

**THERMODYNAMIC PERFORMANCE ASSESSMENT OF THREE BIOMASS-
BASED HYDROGEN PRODUCTION SYSTEMS**

By

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Abstract

Hydrogen is likely to be an important energy carrier in the future. It can be produced by the steam reforming of natural gas, coal gasification and water electrolysis among other processes. However current processes are not sustainable because they use fossil fuels or electricity from non-renewable resources. In this context, this thesis focuses on biomass based-hydrogen production and considers three plants intended for sustainable producing hydrogen using. These three systems are analyzed thermodynamically using Aspen Plus and their performances are examined and compared in regards to hydrogen yield. Therefore, comparisons of the systems are made based on several factors, including energy and exergy efficiencies. In addition, an economic analysis is performed in order to determine the minimum hydrogen production cost for these three systems. The results are expected to be useful to efforts for the design, optimization and modification of hydrogen production and other related processes. In the three system considered, the gasifiers are modelled using the Gibbs free energy minimization approach and chemical equilibrium considerations. Gasification, which is characterized by partial oxidation, is a vital component of several clean energy technologies including the ones considered here. Parametric analyses are carried out of several factors influencing the thermodynamic efficiency of biomass gasification.

The energy efficiencies were found to be between 22-33% for all systems. However the exergy efficiencies range from around 22 to 25%. It was also found that gasifier produces the greatest quantity of entropy, due to its high irreversibility, and merits attention from those seeking to improve efficiencies. It was found that the hydrogen production cost range varies between 1.28 and 1.84 \$/kg for the three systems; this is higher than the cost for that produced from conventional oil.

Keywords: Biomass, Gasification, Hydrogen, Thermodynamics, Energy, Exergy, Steam Methane Reformer, Gasifier, Oil palm shell, Gibbs energy, Economics, Hydrogen Price.

Abstrait

Hydrogène promet d'être une source d'énergie très important dans l'avenir. Il peut être produit par le reformage à vapeur des gazes naturelles, par la gazéification du carbone, ou par électrolysis de l'eau. Pourtant le processus actuel n'est pas un processus durable car on utilise toujours des combustibles fossiles ou l'électricité dérivée des sources d'énergie non renouvelable.

Dans ce contexte, cette thèse se concentre sur la production de la biomasse avec l'hydrogène, elle examine trois plantes différentes considérées pour la production de l'hydrogène comme énergie durable. On a analysé les trois systèmes différents (par le reformage des gazes naturelle en navire a vapeur, le gazéification du carbone, et électrolysis de l'eau) en utilisant le système Aspen Plus qui est un système thermodynamique. Les résultats de ce teste étaient évaluée en termes de leur rendement d'hydrogène. Ces comparaisons étaient faites basées sur plusieurs facteurs incluant l'efficacité de l'énergie et de l'exergie. Nous avons aussi fait une analyse économique pour déterminer le prix minimum de vente de l'hydrogène pour ces trois systèmes. Les résultats de ces expériences seront utiles pour la conception du design, de l'optimisation, et de la modification de la production d'hydrogène et d'autres processus relatifs.

Ces trois systèmes prennent en considération les gazogènes modelés sur le design de Gibbs qui utilise une approche de minimal de l'énergie libre et un équilibre chimique. La gazéification est caractérisé par une oxydation partielle qui est essentielle pour la création de plusieurs technologies d'énergie propre incluant les méthodes considères ici. Les analyses paramétriques étaient effectuées en utilisant plusieurs facteurs qui ont influencées l'efficacité thermodynamique des gazes de la biomasse.

Tous les rendements énergétiques pour tous les systèmes avaient un résultat d'entre 22-33%. Pourtant le rendement de l'exergie était entre 22-25%. Aussi, ils ont découvrent que la gazéification est le meilleur producteur de l'entropie, parce que l'entropie est irréversible et mérite l'attention de ceux qui cherchent a améliorer le rendement énergétiques. En plus, pour les trois systèmes, le prix de vente de l'hydrogène est entre 1.28\$ et 1.84\$/kg qui est plus élevée que le prix actuel du pétrole brut classique.

Légende: Biomasse, Gazéification, Hydrogène, Thermodynamique, Énergie, Exergie, La Reformation des Gazes Naturelle en Navire a Vapeur, Gazéification, Paume de Pétrole Shell, Économique, Gibbs Énergie, Prix d'Hydrogène

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Nomenclature

| | |
|-------------|---------------------------------------------|
| C_p | Specific heat at constant pressure, kJ/kg-K |
| \dot{E} | Energy flow rate, kJ/h |
| \dot{E}_x | Exergy flow rate, kJ/h |
| ex | Specific exergy, kJ/kg |
| h | Specific enthalpy, kJ/kg |
| HHV | Higher heating value, MJ/kg |
| LHV | Lower heating value, MJ/kg |
| \dot{m} | Mass flow rate, kg/h |
| m_i | Inlet mass flow rate, kg/h |
| m_o | Outlet mass, kg |
| P_o | Reference-environment pressure, kPa |
| Q | Heat, kJ |
| R | Universal gas constant, kJ/kmol-K |
| S | Entropy, kJ/K |
| T | Temperature, K |
| T_0 | Reference-environment temperature, K |
| \dot{W} | Work rate, kJ/h |

x Exergy ratio

Greek Symbols

Δ Difference

ψ Exergy efficiency, %

η Energy efficiency, %

β Correlation factor

Subscripts

bio Biomass

biomoist Biomass moisture

cg Cold gas

dest Destroyed

drybio Dry biomass

en Energy

gen Generated

i, j Components

in Input

meth Methane gas (CH₄)

out Output

st Steam

| | |
|------------------|--------------------|
| <i>sys</i> | System |
| <i>net</i> | Net system |
| <i>prodg</i> | Produced gas |
| <i>unconcarb</i> | Unconverted carbon |

Superscripts

| | |
|-----------|----------|
| <i>ch</i> | Chemical |
| <i>ph</i> | Physical |

Acronyms

| | |
|------------------|------------------------------|
| <i>A</i> | Air Cooler |
| <i>BCL</i> | Battelle Columbus Laboratory |
| <i>COMB</i> | Combustion |
| <i>COMP</i> | Compressor |
| <i>COOL</i> | Cooling |
| <i>CYC</i> | Cyclone |
| <i>DEARA</i> | Deaerator |
| <i>DRY-FLASH</i> | Condenser |
| <i>DRY-REACT</i> | Dry reactor |
| <i>ER</i> | Equivalence ratio |
| <i>EC</i> | Economizer |

| | |
|----------------|-----------------------------------------------|
| <i>FLSHD</i> | Flash reactor |
| <i>H</i> | Heater |
| <i>HE</i> | Heat exchanger |
| <i>HPTUR</i> | High pressure turbine |
| <i>HTS</i> | High-temperature shift |
| <i>LPTUR</i> | Low pressure turbine |
| <i>LTS</i> | Low-temperature shift |
| <i>M</i> | Mixer |
| <i>NASA</i> | National Aeronautics and Space Administration |
| <i>P</i> | Pump |
| <i>PRE</i> | Pre-heater |
| <i>PSA</i> | Pressure swing adsorption |
| <i>REFOR</i> | Reformer |
| <i>R-GIBBS</i> | Gibbs reactor |
| <i>R-Stoic</i> | Stoichiometric reactor |
| <i>R-Yield</i> | Yield reactor |
| <i>S</i> | Splitter |
| <i>SDRUM</i> | Drum tank |
| <i>STBR</i> | Steam-biomass ratio |

| | |
|----------------|-------------------------|
| <i>SYNCOOL</i> | Syngas cooler |
| <i>T</i> | Tank |
| <i>TIC</i> | Total installed cost |
| <i>TINC</i> | Total indirect cost |
| <i>TPI</i> | Total project cost |
| <i>VPTUR</i> | Vacuum pressure turbine |
| <i>WGS</i> | Water gas shift |
| <i>WHB</i> | Waste heat boiler |

Chapter 1

INTRODUCTION

Biomass, a significant energy source globally, is being investigated in various countries as a potentially significant renewable resource. Biomass is derived from solar energy, and forms of biomass include wood, municipal solid wastes and industrial residues. As a renewable resource, biomass can contribute to renewable hydrogen production. Biomass energy can be used as fuel for electricity generation, transportation, heating and cooling, etc. Biomass is relatively clean compared to other sources of energy, as it releases no net CO₂ emissions when carefully managed. CO₂ is fixed by photosynthesis during biomass growth and is released during utilization. Biomass can be converted to a fuel gas through thermochemical gasification, which is reported to be one of the most cost effective conversion processes for biomass (Corradetti *et al.*, 2007). Biomass can also be converted to hydrogen, which can be used as a fuel in combustion engines and fuel cells cleanly and efficiently.

When we consider hydrogen production methods, current processes are not sustainable because they use fossil fuels or electricity from non-renewable resources. Hydrogen production can be made sustainable if it is produced from sustainable energy resources. In this regard, alternative thermochemical (pyrolysis and gasification) and biological (biophotolysis, water–gas shift reaction and fermentation) processes are practical and can be more sustainable than present processes in Manish *et al.* (2008). Many researchers are focusing their research on the gasifier portion of this process, as gasification appears to be more favourable for hydrogen production than pyrolysis.

Gasification, which is characterized by partial oxidation, is a vital component of several clean energy technologies. Consequently, gasifier modelling and simulation, using programs such as Aspen Plus, has been ongoing. Currently, however, 80–85% of the world's total hydrogen production is derived from natural gas via steam methane reforming (SMR) (Granovski *et al.*, 2007). Although much research has been reported on

the production of hydrogen by SMR, most of the studies have concentrated on the analysis of the reforming reactor. In this study, the gasifier is the most significant part of the system; therefore it is analysed in detail.

Exergy analysis is a tool for understanding and improving efficiency, and is used throughout this investigation in addition to energy analysis.

The aim of the present work is to investigate hydrogen production by thermochemical biomass gasification using energy and exergy methods, and to evaluate the potential of hydrogen production from biomass thermodynamically and economically. A parametric analysis of factors influencing the thermodynamic efficiency of biomass gasification is carried out. Three systems considered here include syngas production as an input for producing hydrogen in the hydrogen plant.

1.1 Motivation and Objectives

Considering increasing human energy consumption, mankind needs to find new forms of energy sources for the next generation for two reasons. One is the environmental aspect, and the second is the diminishing supply of fossil fuels. These factors are encouraging researchers and society to find new energy resources and technologies. There is a vital need for a process that can convert biomass into useful energy products such as hydrogen, oil, etc. Although hydrogen is not an energy resource, it has a great capability of being a widely used fuel in the future if it is produced at lower cost in a sustainable way. Also hydrogen is clean, environmentally benign and convenient for transportation. There are many ways to produce hydrogen as previously mentioned. Since a large portion of hydrogen is produced from natural gas or coal, a promising sustainable technology for producing hydrogen is the gasification of biomass which can reduce the overall green gas emission. Gasification of biomass has already been used for the purpose of producing electricity through a Rankine cycle in several commercial plants. Some countries do not have enough fossil fuels while they have an abundance of biomass residues and wastes. These bio-organic materials can be used as a fuel to produce a significant amount of hydrogen.

The Canadian government has a goal of supplying 20% of its electricity from renewable sources by 2010 and Ontario plans to install smart meters in every house hold by 2010, also Canada is bound by the Kyoto protocol and aims at reducing its carbon emissions by 5.8% below 1990 levels by 2012. From this perspective, it is expected that gasification systems will gain significant importance to produce electricity and hydrogen.

This thesis mainly considered three biomass-based hydrogen production plants, simulations were performed using the Aspen Plus software and the process economic analysis software, Icarus was used. The objectives include performing the following tasks:

- Energy analysis of three biomass-based hydrogen production plants
- Exergy investigations of three biomass-based hydrogen production plants
- Performance comparison of these systems through energy and exergy efficiencies
- Economic evaluation of these three systems

In order to implement renewable energy from biomass, reliable data must be available to prove the availability of biomass as a sustainable and dependable source of renewable energy in the long run. Thus, the main objective of this thesis is to examine the potential of biomass for conversion to hydrogen, through gasification, reforming and shift reactions, and thus to be a source of renewable energy to show hydrogen to be an economically feasible final product from biomass gasification.

Even though the simulated hydrogen production systems have already been investigated in some aspects, there are not many studies for the detailed exergy and detailed economic analysis are available for the biomass based hydrogen production systems. This study goes further. In this thesis, the goal is to include an exergy analysis to determine where the greatest exergy losses take place, allowing designers or researchers in the field to get an in-depth understanding of biomass based hydrogen production. In addition, some improvements are recommended. The second objective of the present work is to investigate hydrogen production by thermochemical biomass gasification using energy and exergy methods, and to evaluate the potential of hydrogen production from biomass including an economic analysis which is aimed to estimates minimum hydrogen

production cost for these three systems. Parametric analyses of factors influencing the thermodynamic efficiency of biomass gasification are also carried out for each of the three systems considered. All of the systems include syngas production as an input for producing hydrogen in a hydrogen plant.

Chapter 2

BACKGROUND

As mentioned earlier, hydrogen is likely to be an important energy carrier in the future. It can be produced by the steam reforming of natural gas, coal gasification and water electrolysis among other processes. This section will identify the details of hydrogen production techniques and how hydrogen impacts our lives.

Hydrogen is considered a potential fuel as an energy carrier for the twenty first century, mainly due to its environmentally benign and sustainable character.

