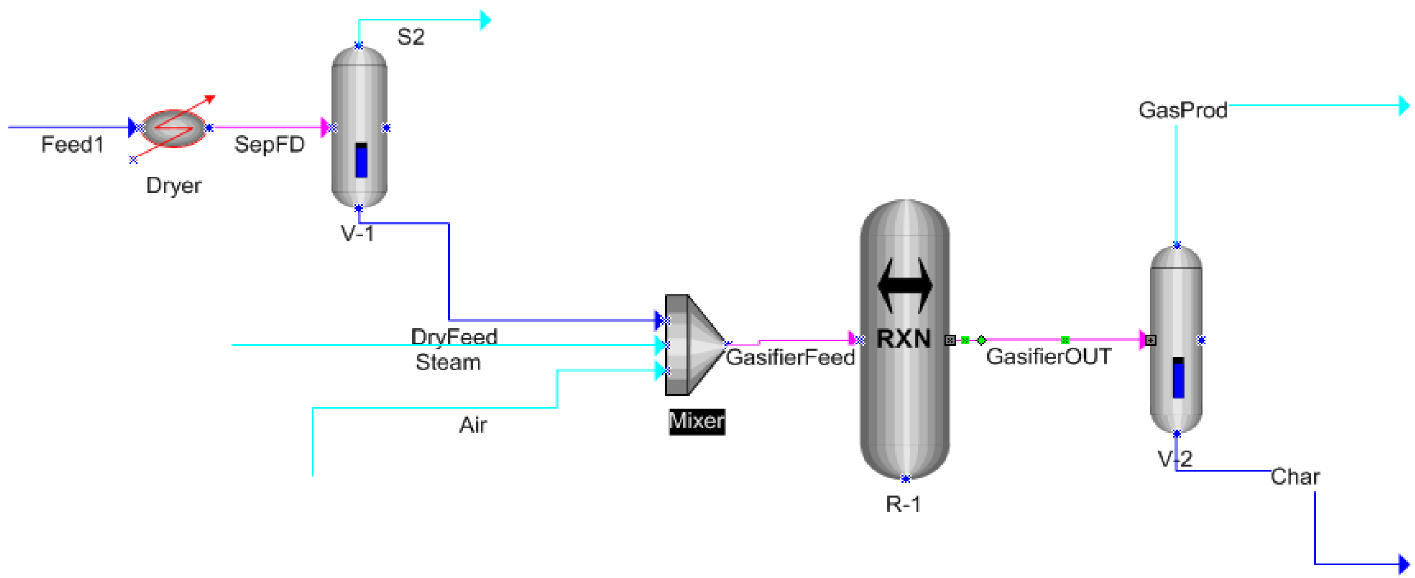

Figure 6: PFD of Hydrogen Plant

From Figure 6 above, the heat exchanger and the separator act as the dryer in the plant where the water content in the biomass feedstock is removed. The gasifying agents of steam and air are then added with a ratio of 1:1 steam to air ratio to enter the gasifier [5]. In the gasifier, based on the literature review, the operating temperature is in a range between 800^{o}C and 1300^{o}C and a pressure of 800 bar [10]. The final separator acts as the hydrocyclone where un-burnt carbon and un-reacted biomass are separated from the gas mixture.

From the iCON results, Figure 7 shows the mass of hydrogen in the gasification product per unit hour at the different gasification temperature ranges stated in the literature.