2.1. Hydrogen

In 1766, Cavendish, studied the component effects of the dilute acids on metals like Zn, Fe and tin, and found that a similar gas was obtained in each case. He called this gas inflammable air since it burned when ignited. The name hydrogen (Greek hydro for "water" and genes for "forming") was given to the gas by Lavoisier who found that the gas when burned in air produced water. Hydrogen with atomic weight 1.00797 and atomic number 1 is the first element in the periodic table having the electronic configuration $1s^1$. Three isotopes of hydrogen; ^1H , ^2H and ^3H with atomic weight 1, 2 and 3 are known. These are hydrogen, deuterium and tritium, respectively. Hydrogen is a colourless, tasteless and odourless gas. It is the lowest density element known with density of 0.0695 kg/m^3 .

2.2 Uses of Hydrogen

Although hydrogen can widely be used applications, some industrial uses of hydrogen gas are summarized (Goyal *et al.*, 2006) in various sectors:

- Chemical feedstock for production of certain chemicals.
- Ammonia manufacturing, petroleum refining and petrochemicals production.

- Hydrogenation of unsaturated oils of soybeans, fish, cottonseed, corn, peanut and coconut.
- Hydrogenation of inedible oils and greases for manufacturing soaps and animal feed.
- Production of float glass.
- Oxy-hydrogen cutting of glass.
- Energy storage technology.
- Electronics industry.
- Production and processing of silicon.
- An alloying element in various amorphous materials.
- A fuel for rocket propulsion.
- Fuel cells.

2.3 Hydrogen Production Methods

Different process routes of hydrogen production from biomass can be broadly classified as follows in the subsequent subsections (Nath *et al.*, 2003).

2.3.1 Steam Methane Reforming

Hydrogen production using steam methane reforming (SMR) involves three steps (Midilli *et al.*, 2007). Methane is catalytically reformed at an elevated temperature and pressure to produce a syngas (a mixture of H₂ and CO). Steam is used to promote the second step, the conversion of syngas to H₂ for which the main reaction is $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$. The third step, purification, is conventionally accomplished by pressure swing adsorption (PSA) to remove water, methane, CO₂, N₂ and CO, producing hydrogen with a purity of over 99.99%. Alternatively, chemical absorption of CO₂ may be achieved using an amine contactor, followed by methanation to eliminate CO and CO₂ impurities represented by Turner *et al.* (2008). After separation of the H₂, CO₂ can be removed from the remaining process gas for sequestration if desired. SMR (without CO₂ sequestration) has a high efficiency and is currently the most favourable hydrogen production method primarily due to the low cost of the natural gas feedstock and the system (Bilgin *et al.*, 1986).

2.3.2 Partial Oxidation/Autothermal Reforming of Methane

Partial oxidation and autothermal reforming of methane are similar to SMR. The partial oxidation process directly oxidizes methane in a one-step reaction (the main reaction is $\text{CH}_4 + 0.5\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$.) while autothermal reforming combines partial oxidation and the reforming reaction, catalytically reacting methane with a mixture of steam and oxygen. This differs from SMR which treats methane with steam only. Studies indicate that, despite advances in partial oxidation and autothermal reforming processes which their hydrogen production efficiencies around 66-76% for both processes, SMR is still a more cost effective production technique for hydrogen in Midilli *et al.* (2007).

2.3.3 Coal Gasification

Coal gasification involves three principal steps: conversion of coal feedstock with steam to a syngas, catalytic shift conversion, and product purification. In the first step, coal is chemically reacted with high-temperature (approximately 1330°C), high-pressure steam to produce raw synthesis gas. In the second step, the syngas passes through a shift reactor converting a portion of the carbon monoxide to carbon dioxide. In the third step, the hydrogen product is purified. Physical absorption removes 99% of H₂S impurities, and about 85% of the H₂ in the shifted syngas is removed as 99.999% pure H₂ in a pressure swing adsorption (PSA) unit. If CO₂ sequestration is applied, a secondary absorption tower removes CO₂ from the remaining shifted syngas. The waste gas is burned to produce electricity. The purification equipment to supply pure O₂ feed contributes significantly to the overall system cost. The energy conversion efficiency for hydrogen production in a conventional coal to hydrogen plant is reported to be at 64% (HHV) without the CO₂ capture (Stiegel *et al.*, 2006). This efficiency is much lower than that for a steam methane reforming process, which is at 70-80% (Feng *et al.*, 2007). In addition, coal gasification is currently more expensive than natural gas reforming because of the gasifier and the need for O₂ for the reaction process.

2.3.4 Water Decomposition

There are many studies about latest advances in thermochemical hydrogen production ongoing. Recently, University of Ontario Institute of Technology (UOIT) has made significant contributions to water decomposition such as Rosen *et al.* and Orhan *et al.* (2008). The main concern in their study was that using the copper-chlorine (Cu-Cl) cycle to produce hydrogen.

Endothermic water splitting processes can be used for hydrogen production processes. Thermochemical processes can use heat from nuclear, solar or other technologies. These processes are more expensive than fossil fuel processes. However they do not produce harmful emissions or consume large quantities of non-renewable sources. Examples of thermochemical processes include the sulphur-iodine and the copper-chlorine thermochemical cycles. In water splitting via electrolysis, electricity supplies the energy required. The electricity can be produced using fossil fuels or cleaner alternatives like nuclear, wind, solar and water power. Water decomposition processes are attractive because the material feedstock is water and no carbon dioxide is released in the processes.

2.3.5 Photosynthetic and Photobiological Processes

Photosynthetic and photobiological processes use solar energy to produce hydrogen. During the photosynthetic process, hydrogen is produced by the reduction of H^+ ions in an aqueous solution to H_2 . Green algae contributes to the reduction by producing the reduction catalyst and by providing an electron source. Hydrogenase enzymes found in green algae act as the catalyst. Electrons are provided by suppression of the first step of photosynthesis, which would normally pull electrons from water to produce oxygen. A significant part of the potential cost of the process is attributable to the high cost for the biological system (higher material cost for hydrogen impermeable materials and sterilization costs) and the cost of compression using pressure swing adsorption.

2.3.6 Biomass Pyrolysis and Gasification

Different routes for biomass conversion to hydrogen-rich gas are shown in Fig. 1.1. Biomass can be converted into useful forms of energy products using a number of different processes as previously mentioned. The choice of process type is directly related to the quantity of biomass feedstock. Many researchers agree that the direct use of biomass to produce heat by combustion is an inefficient way of utilizing its energy and it contributes to enhance environmental pollution. Pyrolysis and gasification of the waste materials have been found to be the most favourable thermo-chemical conversion processes for utilizing renewable biomass energy.

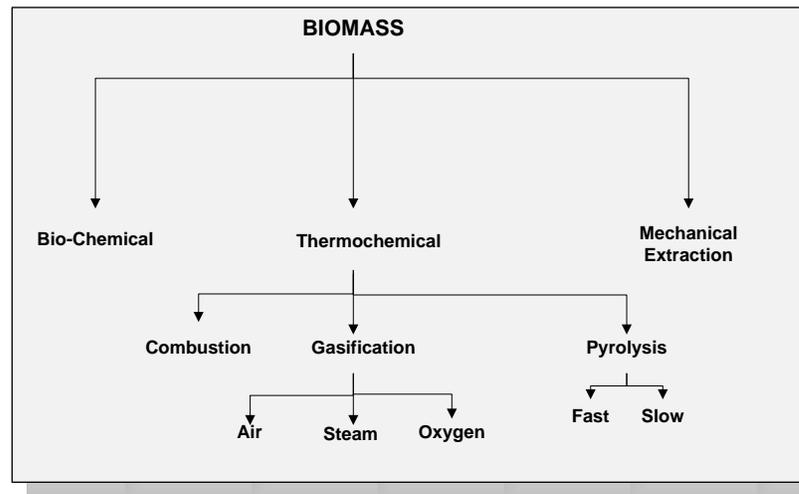


Fig. 1.1: Biomass conversion technologies for producing hydrogen.

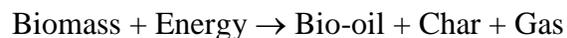
It can be seen in Figure 1.1 that thermo-chemical conversion processes comprise three different processes as described below (Goyal, 2006):

- (i) **Combustion:** The burning of biomass in air, i.e., combustion is a process to obtain a range of outputs like heat, mechanical power or electricity by converting the chemical energy stored in biomass. Combustion of biomass produces hot gases in the temperature range of 800–1000°C.
- (ii) **Gasification:** Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900°C. Many gasification methods are available for producing fuel gas. Based on throughput, cost, complexity and efficiency

issues, circulated fluidized bed gasifiers are suitable for large-scale fuel gas production.

Fig. 1.1 shows hydrogen can be produced from biomass with two common processes: direct gasification and pyrolysis to produce liquid bio-oil for reforming. These processes are explained below:

- (iii) **Pyrolysis:** Pyrolysis is the conversion of biomass to liquid, solid and gaseous fractions by heating the biomass in the absence of air at around 500°C temperature (Hamelinck, 2002). In addition to gaseous product, pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of the various energy fuels and chemicals. Pyrolysis reaction is an endothermic reaction as mentioned below:



Currently commercial biomass gasification processes for hydrogen production do not exist, but demonstration plants have been constructed for producing electricity or other chemicals. Some examples follow:

- The gasification process of BIOSYN, Inc. is an oxygen-blown gasification process that uses a bubbling fluidized bed gasifier with a bed of silica or alumina. The syngas generated is used for methanol production and has been tested since 1984 in a 10 ton/h demonstration plant in St-Juste de Bretennieres, Quebec, Canada.
- In the Fast Internal Circulation Fluidized Bed (FICIB) process, biomass is gasified in the gasification zone of a reactor with circulating bed material, with steam at 850-900°C. This material is circulated to the combustion zone where char is burned to supply thermal energy. A demonstration plant producing 2 MW of electrical power was constructed in Gussing, Burgenland in Fall, 2001.
- Although still in the demonstration phase, the Battelle Columbus Laboratory (BCL) gasifier displays a high efficiency that is comparable to that of gas production. As an indirectly heated gasifier, the BCL gasifier consists of two main reactors: one where biomass is gasified with steam and a second where combustion occurs. The first

reactor provides char and air to the second. Combustion heat is transferred to the gasifier by re-circulating hot material.

Biomass gasification and pyrolysis are not generally considered economically competitive with coal gasification, except possibly in areas with no established natural gas infrastructure or coal availability. Some biomass processes yield by-products such as methanol that can be sold on chemical markets, making biomass slightly more competitive.

In recent years, some pilot plants have been built using various approaches including directly or indirectly heated gasifiers, air or oxygen-blown gasifiers, and atmospheric or pressurized gasifiers. When producing hydrogen, air-blown gasifiers are not preferred for gasification because the syngas generated is rich in nitrogen and because costs significantly increase with such a process since the hydrogen plant and other equipment are expensive. Utilizing indirectly heated gasifiers avoids the drawback of oxygen gasifiers since the air does not mix with the syngas and combustion occurs in a separate reactor.

There also exist other hydrogen production technologies:

- Fast pyrolysis followed by reforming of carbohydrate fractions of bio-oil.
- Direct solar gasification.
- Miscellaneous novel gasification process.
- Supercritical conversion of biomass.
- Microbial conversion of biomass.
- Thermal decomposition of hydrocarbon fuels.
- Thermocatalytic CO₂-free production of hydrogen from hydrocarbon fuels.
- Superadiabatic decomposition of hydrogen.
- Absorption enhanced reaction process (SERP).
- Photoelectrochemical hydrogen production.
- Biological H₂ from fuel gases and from H₂O.
- Two-phase photobiological algal H₂-production system.

Chapter 3

LITERATURE REVIEW

It is expected that by 2050 the world energy demand will have significantly increased. In addition, due to problems caused by greenhouse gas emissions, the world also needs low-emission and low-carbon energy suppliers to eliminate air pollution; the most promising sources today are solar energy, wind energy, biomass, bio-fuels, geothermal energy, and hydro-electricity. One of the options is to produce hydrogen from biomass to achieve sustainable and emission-free energy. Hydrogen is the lowest atomic mass atom in nature and hydrogen may help addresses challenges in this century as an energy carrier.

One question that is often debated by the researchers is if hydrogen will be a future fuel. For instance, Shinnar (2004) stated negative points about hydrogen; these points were summarized by Elnashaie *et al.* (2007). Although there are challenges to the hydrogen economy, a great number of researchers suggest that hydrogen is one of the most promising future fuels, and studied positive sides of hydrogen (Hirsch, 2004) and some points can be given as follows (Elnashaie *et al.*, 2007):

1. “H₂ supply on earth is infinite”.
2. “In internal combustion engines, H₂ burns without emission of CO₂, particulates and SO_x”.
3. “In fuel cells, H₂ can be converted to electric power at attractive efficiencies with negligible emissions”.

From the brief discussion above, in conclusion, hydrogen is a very promising clean fuel. In this thesis, we will concentrate on hydrogen production. Before that it would be interesting to give a definition of the hydrogen economy. Shell provides the following definition of a hydrogen economy:

“The hydrogen economy is a world fundamentally different than the world we know now. In the hydrogen economy hydrogen is available to everyone, everywhere—from the corner fuelling station to the large industrial facility on the outskirts of town. Countries

will not be dependant anymore on a single source of fuel. Hydrogen is produced, cleanly and cost-effectively, from a variety of sources like renewable, such as biomass and water, fossil fuels or even nuclear energy, using advanced technologies to ensure that any carbon released in the process does not escape into the atmosphere. Hydrogen is delivered and stored routinely and safely. Hydrogen-powered fuel cells and engines are as common as the gasoline and diesel engines of the late 20th century; they power our cars, trucks, buses and other vehicles, as well as our homes, offices and factories”.

3.1. Experimental Studies

The number of experimental studies regarding biomass gasification is large, and most of them are related effect of catalysis on the hydrogen yield and pyrolysis. However some of them are investigating the effect of temperature on produced H₂. For example, Skoulou *et al.* (2008) presented an experimental study with bubbling fluidized bed gasifier. The target of this study was H₂ enrichment of the product gas with the reactor temperature range between 750-850°C and equivalence ratio 0.2-0.4. The data obtained from several experiments indicate that olive kernels produced maximum H₂ and CO production while at 750°C and equivalence ratio (ER) = 0.2.

Brown *et al.* (1984) carried out with Pacific Northwest Laboratory (PNL) an experimental study to observe the effect of the both primary (alkali carbonates, potassium carbonate, and sodium carbonate) and secondary catalysis (nickel-based) on the gasification of different feedstocks in continuous fixed and fluidized-bed reactors. The results were very interesting that primary catalysts (alkali carbonates) alter pyrolysis reaction pathways and catalyze various secondary reactions, significantly changing the final product distribution. Alkali carbonates do catalyze the reaction of biomass char with steam, but they have little net effect on char yield in the fluidized bed. The physical characteristics of the gasifier, residence time, superficial gas velocity, and the particle size of the biomass appear to have a much larger effect on overall conversion than do primary catalysts. In addition, although nickel catalysts are the most effective catalysts for maximizing production of specific gases, nickel catalysts can unfortunately be easily deactivate by carbon deposition, sintering or sulphur poisoning.

Maschio *et al.* (1992) claimed pyrolysis is a promising route for biomass utilization by illustrating results of his experiments. They stated that a large number of research projects in the field of thermochemical conversion of biomass and particularly on biomass pyrolysis have been carried.

Turn *et al.* (1998) carried out a parametric experimental study using a bench-scale fluidized bed gasifier. The aim of this study was to determine the effects of reactor temperature, equivalence ratio (ER), and steam to biomass (STBR) ratio on the hydrogen production yield. They concluded that the hydrogen yield potential was the most sensitive to equivalence ratio and the highest hydrogen yield potential, 128 g H₂/kg of dry, ash free biomass (sawdust), at the temperature of 850°C, ER=0, and STBR=1.7.

Balasubramanian *et al.* (1999) have proposed the use of a CO₂ sorbent for enhancing the hydrogen yield of conventional steam methane reforming. This innovative method could be applied to any carbonaceous material such as coal, hydrocarbons or biomass. Also, Mahishi *et al.* (2006) conducted an experimental study in order to observe rich hydrogen yield gas. They did southern pine bark steam gasification in the presence of calcium oxide sorbent at various temperatures in the range of 500-700°C. It was observed there was a huge difference on hydrogen yield and carbon conversion efficiency (hydrogen yield by 48.6% and carbon conversion by 83.5%, respectively) with sorbent and without sorbent. And they also suggested that it is possible to operate the gasifier with lower temperature with sorbent due to the hydrogen yield for the sorbent case at 500 and 600°C was more than the conventional hydrogen yield at 700°C.

Gronli *et al.* (2000) developed a mathematical model for wood pyrolysis and compared of experimental measurements with model predictions. They argued that the development of thermochemical processes for biomass conversion and proper equipment design require knowledge and good understanding of the several chemical and physical mechanisms that constitute with the thermal degradation process. From this perspective, mathematical modelling of single-particle pyrolysis represents a very useful understanding of some of these processes.

Recently, Lv *et al.* (2003) have conducted experimental studies on biomass gasification with emphasis on hydrogen production. The researchers found that high gasification temperatures ($> 800^{\circ}\text{C}$) and small biomass particle size (0.2–0.3 mm) favour a high hydrogen yield. The group conducted further studies to determine the effect of in-bed use of dolomites and nickel-based catalyst on the hydrogen yield (Lv *et al.*, 2004). They found that the dolomite and Ni catalyst had a strong influence on the hydrogen yield which reached about 130 g/kg biomass. Finally the group did non-catalytic studies to compare biomass steam gasification versus biomass air gasification and found that steam gasification produces a hydrogen rich gas with lower heating values (LHV) exceeding 11 MJ/Nm³ (Lv *et al.*, 2007).

Lv *et al.* (2004) conducted a series experiments to investigate the effects of reactor temperature, steam to biomass ratio (STBR), equivalence ratio (ER) and biomass particle size on gas composition, gas yield, steam decomposition, low heating value and carbon conversion efficiency. This study showed that higher temperature favoured hydrogen production and gas yield but did not always favour gas heating value that means too high temperatures make the gas heating value lower. Also smaller biomass particles produced more CH₄, CO, C₂H₂ and less CO₂. One can contribute this idea with saying smaller particles have a better interaction with other molecular particles.

Lv *et al.* (2004) carried out a kinetic study on biomass fast catalytic pyrolysis with selected various biomass resources. The results showed that both calcined dolomite and a nickel-based catalyst improved the production of H₂. The nickel-based catalyst affects the hydrogen content to enhance almost two times more. Garcia *et al.* (1998) have conducted an experimental program in a fluidized bed at a temperature ranging between 650-700°C. This study was carried out in a bench-scale plant based on Waterloo fast pyrolysis process technology. The influence of the catalyst weight/biomass flow rate ratio (W/mb) was analysed on the product distribution and on the quality of gas product obtained. When the W/mb ratio increases, H₂ and CO yields increase while CO₂, CH₄ yields decrease.

Yang *et al.* (2006) conducted an experimental study on biomass pyrolysis. After the pyrolysis process, there are three chemical phases that occur in which solid, liquid and gas. This experiment also corresponds to some other pyrolysis study results showing temperature had a great role on the yield and quality of different products from biomass pyrolysis. It is favourable to conduct pyrolysis over 300°C to eliminate devolatilization. Increasing temperature will allow for an elevated hydrogen yield.

Zhang *et al.* (2006) demonstrated a technology for synthesis of liquid fuel from syngas, often known as a GTL (gas to liquid) process, which was developed about half a century ago. The process basically includes pre-treatment, biomass is gasified to produce syngas, after cleaning this gas, it enters in the FT reactor, FT off-gas is recycled or combusted to produce electricity. The liquid FT products are further treated to make a targeted fuel.

Hrabovsky *et al.* (2006) conducted a pyrolysis and gasification of wood in arc plasma with plasma produced in the torch with a dc arc stabilized by combination of argon flow and water vortex. The torch generates an oxygen-hydrogen-argon plasma jet with extremely high plasma enthalpy and temperature for syngas production in the experimental study. It was observed that a first advantage of having plasma offers better control of process temperature, higher process rates, lower reaction volume and especially optimum composition of produced syngas. A second benefit was syngas with a calorific value more than two times higher than the power spent for the process was produced.

Aznar *et al.* (2006) carried out an experimental study and examined the effect of adding a CO-shift reactor downstream from a fluidized-bed biomass gasifier and steam-reforming catalytic bed. The main gasifying agent used was a mixture of H₂O and O₂. Although the overall gasification process (advanced fluidized bed gasifier + steam reforming bed + two CO-shift reactors) is complex and could result in high cost, generating an exit gas with 73% vol. H₂ corresponds to 0.14 kg of H₂/kg of biomass on a dry basis, and with only 2.6% vol. CO produced.

Zabaniotou *et al.* (2007) conducted an experimental study of two systems in which fast pyrolysis at high temperature and fixed bed air gasification of rapeseed residues. They depicted comparing the two thermochemical methods with concluding that high temperature fast pyrolysis had better results than gasification. They agree that increasing temperature made a positive effect on syngas ($\text{CO} + \text{H}_2$) yield for both processes.

Wang *et al.* (2008) studied four different biomass samples (legume straw, corn stalk, cotton stalk, wheat straw) by using “deoxy-liquifaction” which is almost the same “pyrolysis”. The purpose of the work was to remove the oxygen in biomass to the greatest degree to produce the bio-petroleum at a low temperature with water at a medium temperature. Each sample weight and moisture content was prepared 5g and with 15% water. Working conditions were 350°C, 12-13 MPa for 2-3 h, also distillation temperature of 101-450°C. At the end of the experiment it was concluded that according to the standard for bio-petroleum, only legume straw oil and corn stalk oil could be called bio-petroleum; this means that H/C molar ratio was higher than 1.65. Oxygen content was lower than 6% with the HHV higher than 40 MJ/kg.

Tanaka *et al.* (2008) conducted an experimental study to investigate the possibility of effective hydrogen production from food waste instead of fossil fuels was investigated. The second objective was to clarify the effects of adding ash containing alkali components in order to establish a highly efficient system for producing hydrogen from food waste together with residual ash. It was concluded that hydrogen production is increased by adding food ash containing alkali components, and adding ash promotes more hydrogen production than calcium oxide under pyrolysis condition.

3.2 Hydrogen Economy

Voogt *et al.* (2001) have made a point relating to the political side of hydrogen economics the accomplishments of utilizing renewable energy vary significantly depending heavily on characteristics such as government policy and the attitudes and behaviours of relevant policy makers.

Tijmensen *et al.* (2002) have reviewed the technical feasibility and economics of biomass integrated gasification—Fischer Tropsch process in general, identifying the most promising system configurations and key R&D issues essential for the commercialization of this technology.

Goswami *et al.* (2003) presented the modeling results for the hydrogen production costs, steam methane reforming (SMR) was currently the cheapest method of hydrogen production and electrolysis powered by the PV powered electrolysis was the most costly, they also added that the economic analysis of different H₂ production technologies seems to be incomplete without consideration of environmental cost associated with these processes.

Besides direct combustion, biomass can be converted through other processes to generate energy, like gasification to produce hydrogen as discussed in this thesis. Vehicles powered by hydrogen fuel cell technology are three times more efficient than a gasoline-powered engine (Momirlan and Veziroglu, 2005). This technology is already used by several major car producers, which include BMW, American Honda Company and also Toyota Motors. These vehicles are powered by a fuel cell in combination with a nickel metal hydride battery (Momirlan and Veziroglu, 2005). In addition, these hybrid systems have been used by North American and European manufacturers' experimental vehicles and also any mobile application where a surge in output is needed. Furthermore, the hybrid concept allows the fuel cell stack to run at maximum efficiency by allowing the buffer action of the storage device (NiMH batteries, ultracapacitors, etc.). This environmental-friendly technology is expected to have been taken into effect in near future with Kyoto protocol, demanding the industry to reduce GHG emissions through reduced diesel use (Nath and Das, 2003). For example, the UK Government has set out its ambition of securing 20% of electricity from renewable sources by 2020 (Gross, 2004), while Netherlands stated its goal of 10% renewable energy by 2020 (Agterbosch *et al.*, 2004). For instance, Germany has the most successful industrial development of renewable energy. This accomplishment is mainly related to the parliament energy policy. In short, the dynamic growth of renewable energy in Germany has been driven

largely due to the reduction of taxes by government and social awareness for renewable energy technologies.

Braccio *et al.* (2006) conducted an economic analysis to investigate the effect of different parameters and variables on the cost of hydrogen produced using low to medium capacity (1.3 MW, 10 MW, 20 MW) gasification plants. It was concluded additional significant cost reduction could be obtained with the increase of plant size and the cost of produced hydrogen gas found to be nearly 11 to 12 €/GJ with a refuelling station, compression brings some additional cost to nearly 5 €/GJ. Therefore in this study, the cost of hydrogen produced using biomass has been estimated to be 16 to 17 €/GJ which is quite higher than the result declared in the next paragraph hydrogen production cost.

Lv *et al.* (2007) undertook a study on the economic efficiency of hydrogen production from biomass residues in China, the basic system for hydrogen production consist of oxygen-rich air downdraft gasifier plus CO-shift reaction in a fixed bed. The cost sensitivity analysis on this system results in a cost of 1.69\$/kg H₂ available with the capacity of this system is 266.7 kg biomass/h (6.4 ton/day).

Elnashaie *et al.* (2007) investigated ranges of hydrogen production capacity for the cost estimation varies from a pilot plant of 100 kg H₂/day to a very large industrial plant of 10,000,000 kg H₂/day. The results show that the hydrogen production cost generally decreases from a cost of 2.224 \$/kg H₂ for a small pilot plant of 100 kg H₂/day to a much lower cost of 0.625 \$/kg H₂ for a very large plant of 10,000,000 kg H₂/day. The comparison of the economics of hydrogen production shows that the hydrogen production cost using this novel autothermal reformer-regenerator process is lower than the cost reported by the most economical steam methane reforming in industrial fixed-bed reformers. For example, with the same capacity of 100 kg H₂/day, the hydrogen cost in an industrial steam methane reforming process is around 9.10 \$/kg H₂, while the hydrogen costs are 2.054 \$/kg H₂ for methane feed and 2.224 \$/kg H₂ for heptanes feed in this novel autothermal reformer-regenerator system; the cost reductions are 77.43% for methane and 75.56% for heptane, respectively. If the hydrogen production capacity is a typical industrial-plant capacity of equivalent to 214,286 kg-H₂/day, the reported

hydrogen cost in industrial fixed-beds by steam methane reforming is about \$0.739–0.966/kg H₂, while using this autothermal process, the hydrogen costs are \$0.664/kg H₂ for heptane steam reforming and \$0.501/kg H₂ for steam methane reforming, respectively. The cost reductions are 10.2%–31.3% for steam reforming of liquid/higher hydrocarbons and 32.2% – 48.1% for methane steam reforming, respectively. Therefore, the comparison suggests that this autothermal circulating fluidized bed membrane reformer can be a more efficient and more economical pure hydrogen producer.