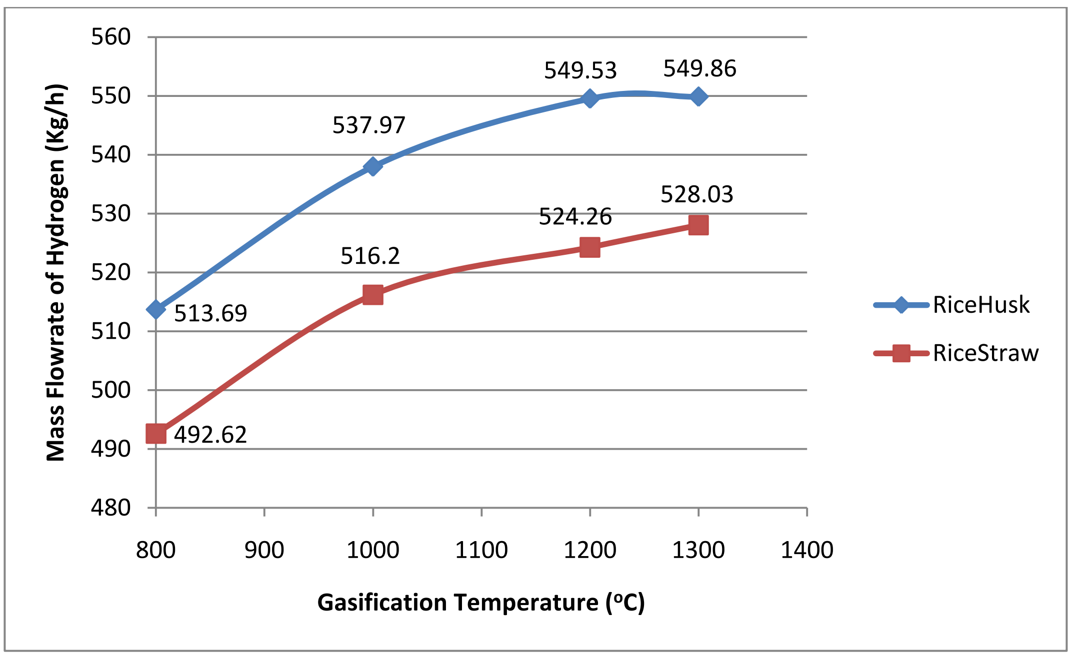

Figure 7: Mass of Hydrogen in the Gasification Product

From the above Fig. 7, the mass of hydrogen gas in the gasification product increases as the gasification temperature increases this shows a similar trend as the one stated in the literature [5, 8].

From the iCON results, Figure 8 below shows the mole fraction of the product gas from rice husk at the different gasification temperatures.

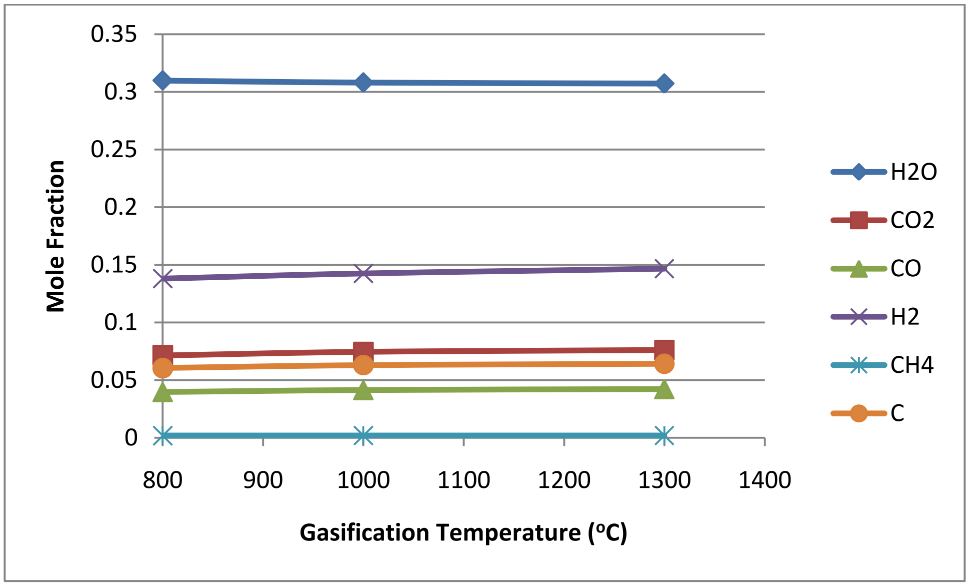

Figure 8: Mole Fraction of Product Gas from Rice Husk

From the iCON results, Figure 9 below shows the mole fraction of the product gas from rice straw at the different gasification temperatures.