3.3 Exergy Analysis

Extensive exergy analyses have been reported using devices, technologies and systems, in a variety of fields. Some examples include exergy assessments of power plants for transportation and power generation, chemical and metallurgical processing facilities and building systems.

Rosen *et al.* (1987) points out that an important commercial process for the production of hydrogen from fossil fuels is the Koppers-Totzek (KT) coal gasification process. The principal findings of this study of the KT process were that its energy and exergy efficiencies are 59% and 49%, respectively.

Rosen *et al.* (1987) reported energy and exergy analyses and comparisons of two production processes for hydrogen and electricity from coal. To produce electricity, conventional coal-fired steam power plant, and to produce hydrogen, a Koppers-Totzek coal gasification plant was taken into consideration. It seems that researchers tend to study more profoundly to improve renewable fuels than fossil fuels because of environmental issues (such as global warming).

Rosen *et al.* (1988) performed energy and exergy analyses of a production process for methanol from natural gas. The process involved generation of synthesis gas by steam-methane reforming, compression of the synthesis gas, methanol synthesis and distillation of the crude methanol. The energy and exergy efficiencies for the overall processes were found to be 39% and 41%, respectively.

Rosen *et al.* (1990) investigated the thermodynamic performance of the steam-methane reforming (SMR) process for producing hydrogen from natural gas. The analysis results indicate that the principal exergy losses occur in the reformer and are due to the irreversibilities associated with combustion and heat transfer across large temperature differences. Overall energy and exergy efficiencies for methane fed SMR were calculated to be 86.0% and 78.5%, respectively.

Lede *et al.* (1999) carried out a study on using solar energy for thermochemical conversion of biomass. The study highlights the technical and economic benefits and also lists the difficulties of using solar energy as a source of heat for gasification and pyrolysis of biomass. Prins *et al.* (2003) studied the energetic and exergetic aspects of biomass gasification in the presence of steam and air. They concluded that the choice of gasification medium should be governed mainly by the desired product gas composition.

Schuster *et al.* (2001) conducted a parametric modeling study of a biomass gasification system. A decentralized combined heat and power station using a dual fluidized bed steam gasifier was simulated. The group predicted net electricity to biomass efficiency of about 20%. Carapellucci *et al.* (2002) studied the thermodynamics and economics of biomass drying using waste heat from gas turbine exhaust and concluded that using gas turbine exhaust for biomass drying enhances the economic feasibility of biomass fired power plants.

Prins *et al.* (2003) studied energy and exergy analyses of the oxidation and gasification of carbon. The objective of his study was to quantify exergy losses throughout the gasification process, and to compare the results with combustion processes finalizing the differences between combustion and gasification. They claim that gasification is more efficient than combustion since exergy losses due to internal thermal exergy exchange are reduced from 14-16 to 5-7% of expended exergy, while the chemical reactions are relatively efficient for both processes. They suggest that optimum gasification temperatures should be in the range of 1100-1200 K (for atmospheric pressure) and 1200-1300 K (for 10 bar pressure).

Lutz *et al.* (2003) presented a thermodynamic analysis of hydrogen production by steam reforming. In this system, the reformer heat demand is supplied from a fractioned produced stream. Apart from this study, Ahmed and Krumpelt (2001) investigated a global analysis of the efficiency of steam reforming for a variety of hydrocarbon fuels, with an emphasis on partial oxidation and autothermal reforming.

Kearns *et al.* (2004) applied a second law analysis to pressure swing adsorption which is a popular gas separation technology for the process industries such as air separation, hydrogen purification, and isomer separation. Exergy functions were illustrated as binary linear isotherm theory to a four-step skarstrom cycle.

Rao *et al.* (2004) consider a counter current fixed-bed gasifier for municipal residue-based gasification. Refuse derived fuel (RDF) pellets and they compared with the mass and energy performance features of gasifier with other biomass and residual fuels. The mass conversion and cold gas efficiency (CGE) of the gasifier were observed to be 83% and 73%, respectively for RDF pellets. His study aims to identify the sources and magnitudes of the inefficiencies and irreversibilities in terms of energy conversion.

Pellegrini *et al.* (2005) presented a simplified model for the gasification process based on chemical equilibrium considerations consisting minimization of the Gibbs free energy of the produced gas had been coded EES programming language. Furthermore they performed a parametric study evaluating the moisture in biomass, temperature of air, temperature of biomass, volume of steam added and thermal losses. In addition some of his results also were compared with those found in the literature and real systems.

Tsatsaronis *et al.* (2005) presented a novel process; the so called hydrogen and electric power from Carbon-Containing Substances and Process heat (HECAP) process. This process was described as one of the most prominent hydrogen production techniques which were invented in 1973. In addition, the process can be described as a contribution idea which perhaps could be called hydrogen and electric power from sustainable carbon-containing substances and process heat (HESCAP). HECAP is simulated by using Aspen Plus. Basically, in this process, hydrogen gas is generated in the electrolytic unit and released as product from the process, while the sulphuric acid solution is used as an

oxidizer for coal combustion. In this process, not only hydrogen is able to be produced but also electric energy can be produced as well. They also include a thermodynamic analysis of this process to prove hydrogen and electric energy are generated with high efficiency. They claim that this process is a true “zero emission process” because no NO_x is formed during coal combustion with sulphuric acid since no air is needed and the combustion products SO₂ and CO₂ are removed as compressed liquids from the overall process. Furthermore, thermodynamic losses of the combustion reaction are reduced when sulphuric acid is used as an oxygen carrier. They also say that SO₂ removal is easier from the combustion gas and the combustion product CO₂ is separated by using integrated CO₂ capture system without any additional energy penalty.

There are many studies about exergetic evaluations of biomass gasification; one of them is Ptasinski *et al.* (2005), the purpose of their study was that comparing different types of solid biofuels (straw, untreated wood, treated wood, grass plants) or liquid biofuels (vegetable oil) for their gasification energy, exergy efficiencies and benchmark this against the gasification of coal. They concluded that biomass could replace coal as a gasification feedstock from a thermodynamic point of view, the result they calculated by using Aspen Plus for gasification based on chemical and physical exergy showing higher efficiencies than for solid biomass almost 84% to 76-78%. In contrast, the vegetable oils result is similar to the gasification of coal and both could be considered as high-quality fuels.

Jand *et al.* (2006) claim that none of the available kinetic models for biomass gasification, regardless of complexity, is able to predict the yield, composition, and calorific value of the gasification resulting gaseous fuel. For this reason a method is described for significantly improving the predictive capability of equilibrium-based calculation tools for the estimation of fuel gas composition in high-temperature biomass gasification processes. They followed two different approaches: the series reactor method and the Gibbs minimization model. Their numerical part is taken from Smith *et al.* (1982) and it has been coded in MATHCAD11. Almond shell and sawdust are considered as biomass and calculation tool equilibrium results are compared with previously published

results and additional some experimental results are compared with the results of the thermodynamic limit computations.

Weber *et al.* (2006) investigated overall energy efficiency of hydrogen production from biomass via an integrated process based biomass gasification (air blown type was used). The results obtained from the literature of experimental studies show that such an integrated system can generally have overall energy efficiency of 40-60% (HHV basis), depending on biomass properties and process configuration. Significant efficiency improvements can be achieved if the gasifier operates at a similar pressure to the reformer, which typically operates at elevated pressures. Analysis further suggests that the gasification with steam and other oxidizer is the most energy efficient way for hydrogen production and such a strategy also delivers a high amount of hydrogen. Other strategies for efficiency improvements include increasing reaction conversion in the reformer, enhancing CO conversion in the shift reactor and improving process heat recovery.

Kelly-Yong *et al.* (2007) say that although there has been some successful industrial-scale production of renewable energy from biomass, generally this industry still faces a lot of challenging, including availability of economically viable technology, sophisticated and sustainable natural resources management, and proper market strategies under competitive energy markets they also highlighted the development and the implementation of suitable policies by the local policy-makers is still the single and most important factor that can determine a successful utilization of renewable energy in a particular country. Also, they presented the potential availability of oil palm biomass that can be converted to hydrogen through gasification in supercritical water (temperature > 374°C, pressure > 22 MPa). It is interesting to note that with an annual world oil palm biomass production of about 184.6 million tons, the maximum theoretical yield of hydrogen potentially produced by oil palm biomass via this method is 2.16×10^{10} kg H₂ yr⁻¹ with an energy content of 2.59 EJ/yr, meeting almost 50% of the current worldwide hydrogen demand.

Mahishi *et al.* (2007) conducted a thermodynamic analysis of hydrogen production from biomass using equilibrium modeling. In order to figure out optimum gasification process conditions which means maximum hydrogen production they looked at the effects of process parameters such as temperature, pressure, steam-biomass ratio and equivalence ratio. They concluded that the maximum amount of hydrogen is 1.54 mol that can be produced when the equilibrium in pure air gasification is operated by $P=1$ atm, $T=1000$ K, $STBR=3$ and $ER=0.1$ stated conditions at a thermodynamic efficiency of 54%.

Among the alternative processes of hydrogen production Gomri *et al.* (2007) compared those process, a two-step water-splitting solar thermochemical cycle and the SMR process. In this study, energy and exergy efficiencies are evaluated for hydrogen production by steam methane reforming and for the overall ammonia production process. Further a process of hydrogen production based on solar thermochemical process (Zn/ZnO redox reactions) was presented. They identified in their results that Zn/ZnO redox reactions could be an alternative process to replace SMR. Furthermore, ammonia can be produced using concentrated solar energy with an exergy efficiency of the process approximately 20%. It is also known that ammonia is a good energy carrier that can be reformed to produce hydrogen and nitrogen by product. There are many applications of ammonia; production of fertilizers, plastics, fibers, intermediates for dyes and pharmaceuticals and manufacture of explosives and use as a solvent and refrigerant.

Although CO_2 emissions from using biomass as a fuel in the gasification is sustainable due to this carbon dioxide is fixed by photosynthesis, there are some studies on carbon dioxide (CO_2) capture, for example, Florin *et al.* (2007) argued the steam gasification of biomass, coupled with CO_2 capture, is a promising process for exploiting renewable biomass resources for the production of H_2 . Based on the model, they predicted a maximum H_2 concentration of 83% mol, with a steam- to-biomass ratio of 1.5

Simpson *et al.* (2007) performed hydrogen production via steam methane reforming (SMR) using exergy analysis, SMR model was developed using a chemical equilibrium model with detailed heat integration. They concluded global thermal and exergy efficiencies of the base-case system are 66.7% and 62.7%, respectively. They states that

the majority of the exergy destruction occurs within the reformer, mostly due to high irreversibility of combustion and heat transfer.

It is widely acknowledged that the solution to the global problems would be to replace the existing fossil fuels with hydrogen as the universal energy carrier declared by Conte *et al.* (2001). From this perspective, Ptasinski *et al.* (2008) presented an efficiency analysis of hydrogen production processes from a variety of biomass feedstocks by a thermochemical method-gasification as well as biochemical methods-fermentation and anaerobic digestion. Aspen Plus was used for the mass and energy balances. It was discovered that the exergetic efficiency of hydrogen production by gasification of more dry feedstocks, such as vegetable oil and straw (65.7-79.1%), is comparable to that of the current hydrogen production by SMR (78.0%). However the exergetic efficiency for H₂ production from sludge, manure and various household organic wastes are lower both for gasification (35.8-40.3 %) as well for biochemical processes (29.1-36.3%).

Dilmac *et al.* (2008) illustrated a study of hydrogen production via catalytic steam reforming of natural gas processes were taken using a real petroleum refinery. The energy and exergy efficiencies were calculated and the data was calculated by using Simsci/ProII simulation software. They deduced that steam reformer exergy efficiency were found to be 78.23% while energy efficiency was 94.33% and the shift reactor exergy efficiency was 98.10 when energy efficiency was 99.44%.

There are many studies about pure hydrogen production and CO₂ capture. In one, Eltron Research Incorporation recently developed a membrane to operate high H₂ separation rates with essentially 100% selectivity to H₂. These membranes are designed to operate at the same conditions as high-temperature water-gas shift (WGS) reactors (320-440°C) and they claim some of the advantages of the membrane are CO₂ capturing even though high pressure, the membrane cost is low with long membrane life, membrane is able to work with biomass, hydrogen recoveries 90% or higher are possible, the membranes can be integrated with commercial high temperature water-gas shift catalysts.

Toonssen *et al.* (2008) considered five different commercial or pilot scale gasification systems with five different gasifiers sequentially, Battelle, Varnamo, Fast internal circulating fluidized bed (FICFB), Institute of Gas Technology (IGT), Blaue Turm gasifiers for the design of the hydrogen production plant that generates almost pure hydrogen. And they made a comparison among the gasifiers with respect to thermodynamic performances (hydrogen yield and exergy efficiency) depend on two different gas cleaning processes, low temperature gas cleaning (LTGC) and high temperature gas cleaning (HTGC). They concluded LTGC processes based on the Battelle and FICFB gasifier are performing better hydrogen production than the HTGC processes, and the Blaue Turm it is the HTGC process, which is better performance. Finally, the Blaue Turm HTGC process has the highest hydrogen yield (0.106 kg H₂/kg dry biomass), while Battelle LTGC has the highest exergy efficiency (50.7 %). And highlighted in that comparison, these processes are different due to moisture content of the biomass different however it seems that the lower moisture content has a positive influence on the performance on the system. In addition Cycle-Tempo computer program was used for thermodynamic evaluation in this study.