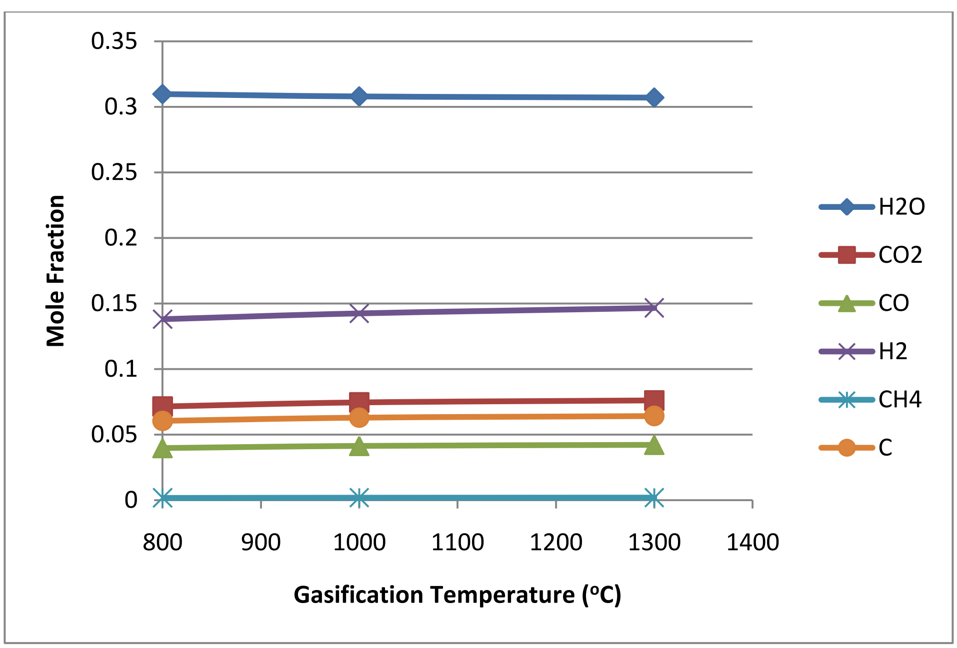

Figure 9: Mole Fraction of Product Gas from Rice Straw

Figures 8, 9 above show an increase in the mole fractions of hydrogen and carbon monoxide and a decrease in mole fraction of water as the gasification temperature increases for both rice straw and rice husk which is a similar trend to the literature due to the reduction of water and carbon dioxide at higher gasification temperatures.

Figures 7-9 above shows that the optimum gasification temperature for the production of hydrogen with respect to the yield of hydrogen is 1,300^{o}C which yields approximately 550 Kg of hydrogen from 8,350 Kg of rice husk used as a feedstock and approximately 528 Kg of hydrogen from 8,350 Kg of rice straw used as feedstock.

Table 10 below shows the mass fraction and operating conditions of rice husk gasification at the optimum temperature of 1,300^{o}C obtained from the iCON simulator.

Table 11 below shows the mass fraction and operating conditions of rice straw gasification at the optimum temperature of 1,300^{o}C obtained from the iCON simulator.

Table 10: Mass Fraction and Conditions in the Streams at 1300°C Gasification for Rice Husk

	FEED1	SEPFD	DryFeed	S2	Steam	Air	GasifierFeed	GasifierOUT	Char	GasProd
Vap.Frac.	0	0.0291	0	1	1	1	0.8443	0.9504	0	1
T (°C)	25	105	105	105	1300	1300	1103.27	1300	1300	1300
P (KPa)	101.352	101.352	101.352	101.352	800	800	101.352	800	800	800
MolFlow (Kgmol/hr)	342.64	342.64	332.66	9.98	1110.17	693.22	2136.06	2348.95	116.45	2232.50
MassFlow (Kg/hr)	8350	8350	8170.21	179.79	20000	20000	48170.21	48231.29	1398.87	46832.42
Mass Fraction										
O_2	0	0	0	0	0	0.23301	0.09674	0.06572	0	0.06769
N_2	0	0	0	0	0	0.76699	0.31845	0.31805	0	0.32755
H_2O	0.02153	0.02153	0	1	1	0	0.41519	0.40970	0	0.0.42194
CO_2	0	0	0	0	0	0	0	0.11837	0	0.12191
CO	0	0	0	0	0	0	0	0.04443	0	0.04576
H_2	0	0	0	0	0	0	0	0.0114	0	0.01174
CH_4	0	0	0	0	0	0	0	0.00332	0	0.00342
C	0	0	0	0	0	0	0	0.02899	0.99962	0
RiceHusk	0.97847	0.97847	1	0	0	0	0.16961	0.00001	0.00038	0

Table 11: Mass Fraction and Conditions in the Streams at 1300°C Gasification for Rice Straw