Turpeinen *et al.* (2008) also investigated, by using Aspen plus and HSC chemistry software, producing hydrogen by steam reforming including thermodynamic analysis. That study focused on four compositions: natural gas, biogas (aneorobic digestion or fermentation), refinery gas (Crude oil distillation) and hydrogen-rich gas produced from a coke oven (coke oven plant). They concluded that the biogas and coke oven proved to be a potential candidate for hydrogen production and they are competitive compared to the processes of natural gas.

Chapter 4

SYSTEMS DESCRIPTIONS

In this chapter, it will be focused on the hydrogen production systems and their features in details. Before starting this section it would be better to note that not many systems were proposed or studied for biomass based hydrogen production through gasification in the literature. It is necessary to define the scope of the present study. The approach to preparing this thesis has three stages. The first stage consists of the selecting the three most favourable biomass based hydrogen production plants described in detail, and making improvements as can be seen below in the block flow diagram and detailed system design which will be explained. For system 1, there is a limited amount of information and results available in the literature. For this reason there are many assumptions and modifications made in the simulation, in contrast to system 2 and system 3, which have very detailed thermodynamic evaluations including an economic analysis available in the various studies. Since system 1 is simulated it has a different approach to gasification than in system 2 and system 3. Furthermore the simulation in system 1 will allow for an energy and exergy comparison to systems 2 and 3. The second stage of study seeks to make improvements to the existing study of those systems. This stage uses simulation and exergy analysis. Finally, the third stage consists of an economic evaluation for these systems, to figure out the minimum hydrogen production cost. Stage two and stage three of this study is explored further in following chapters.

4.1 Hydrogen Production System 1

As can be noted below Figure 4.1, the block and process diagram of the hydrogen production system were designed and proposed by Elbaccouch *et al.* (2004) for the gasification of bagasse with a capacity of 900 kg/h flow rate producing 17 kg/h hydrogen.

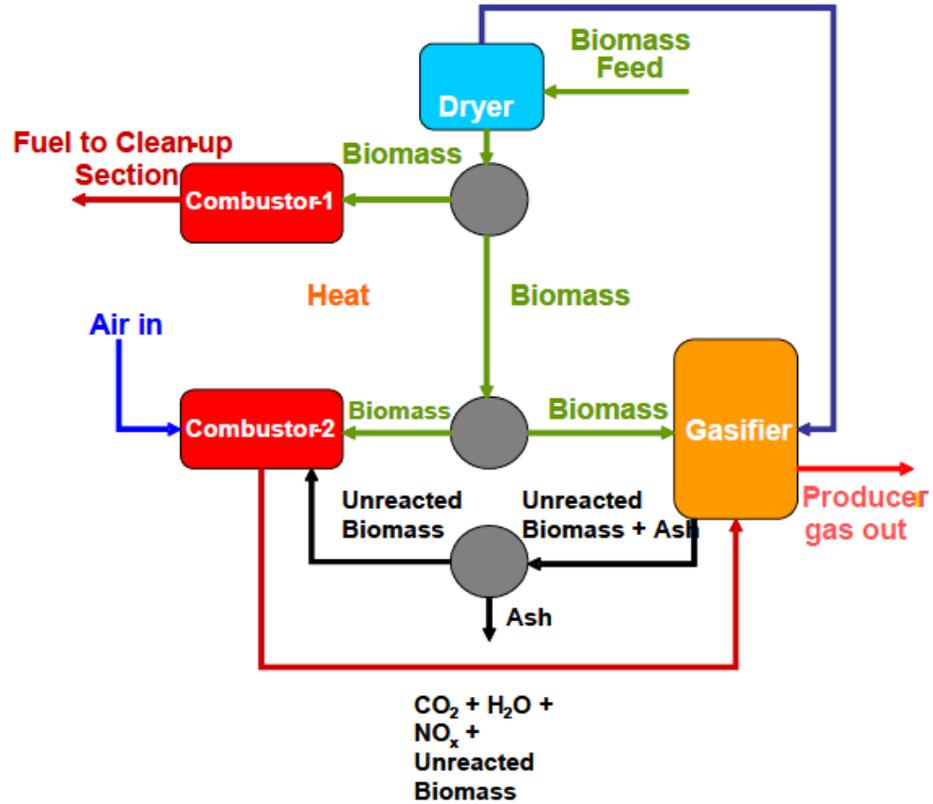


Fig. 4.1: Gasifier approach of system 1 (Reported by Elbaccouch *et al.*, 2004).

First, the combustor1 provides enough energy for the clean-up section where the combustor 2 provides heat for the gasifier. In Fig.4.1, the gasifier heat demand is supplied by the combustor 2, which is fed by the biomass, meaning the gasifier energy is supplied by biomass, which makes a huge difference from the indirectly heated gasifier approach which will be discussed further with system 2 and system 3

There are four steps for producing hydrogen in the below diagram (Figure 4.2). Step one is where biomass enters the drier section. The second step is where the biomass splits; flowing into the gasifier and into the combustor (the split ratio for biomass to the combustors is 0.47). The third step consists of the syngas clean-up after the gasifier and the combustion procedures are completed. Finally the fourth step is the PSA process for the purification of the syngas.

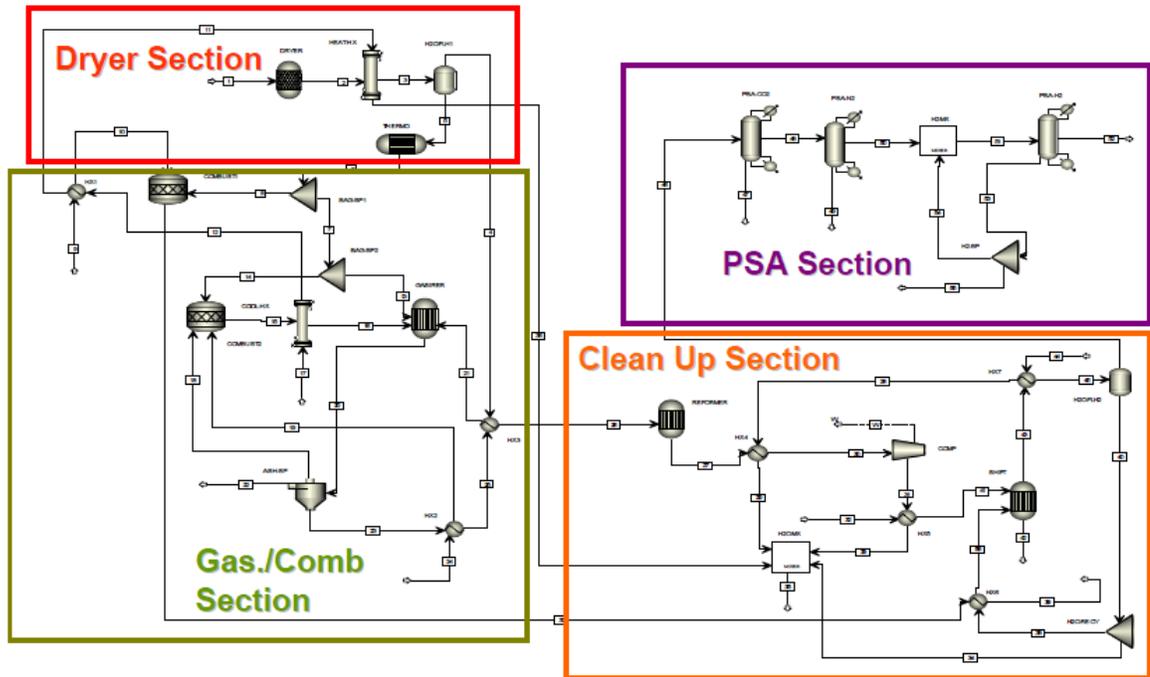


Fig. 4.2: Process diagram of system 1 (Reported by Elbaccouch *et al.*, 2004).

The reason this system taken into consideration is because there are some important differences that must be highlighted in this system such as upon completion of the drying process; where biomass dries without mixing with the syngas providing useful evaporated water for the steam-fed gasifier unlike system 2 and 3. In addition, this system has a unique approach for the biomass allocation; biomass splits into two parts twice to supply the energy demand for the gasifier and the shift reactor.. Furthermore, the results identify that there is an insignificant amount of CH_4 produced from the gasifier in the syngas section for this reason. Hydrogen yield is not increased during the outlet of the reformer. It might be understood that the reformer reactor in this plant is for the purpose of cleaning the syngas.

4.2. Hydrogen Production System 2

As mentioned before, we can produce either electricity or hydrogen through gasification. However there are some examples exist which produce electricity and hydrogen concurrently (Spath *et al.*, 2005). Fig. 4.3 shows the first part of the hydrogen plant of system 2 and system 3 which is syngas production through gasification. This system

reported by the FERCO SilvaGas process (Babu, 2003), employs the low-pressure Battelle (Columbus) gasification process (The process was developed by US DOE Biomass Power Program, FERCO, Battelle Columbus Laboratory, Burlington Electric Department, Zurn Industries, OEC/Zurn, and NREL) which consists of two physically separate reactors; a gasification reactor in which the biomass is converted into a gas mixture and residual char at a temperature of 850° to 1000°C, and a combustion reactor that burns the residual char to provide heat for gasification.

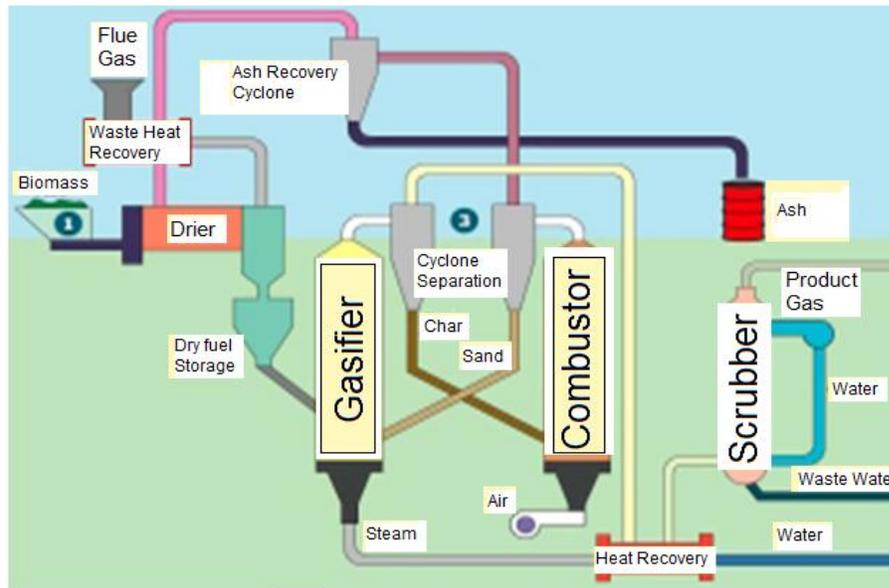


Fig. 4.3: System 2 and system 3 gasifier approach (Reported by Babu, 2003).

Heat transfer between reactors is accomplished by circulating sand between the gasifier and combustor. Since the gasification reactions are supported by indirect heating, the primary fuel gas is a medium calorific value fuel gas. A typical product gas composition obtained in pilot plant tests, at steam to biomass (wood chips) ratio of 0.45, is 21.22% H₂, 43.17% CO, 13.46% CO₂, 15.83% CH₄ and 5.47% C₂H₄ or C₂H₆. A 200 tonne per day capacity Battelle demonstration gasification plant was built at the McNeil Power plant in Burlington, Vermont. The plant size is 182 dry tons per day of biomass feed. The gas produced burned in the boiler of the 50 MW power plants.

As can be seen in Fig. 4.4, this system was divided into two parts. The first is the gasification plant in Fig. 4.3; which produces syngas for the second part of the system, which is the hydrogen plant. The red square outline represents syngas production which is detailed in Fig. 4.4. Produced syngas travels through the syngas compression, into the ZNO-bed, to the Steam Reformer, onto the HTS and the LTS and finally it goes through the PSA for cleaning. This hydrogen production process was simulated using Aspen Plus and its energy and economic evaluation was reported by Corradetti *et al.* (2007). The typical wood composition $\text{CH}_{1.54}\text{O}_{0.67}$ had been used in this study, the delivered biomass moisture was 30%wt with 1856 tons per day biomass inlet corresponding to 1300 dry tons per day. As a result, the amount of produced hydrogen is 4.632 t/h. For a biomass cost equal to \$20/t, the produced hydrogen cost was \$11.8/GJ. And also this hydrogen production system's exergy efficiencies were determined by Cohce *et al.* (2010). Further explanation about this process will be explained in detail following simulation chapters. Note that dashed lines represent heat fluxes.

4.3 Hydrogen Production System 3

As can be seen below Figure 4.5, system 3 is proposed and designed in Aspen Plus in detail by NREL (Spath *et al.*, 2005). Both energy and economic investigations were conducted as proof that hydrogen can be an economically feasible product. Fig. 4.5 shows block flow diagram of biomass based hydrogen plant system 3 reported by NREL, the feedstock used in this analysis is hybrid poplar wood chips delivered at 50 %wt moisture. The plant capacity is arranged to be 2000 dry tonne/day and the feedstock cost is assumed to be \$30/dry ton (delivered). Systems 2 and 3 have almost the same approach regarding low pressure indirectly heated gasifier selection which could be seen in red lines in Fig. 4.5. The process broadly consists of:

- Feed handling,
- Drying,
- Gasification and tar reforming,
- Gas clean up and compression,
- Shift conversion (HTS and LTS),
- Hydrogen purification
- Integrated a steam and power generation cycle.