	FEED1	SEPFD	DryFeed	S2	Steam	Air	GasifierFeed	GasifierOUT	Char	GasProd
Vap.Frac.	0	0.0291	0	1	1	1	0.8463	0.9511	0	1
T (°C)	25	105	105	105	1300	1300	1103.21	1300	1300	1300
P (KPa)	101.352	101.352	101.352	101.352	800	800	101.352	800	800	800
MolFlow (Kgmol/hr)	337.27	337.27	327.45	9.82	1110.17	693.22	2130.84	2341.78	114.62	2227.14
MassFlow (Kg/hr)	8350	8350	8173.03	176.97	20000	20000	48173.03	48450.63	1376.95	47073.66
Mass Fraction										
O_2	0	0	0	0	0	0.23301	0.09674	0.06591	0	0.06784
N_2	0	0	0	0	0	0.76699	0.31843	0.31661	0	0.32587
H_2O	0.02119	0.02119	0	1	1	0	0.41517	0.41036	0	0.42236
CO_2	0	0	0	0	0	0	0	0.12319	0	0.12679
CO	0	0	0	0	0	0	0	0.04354	0	0.04481
H_2	0	0	0	0	0	0	0	0.01090	0	0.01122
CH_4	0	0	0	0	0	0	0	0.00108	0	0.00112
C	0	0	0	0	0	0	0	0.02841	0.9996	0
RiceHusk	0.97881	0.97881	1	0	0	0	0.16966	0.00001	0.0004	0

4.5 Findings

From the iCON simulator at the optimum gasification temperature is estimated to be 1300^{o}C, the hydrogen yields 549.84 Kg/hr from 8,350 Kg/hr of rice husk and 528.03 Kg/hr from 8,350 Kg/hr rice straw.

The ratio of hydrogen to rice husk is 0.066 Kg hydrogen for every Kg of rice husk used.

The ratio of hydrogen to rice straw is 0.063 Kg hydrogen for every Kg of rice straw used.

From chapter 2, the estimated rice husk in Egypt is 0.6 Mton/year, thus, the maximum yield of hydrogen production from rice husk is 39,600 ton/yr. The estimated rice straw in Egypt is 3 Mton/yr, thus, the maximum yield of hydrogen production from rice straw is 189,000 ton/yr.

Therefore, the maximum yield of hydrogen production from both rice husk and rice straw is 228,600 ton/yr.

From chapter 2, the hydrogen demand of Egyptian petroleum refineries is estimated to be between 94,500 ton/yr and 160,500 ton/yr.

The hydrogen production from rice husk and rice straw can fully supply the existing petroleum refineries in Egypt with their needs of hydrogen and also produce excess hydrogen that can be sold internally or exported to neighboring countries.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Recommendation

5.1.1 Process Completion

The flowsheet simulation has been done up to after the gasifier where the product gas needs to be further processed to obtain pure hydrogen. The following steps are been recommended to be followed;

1. Acid Gas Removal Unit

   The acid gas removal unit is to remove carbon dioxide from the product gas mixture because of the carbon dioxide enters the chilling train at very low temperatures will freeze to form dry ice and cause blockage to the equipment and pipelines in the chilling train [16]. The Acid gas removal unit consists of a tray or packed column and operates at low temperature and high pressure where DiGlycol Amine (DGA) or other types of amines are used to remove carbon dioxide from the mixture of gas. The rich amine can be regenerated in a stripper at high temperature and low pressure to be re-used again [16].

2. Dehydration Unit

   The dehydration unit is responsible for the removal of water from the product gas mixture as –similar to CO_2- the water at low temperatures tend to freeze causing blockage of the equipment [16]. The dehydration tower is usually a fixed bed with silica gel that absorbs water from the mixture of gas [16].

3. Chilling Train

   The chilling train is a series of refrigeration cycles where the product gas is cooled down to -141^{o}C where methane offgas is separated from hydrogen to leave a pure product of hydrogen that can be 99.99+% purity [16]. The refrigerants used are usually propane refrigerant and ethylene refrigerant to achieve the desired low temperature [16].

5.1.2 Examining Using Different Operating Conditions

Determine the effect of different pressures in the gasifier on the yield of hydrogen produced. Also different steam to air ratios should be examined to determine the best ratio that yields the highest production of hydrogen from biomass.

5.1.3 Economic Potential

Economic potential should be calculated to determine the best profitable operating conditions that would yield the desired amount of hydrogen needed by the petroleum refineries.

5.2 Conclusion

To conclude, the biomass is the next generation of the energy in the world due to the issues arising from the use of fossil fuel from the emissions of greenhouse gases and the instability of the fossil fuel prices. The design of a hydrogen plant for petroleum refineries using biomass as a feedstock will provide a cleaner means to produce hydrogen that satisfies the hydrogen needs of existing petroleum refinery. Rice husk and rice straw are to be used as the feedstock for the hydrogen plant due to their abundance in Egypt.

For this project, the hydrogen demand of the petroleum refineries was fully satisfied by the gasification of rice husk and rice straw in a fixed bed updraft gasifier at a temperature of 1,300^{o}C. The total production of hydrogen is assumed to be 228,600 ton/yr against a demand of only 160,500 ton/yr.

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