Chapter 5

THERMODYNAMIC ANALYSIS

A thermodynamic evaluation of a complex system requires consideration of its components and their characteristics, chemical reactions and thermal losses. Recently, biomass gasification in indirectly heated steam gasifiers has received much attention for the conversion of biomass to combustible gas (Li *et al.*, 2004). In this thesis simulation's, it was considered the energy efficiency of the gasification reaction as the total energy of the desired products divided by the total energy of the process inputs (Ptasinski *et al.*, 2007). For this analysis, the products are taken to be a mixture of H₂O, N₂, H₂, CO₂, CH₄, CO, NH₃ and H₂S. Char is assumed to consist of solid carbon (C) and tar is not taken into account in the simulations.

Simulations are performed with the Aspen Plus simulation software, which is commonly utilized in a wide range of industrial applications. A fortran subroutine is applied to control process yields. In Aspen Plus, streams represent mass or energy flows. Energy streams may be defined as either work or heat streams, of which the latter also contain temperature information to avoid infeasible heat transfer. Mass streams are divided by Aspen Plus into three categories: mixed, solid, and non-conventional (for substances like biomass). Mixed streams contain mixtures of components, which can be in gaseous or liquid phase. The solid phase components in these simulations are solid carbon (C) and sulphur (S). Thermodynamic properties are defined in the Aspen Plus libraries for chemical components. Components present in the mixed and solid stream classes may participate in phase and chemical equilibrium, and are automatically flashed by Aspen Plus at stream temperature and pressure. Non-conventional components are defined in Aspen Plus by supplying standard enthalpy of formation and the elementary composition (ultimate and proximate analysis including particle size distribution) of the components may also be defined. Biomass is characterized in this manner here. Although Aspen Plus calculates enthalpies and entropies for conventional components, ambient temperature and pressure, which are required in evaluations of exergy, are not readily available in the

result output. A property termed availability by Aspen Plus is calculated for conventional components, but this does not include chemical exergy. For these reasons, the excel program is used to calculate total exergy (physical and chemical) for each stream in these simulations.

The following simplifying assumptions are made in the analysis and simulations:

- Char only contains solid carbon and ash, and there is no tar yield.
- The process occurs at steady state and isothermally, and in order to avoid kinetic affects residence time is not considered.
- There is no catalysis included in the simulation or thermodynamic calculation.
- The ZNO-bed is not included in the energy and exergy calculations.
- Pressure swing adsorption (PSA) system is considered as a place where the inlet syngas lost heat and pressure during the process. Thus, just thermophysical calculation takes into consideration.
- All gases behave ideally.
- Ambient air is considered on a volume basis as 79% nitrogen and 21% oxygen.
- Reference air temperature, 25°C and pressure, 1 bar.
- A heat stream is used as a heat carrier in Aspen Plus instead of sand.
- During the processes all the components except the SMR, the HTS and the LTS pressure drops are ignored.
- The Peng–Robinson equation of state with Boston-Mathias modifications were used as the method of solving the equations.

5.1 Balance Equations

Mass and energy (in particular enthalpy) values are evaluated with Aspen Plus. For a general steady-state process, it can be written mass and energy balances, respectively, as

$$\sum_i \dot{m}_i = \sum_o \dot{m}_o \quad (5.1)$$

$$\sum_i \dot{E}_{in} = \sum_o \dot{E}_{out} \quad (5.2)$$

An overall exergy balance can be written for a steady state process as follows:

$$(\sum \dot{E}x_i)_{in} = (\sum \dot{E}x_j)_{out} + \sum \dot{E}x_{dest} \quad (5.3)$$

where

$$(\sum \dot{E}x_i)_{in} = \dot{E}x_{air} + \dot{E}x_{drybio} + \dot{E}x_{biomoist} + \dot{E}x_{st} + \dot{E}x_{meth} \quad (5.4)$$

$$(\sum \dot{E}x_j)_{out} = \dot{E}x_{prodg} + \dot{E}x_{unconcarb} + \dot{E}x_{st} + \dot{E}x_{exh} + \dot{W}_{net} \quad (5.5)$$

Both physical and chemical exergy inlet and outlet values are determined for the Gasification, Combustion, SMR, HTS and LTS product gases. These values are used to assess exergy destructions. Some components possess only physical exergy. The specific flow exergy associated with a specified state is expressible by the sum of specific physical and specific chemical exergy:

$$ex_{prodg} = ex^{ph} + ex^{ch} \quad (5.6)$$

The physical exergy can be defined as

$$ex^{ph} = (h - h_o) - T_0(s - s_o) \quad (5.7)$$

and the chemical exergy contribution can be calculated for an ideal gas mixture as follows:

$$ex^{ch} = \sum_i x_i (ex_i^{ch} - RT_o \ln x_i) \quad (5.8)$$

Here, x_i is the mole fraction and ex_i^{ch} the standard chemical exergy of component i . Standard chemical exergy values used here are taken from model 2 in Szargut *et al.*(1988).

The entropy balance for a steady-flow reacting system can be written as

$$\sum \frac{\dot{Q}_j}{T_j} + \sum \dot{m}_i s_i - \sum \dot{m}_o s_o + \dot{S}_{gen} = 0 \quad (5.9)$$

The exergy destroyed due to irreversibility can be expressed as follows:

$$\dot{E}x_{dest} = T_0 \dot{S}_{gen} \quad (5.10)$$

The physical exergy of biomass is zero when it is entering the system at its assumed input at T_o and P_o . Thermodynamic properties are needed for the calculation of the chemical exergy of biomass. Since such properties for oil palm shell biomass are not available, a correlation factor is used based on statistical correlations developed by Szargut *et al.* (2005);

For solid biofuels:

$$\beta = \frac{1.044 + 0.0160 H/C - 0.3493 O/C [1 + 0.0531 H/C] + 0.0493 N/C}{(1 - 0.4124 O/C)} \quad (5.11)$$

The specific chemical exergy for biomass can then be determined as

$$Ex_{bio(solid)}^{ch} = \beta LHV_{bio} \quad (5.12)$$

Although the magnitude of the physical exergy of biomass is small, it is calculated in these simulations after the drying process. The calculation is performed using the heat capacity of dry biomass which is described by Gronli and Melaaen (2000):

$$C_{p(bio)} = 1.5 + 10^{-3}T \quad (5.13)$$

where $C_{p(bio)}$ is the heat capacity and T is the temperature (K) of the biomass.

The change in specific entropy in Eq. (5.7) can be written for biomass as

$$\Delta s = \int_{T_0}^T \frac{C_p}{T} dT \quad (5.14)$$

where C_p is the specific heat in constant pressure.

Equation (14) can be used to calculate the physical exergy with Eq. (5.7) at the specified temperature.

The heat capacity of solid carbon is determined using Aspen Plus property data and substituted into Eq. (5.7) to find entropy values, which are used for the thermal exergy calculation in Eq. (5.7).

5.2 Energy, Cold Gas and Exergy Efficiencies for BCL Gasification

The overall system performance is based on the simulation results for the three systems which will be displayed in following chapters. The latter can be expressed with the cold gas efficiency. This measure is the ratio of the chemical energy of the produced gas to that of the biomass feed energy content. The cold gas energy efficiency of the BCL hydrogen plant is determined as;

$$\eta_{cg} = \frac{\dot{m}_{prodg} LHV_{prodg}}{\dot{m}_{drybio} LHV_{drybio}} \quad (5.15)$$

Hydrogen is the desired product in this simulation, so the production efficiency can be described as the system efficiency in general. Energy efficiency η and exergy efficiency ψ values are often evaluated for steady-state processes, and can be written here as follows:

$$\eta_{sys} = \frac{\dot{E}_{prodg} + \dot{W}_{net}}{\dot{E}_{air} + \dot{E}_{drybio} + \dot{E}_{biomoist} + \dot{E}_{st} + \dot{E}_{met h}} \quad (5.16)$$

$$\psi_{sys} = \frac{\dot{E}x_{prodg} + \dot{W}_{net}}{\dot{E}x_{air} + \dot{E}x_{drybio} + \dot{E}x_{biomoist} + \dot{E}x_{st} + \dot{E}x_{met h}} \quad (5.17)$$

where \dot{E}_{prodg} is the rate of product energy output, $\dot{E}x_{prodg}$ is the rate of product exergy output and \dot{W}_{net} is the net work output (produced work minus consumed work). Also the energy efficiency of component i may be written as follows:

$$\eta_i = 1 - \frac{(\dot{E}_{out})_i}{(\dot{E}_{in})_i} \quad (5.18)$$

where $(\dot{E}_{out})_i$ and $(\dot{E}_{in})_i$ are the energy output and input rates for component i . Similarly, the exergy efficiency for component i may be written as

$$\psi_i = 1 - \frac{(\dot{E}x_{dest})_i}{(\dot{E}x_{in})_i} \quad (5.19)$$

where $(\dot{E}x_{dest})_i$ and $(\dot{E}x_{in})_i$ respectively, are the exergy destruction rate and the exergy input rate for component i .

The steam-biomass ratio (STBR) can be expressed as

$$\text{STBR} = \frac{\dot{m}_{st}}{\dot{m}_{drybio}} \quad (5.20)$$

Also, the ratio of exergy destruction x_{dest} for a component can be evaluated by dividing its exergy destruction by the total exergy provided to the system. Here, it can be written as

$$x_{dest} = \frac{(\dot{E}x_{dest})_i}{(\sum \dot{E}x_i)_{in}} \quad (5.21)$$

where $(\dot{E}x_{dest})_i$ is the exergy destruction for each component and $(\sum \dot{E}x_i)_{in}$ is the exergy flow of all input material streams.

Chapter 6

ECONOMIC EVALUATION

This section will discuss the economic evaluation for these simulated systems to estimate minimum hydrogen production cost, further discussion will be the methods and sources for determining the capital cost of each piece of equipment within these three plants. A summary of the individual equipment design criteria for these three systems can be found in Appendix 1.

Once the system configurations were set up on Aspen Plus, the data can be collected for simulation calculations. Also some data results can be transferred to Aspen Plus Economic Analyser to estimate most of the component's capital cost. The majority of the costs came from literature and Icarus (an equipment capital cost estimating software tool by Aspen Tech), in order to determine the total project cost, first the purchased cost of the equipment was calculated and then cost factors were used to determine the installed equipment cost. The cost multipliers were taken from Peters and Timmerhaus (2003).

For the biomass based hydrogen plants in this study, in order to estimate TPI (Total Project Investment) these routes are followed;

$$\text{TPI} = (\text{TIC}) + (\text{TINC}) \quad (6.1)$$

where TIC is the total installed cost and TINC is total indirect cost.

As can be seen above equation (6.1); the total project investment (TPI) is the sum of the total installed cost (TIC) plus the total indirect costs (TINC).

6.1 Total Installed Cost (TIC)

To estimate TIC the factors were used of each piece of equipment are shown in Table 6.1. In addition, this method which is called technically factored estimate: based on knowledge of major items of equipment has an expected accuracy is about $\pm 30\%$.

Table 6.1: Cost factors in determining total installed equipment costs.

| | % of TPEC |
|----------------------------------------------|------------------|
| Total Purchased Equipment Cost (TPEC) | 100 |
| Purchased equipment installation | 39 |
| Instrumentation and controls | 26 |
| Piping | 31 |
| Electrical systems | 10 |
| Buildings (including services) | 29 |
| Yard improvements | 12 |
| Total Installed Cost (TIC) | 247 |

6.2 Total Indirect Cost (TINC)

The indirect costs which are the nonmanufacturing fixed-capital investment costs also need to be calculated. These costs were also determined using cost factors taken from Peters and Timmerhaus, (2003). The factors are shown in Table 6.2 and have been put as percentages in terms of total purchased equipment cost, total installed cost, and total project investment.

Table 6.2: Cost factors for indirect costs.

| Indirect cost | % of TIC |
|------------------------------------|-----------------|
| Engineering | 13 |
| Construction | 14 |
| Legal and contractor fees | 9 |
| Project contingency | 15 |
| Total indirect costs (TINC) | 51 |

6.3 Feed Handling, Drying, Gasification and Gas Clean Up Capital Costs

There are several reports available for the biomass handling and drying costs as well as the gasification and gas clean up costs that documented detailed design and cost

estimates. As it can be seen Table 6.3 shows summarized Feed Handling & Drying and Gasifier & Gas Clean up Costs.

Table 6.3: Feed handling, drying, gasifier and gas clean up costs.

| Reference | Scaled Feed Handling and Drying Cost \$K | BCL - Scaled Gasifier and Gas Clean Up Cost \$K |
|-------------------------------|------------------------------------------|-------------------------------------------------|
| Spath <i>et al.</i> (2005) | \$18,840* | \$16,392* |
| 2009 (3% escalation per year) | \$23,170 | \$20,160 |

*2,000 tonne/day plant.

6.4 Other Capital Costs

The cost of reactors, heat exchangers, compressors, blowers and pumps were determined using the energy and material balance from the Aspen Plus simulation along with the aspen process economic analyser (Icarus). The following were the sizing criteria.

The surface area of each heat exchanger was calculated based on the equation $Q = U \times A \times \ln \Delta T$ (where Q is the heat duty, U is the heat transfer coefficient, A is the exchanger surface area, and $\ln \Delta T$ is the log mean temperature difference). The Icarus enables to calculate surface area.

The design information including flow rate, operating temperature and pressure for the blowers and compressors were all taken from the Aspen Plus simulation. The cost of the syngas compressor (K-301) includes the cost of the interstage coolers and condenser vessels.

For the various pieces of equipment, the design temperature is determined to be the operating temperature plus 30°C (Walas *et al.*, 1988). The design pressure is the higher of the operating pressure plus 2 bar or the operating pressure times 1.1 (Walas *et al.*, 1988).

6.5 Operating Costs

There are two kinds of operating costs: fixed and variable costs. The following sections discuss the operating costs for the biomass gasification to hydrogen production plant including the assumptions and values for these costs.

6.5.1 Fixed Operating Costs

The fixed operating costs given in Spath *et al.* (2005) were used as a starting point to develop fixed costs for the biomass gasification-to-hydrogen production plant. The given salaries from 2002 thus, it is assumed 3% wage increase for every year (see Table 6.4).

Table 6.4: Labor costs.

| | Salary | Number | Total Cost |
|---------------------------------------------------|---------------|---------------|-------------------|
| Plant manager | \$110,000 | 1 | \$110,000 |
| Plant engineer | \$65,000 | 1 | \$65,000 |
| Maintenance supervisor | \$60,000 | 1 | \$60,000 |
| Lab manager | \$50,000 | 1 | \$50,000 |
| Shift supervisor | \$45,000 | 5 | \$225,000 |
| Lab technician | \$35,000 | 2 | \$70,000 |
| Maintenance technician | \$40,000 | 8 | \$320,000 |
| Shift operators | \$40,000 | 20 | \$800,000 |
| Yard employees | \$25,000 | 12 | \$300,000 |
| Clerks & secretaries | \$25,000 | 3 | \$75,000 |
| Total salaries (2002 \$) | | | \$2,080,000 |
| Total salaries (2009 \$) (3% escalation per year) | | | \$2,558,137 |

Also since the salaries listed in Table 6.4 are not fully loaded, a general overhead factor was used. This also covers general plant maintenance, plant security, janitorial services, communications, etc. Factors for maintenance, insurance, and taxes were obtained from Peters and Timmerhaus (2003) and can be seen in Table 6.5.

Table 6.5: Other fixed costs items.

| | Factor | Cost |
|---------------------|--------------------------------|-------------|
| General overhead | 95% of total salaries | \$2,430,000 |
| Maintenance | 2% of total project investment | ----- |
| Insurance and taxes | 2% of total project investment | ----- |

An excel worksheet was set up and some of the base case economic parameters used in the spreadsheet are given in Table 6.6.

Table 6.6: Economic parameters.

| Assumption | Value |
|-------------------------------------|---------------------------------------|
| Internal rate of return (after-tax) | 10% |
| Debt/equity | 0%/100% |
| Plant life | 20 years |
| General plant depreciation | 200% DDB |
| General plant recovery period | 7 years |
| Working capital | 5% of Total Capital Investment |
| Start-up time | 6 months |
| Land | 6% of Total Purchased Equipment Cost. |
| Construction period | 2 years |
| Operating Hours per year | 8000 h/yr |
| Feedstock Cost (Dry basis) | \$40/tonne |

6.5.2 Variable Operating Costs

There are many variables, one could count on when the variable operating costs were calculating, however it was neglected some of this variables. The variables, information about them, and costs associated with each variable are shown in Table 6.7. This table shows in particular the assumed variable operating cost for the simulations. However the real plant might have different variables and costs.

Table 6.7: Variable operating costs.

| Variable | Information and Operating Cost |
|------------------------------------------|--------------------------------------------------------------------------------------------|
| Tar reformer catalyst | Neglected |
| ZnO, steam reforming and shift Catalysis | Neglected |
| Gasifier bed material | Neglected |
| Solids disposal cost | \$700.000/yr for 2,000 tonne/day plant* |
| Electricity | Price: 5.8¢/kWh |
| Natural gas | The pipeline composition consists of 100% vol. CH ₄ Price: \$0.1/m ³ |
| LO-CAT chemicals | Neglected |
| Waste Water | Neglected |

Source: Spath *et al.* (2005)

Chapter 7

SYSTEMS STUDIED

In this chapter there will be some improvements, suggestions and alterations made for the systems which are described in chapter 4, for instance, more heat recovery or electricity production from waste heat to increase the overall system efficiency. A comparison study will also be observed for discussion purposes. The aim of this chapter is to describe the simulated hydrogen plants and their features in detail. The hydrogen plants simulations' will be identified with the new block flow diagrams. The simulations were created to remain true the original systems as described in chapter 4. There are some changes in these simulated systems but the general idea was the stick by their original frame which was described in chapter 4. Detailed explanations of the hydrogen process for the three hydrogen plants are available in the following section.

7.1 Model Validation and Systems Configurations

As mentioned earlier there were three systems simulated in this thesis, and system 1 is much different than systems 2 and 3 which will be explained. The gasifier used for system 2 and system 3 in this analysis is a low-pressure indirectly-heated flow entrained gasifier. The gasifier was modeled using correlations based on run data from the Battelle Columbus Laboratory (BCL). The data and correlations for the gasifier can be found in Bain (1992) and the following correlations for gas components can be summarized as:

For H₂ gas correlation:

$$y = 1.8930E - 05x^2 - 2.6448E - 02x + 1.7996E + 01$$

where y is the mol percentage of hydrogen in the dry gas while x is the temperature, T, in units of F, in the dry gas

The same idea for the CO gas correlation:

$$y = 2.8792E - 05x^2 - 1.0290E - 01x + 1.3346E + 02$$

For CO₂:

$$y = 1.4927E - 05x^2 + 3.7889E - 02x - 9.5251E + 00$$

For CH₄:

$$y = -1.6167E - 05x^2 + 4.4179E - 02x - 1.3820E + 01$$

These correlations at the above were substituted in the Aspen Plus by using fortran subroutine together with the R-GIBBS equilibrium block reactor to control outlet yield. The R-GIBBS reactor defined in the Aspen plus library and it uses single-phase chemical equilibrium, or simultaneous phase and chemical equilibrium, these simplified models are presented here for biomass gasification based on chemical equilibrium considerations, with the Gibbs free energy minimization approach. This block reactor is useful when the temperature and pressure are known, and the reaction stoichiometry is unknown. The latter reactor and the decomposed (RYIELD) reactor combined have been used to model the BCL low-pressure indirectly heated gasifier.

Table 7.1: Proximate and ultimate analyses and other data for oil palm shell.

| <i>Proximate analysis (wt% dry basis)</i> | |
|-------------------------------------------|--------------------------------------|
| Volatile matter | 73.74 |
| Fixed carbon | 18.37 |
| Ash | 2.21 |
| <i>Ultimate analysis (wt% dry basis)</i> | |
| C | 53.78 |
| H | 7.20 |
| O | 36.30 |
| N | 0.00 |
| S | 0.51 |
| Moisture content (wt %) | 5.73 |
| Average particle size (mm) | 0.25-0.75 |
| Molecular formula | CH _{1.61} O _{0.51} |
| Lower heating value (MJ/kg) | 22.14 |

Source: (Yang *et al.*, 2006)

For system 1, due to the lack of information and configuration detail, the gasifier was modeled only as an R-GIBBS equilibrium reactor without using any correlations. The feedstock used for these three systems is oil palm shell, delivered at 50 wt% moisture; the ultimate and the proximate analysis for the feed used in this study is given in Table 7.1. The plant capacity is designed for all three systems which are to be 2000 dry tonne/day (83.3 t/h), and the lower heating value (LHV) of the dry biomass is 22,14 MJ/kg. It is also available an overview of settings and properties used with the Aspen Plus simulation tool in Appendix 2.

7.2 Simulation of Hydrogen Production System 1

As mentioned earlier this system was a part of NASA shuttle program (hydrogen production from biomass) and proposed by Elbaccouch *et al.* (2004) for bagasse gasification. In order to continue further study such as exergy calculations, the new current system was redesigned since there was a lack of and some missing data and information from the original proposed system. When the current system was designed almost the same approach was followed as with the original proposed system. Also, the planned capacity is different than the proposed system bringing more alterations and modifications on the current system. Furthermore, the current design has some improvements and suggestions including an increased heat recovery, and less water consumption.

In the first system, biomass which was chosen as oil palm shell enters the drier section where it comprises of the dry reactor (DRY-REACT), the heat exchanger (HX0) and the condenser (DRY-FLSH) with flow rate 4000 t/day (wet basis). The drier process reduces the amount of water in the biomass from 50% to 5.7%. It should be highlighted that this system's drier section is different than other two system since in this system, biomass and drier gas do not mix in the HE0 thus, this provides us with the means to use evaporated water from the biomass after the condensation process. The flow rate becomes 2000 tonne/day (dry basis) after the drier process then goes into the decomposer (DECOMP). The next step, is implemented using decomposed dry biomass which splits into two parts; one part moves to the combustion (COMB1) where some amount of biomass (47%) and

the left over methane (CH_4) and carbon-monoxide (CO) from the PSA combust; and the second part (53%) moves into the splitter (SP2) where some amount of the biomass was split into two parts; one (25%) to the combustor (COMB2) and the second to the gasifier (28%). In addition in this simulation, the COMB1 and COMB2 provide heat for the gasifier. Also, in this system the gasifier reactor is modelled to mimic the minimization of the Gibbs free energy approach which is identified as the R-Gibbs reactor in Aspen Plus, which is different than in system 2 and system 3 where the indirectly heated BCL gasifier is modelled using the graphical correlations for gas components as previously mentioned.

Produced syngas passes through the cyclone (cyc1) to eliminate ash and other impurities such as carbon (solid), NO_x , etc. These impurities enter the combustion. The ash free produced syngas goes through the HE2 and HE3 to reach the reformer where the steam reforming takes place. After the reformer treatment, the syngas passes through the HE4 to enter the compressor (COMP). This process increases the pressure and temperature. The high pressure and high temperature syngas enters into the HE5 and HE6 to connect with the high temperature shift reactor (HTS) where shift reaction occurs. The outlet of this reactor; the syngas passes the HX7 to reach to the pressure swing absorption system to purge the syngas from other unwanted gases in order to produce 99.9% purity hydrogen. Also this current design includes the water tank mixer (MIXER1) to collect all the water and distribute them to the necessary areas to save energy and exergy, since adding as little water to the system contributes to the systems efficiency positively. The same way this system has the turbine (TURB) to assess the extra steam to produce electricity in the system, it also increase the systems energy and exergy efficiency due to the heat recovery phenomena. The results will be discussed at the end.

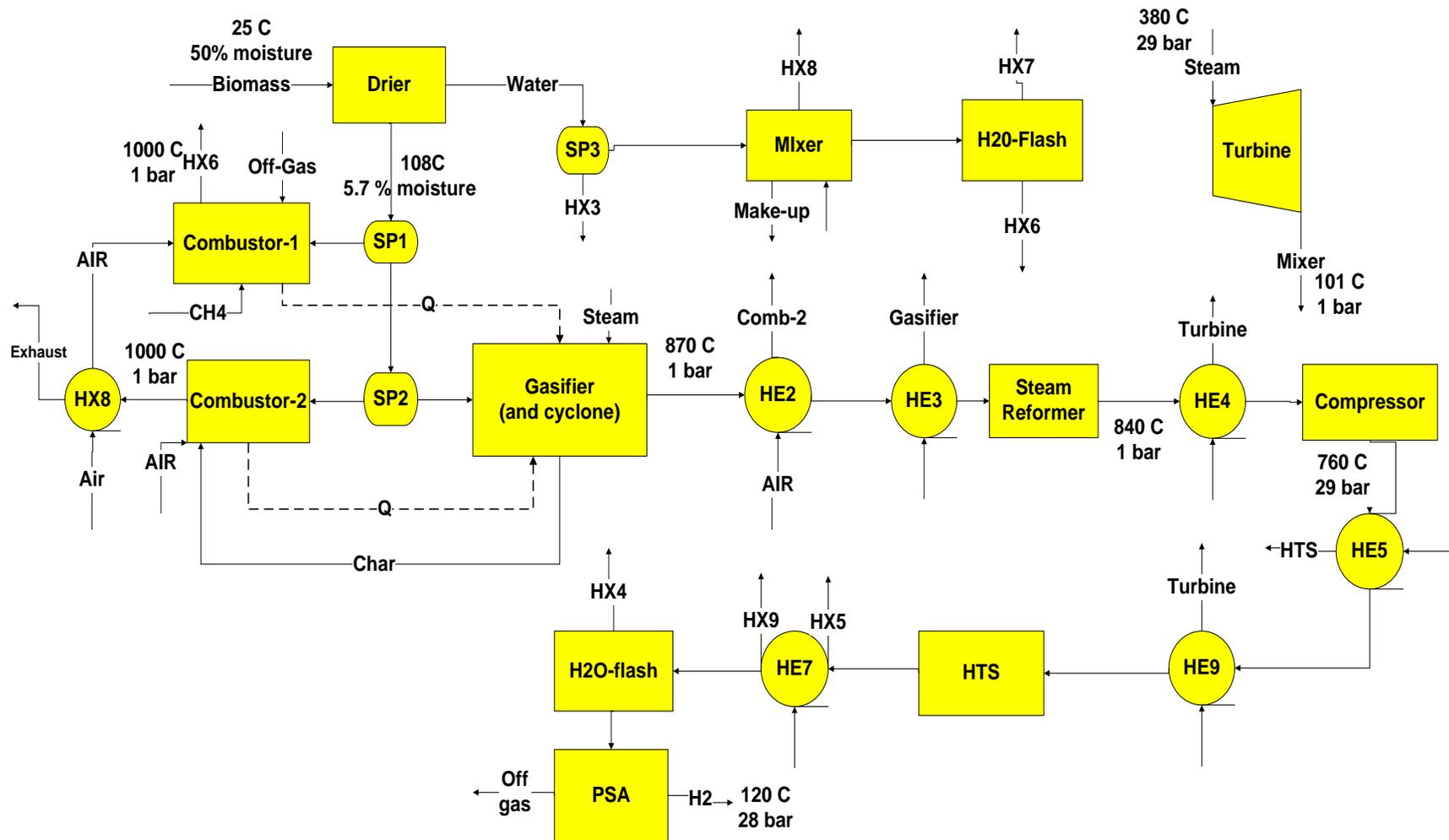


Fig. 7.1: Block flow diagram of simulated system 1.

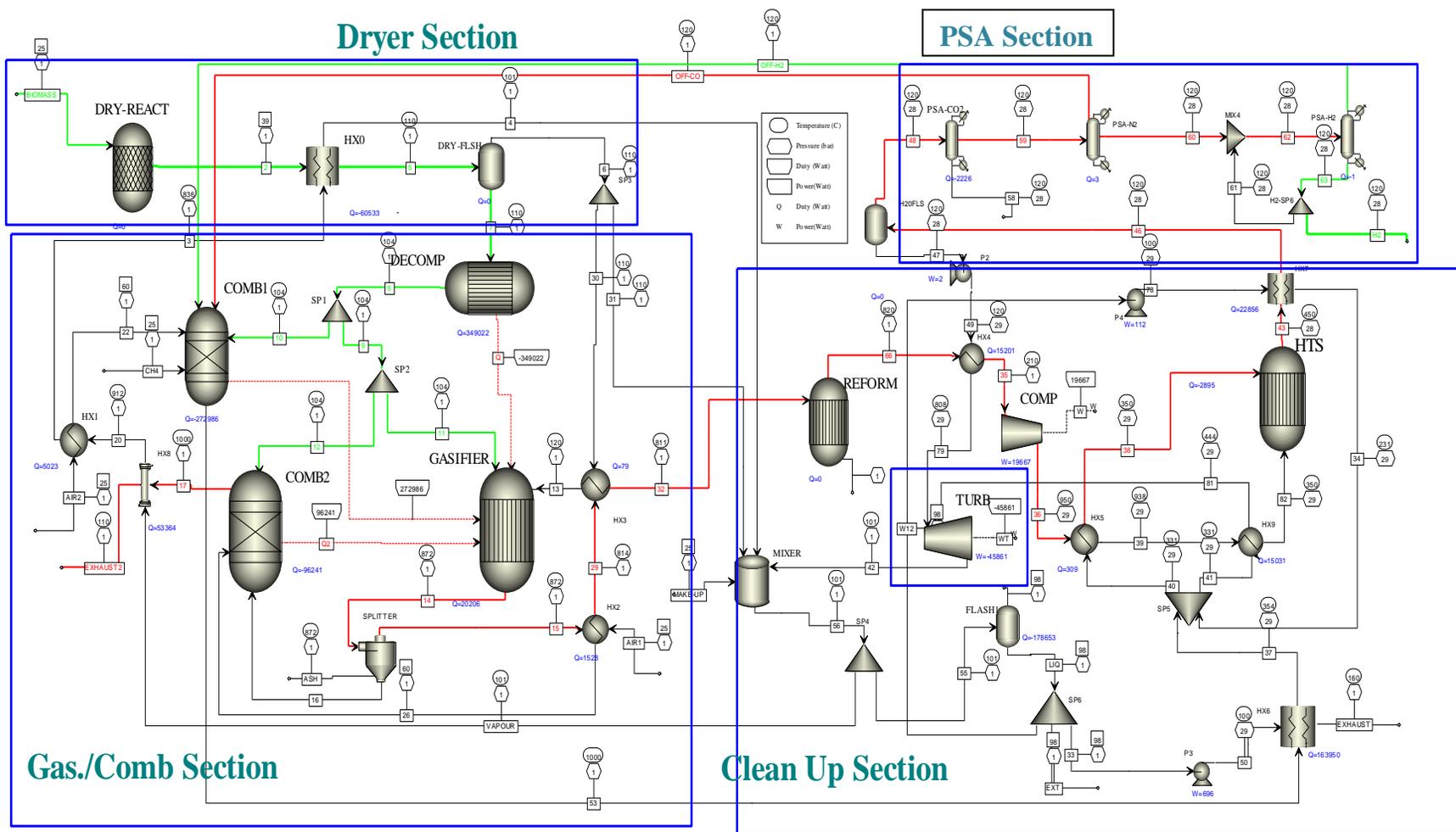


Fig. 7.2: Process flow diagram of simulated system 1.

7.3 Simulation of Hydrogen Production System 2

As can be seen in Fig. 7.3, as a case study, biomass and flue gas are mixed in the dry reactor in order to evaporate the water, and dry the wood from 50% to 5.7% moisture content.

After the drying process is completed in the stoichiometric reactors (RSTOIC) in Fig. 7.4, the gas passes through the decomposition (RYIELD) reactor. Normally the BCL device is an indirectly heated gasifier consisting of two main reactors (Babu, 2002): the gasifier and the combustor. However, in this simulation it contains three main reactors which are yield, Gibbs and the combustor.

First the biomass is decomposed in the RYIELD reactor (this reactor is used in the Aspen plus simulation); this reactor simulates the decomposition of the feed at low temperature (394 K, 1 atm). In this step, biomass is converted into its constituent components including carbon (C), hydrogen (H₂), oxygen (O₂), sulphur (S), nitrogen (N₂) and ash, by specifying the yield distribution according to the biomass ultimate analysis. These components enter the Gasifier reactor (at 1 atm and 1142 K) to produce syngas using steam (at 923 K and 1 atm), as seen in Fig 7.4. The heat of combustion of the actual indirectly heated gasifier system is transferred to the gasifier by recirculating hot inert material, usually sand. In this simulation, however, it is a designed heat stream using just enough heat to supply the gasifier heat demand (see Fig. 7.3). At the same time combustion occurs in a third reactor, which is fed with methane gas (CH₄) from an external supply and char generated by the gasifier. There are two combustors which operate at different temperatures; the first combustor runs at a temperature of 1255 K, while the second runs at 1355 K with 10% excess air.

Figure 7.4 shows that the syngas enters the scrubber which is designed for syngas cleaning. During this process some of the toxic gas is cleaned and water in the syngas is condensed. After entering the scrubber the syngas passes to the separator (SP1), from which part goes to the SMR-COMB. The fraction of the product stream is 0% for this system. After, the syngas passes through the five-stage compressor system, which has

polytropic efficiency of 79% for each compressor stage and a mechanical efficiency of 95%. The syngas is cooled, the preferred method being air cooling as it avoids excess pressure losses. After the compression and cooling processes, the syngas pressure increases from 1 to 31 bars while the temperature increases by 43 K. Before reaching the ZnO-Bed, the syngas is heated to 653 K because the ZnO-Bed cannot function at a lower temperature (Spath *et al.*, 2005). After sulphur cleaning in the ZnO-Bed, the syngas undergoes three main reactions: steam methane reforming (for which the main reaction is $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$), high-temperature shift (for which the main reaction is $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$), and low-temperature shift. It should point out that these reactions are also reversible reactions, and the yield is subject to equilibrium effects which is directly related the temperature and pressure of the system.

The water-gas shift reaction is usually performed in two stages in commercial processes: a high-temperature shift (HTS) in the range of 643–693 K and a low-temperature shift (LTS) in the range of 473–523 K (Spath *et al.*, 2005). It should also point out that there might be some reversible reactions, and the yield is subject to equilibrium effects in this case. The sulphur-free syngas mixes with the steam from the superheater in mixer 1 to drive the SMR. The reforming condition is fixed at 1123 K and 28 bar because methane conversion decreases at high pressure. After the syngas enters the water heat boiler 3 (WHB3), it cools to 677 K before entering the high-temperature shift reactor (HTS). While reducing carbon monoxide in the shift reactor, the hydrogen yield increases by almost 7.5%. As the result can be seen following result section, after the HTS, the syngas passes through a heat exchanger (HE6) and superheater, where its temperature reduces to 473 K. The final treatment for the syngas before pressure swing adsorption (PSA) is the low-temperature shift reactor (LTS), where the carbon monoxide is converted and hydrogen content increased. The outlet of the LTS has the highest hydrogen flow rate (8.98 t/h here).

The PSA unit purifies the syngas by separating the hydrogen from the other components in the shifted gas stream, mainly CO_2 and unreacted CO , CH_4 and other hydrocarbons. Based on studies and data from industrial gas producers, the shifted gas stream must contain at least 70 %mol hydrogen before it can be economically purified in the PSA

unit. For the present analysis, the concentration of hydrogen in the shifted stream prior to the PSA unit is between 60-65% mol. Therefore, part of the PSA unit hydrogen product stream is recycled back into the PSA feed. For a 70 mol% hydrogen PSA feed, a hydrogen recovery rate of 85% is typical with a product purity of 99.9% by volume (Mann, 1995).

For the SMR-COMB unit, air enters at 298 K and 1 atm passes through two heat exchangers (HE2 and HE4). The temperature of the air rises to 1060 K, while concurrently the off-gas from the PSA and the steam methane reformer combustion (SMR-COMB) which is supplied with methane gas at a rate of 0.76 t/h CH_4 passes through the heat exchanger 5 and heat exchanger 3 at 720 K and 1 atm, and enters the SMR-COMB to supply heat for the SMR. In addition the heat exchanger 3 and WHB3 produce the steam for the turbine which produces electricity.

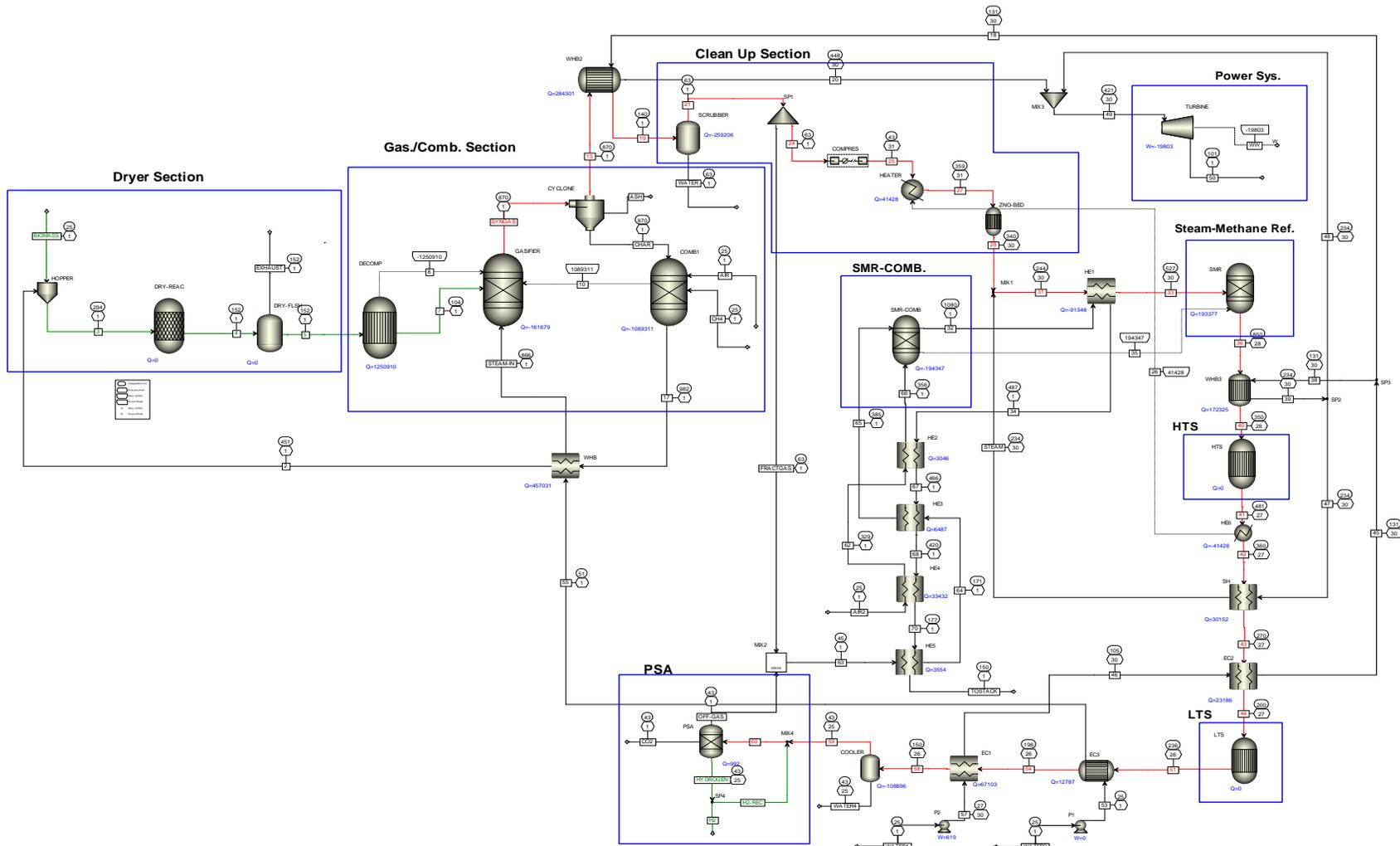


Fig. 7.4: Process flow diagram of simulated system 2.

7.4 Simulation of Hydrogen Production System 3

The process flow diagrams in detail for this process design are included at the end of this thesis in Fig.7.6. In this third system as can be seen in Fig. 7.5 it is divided into ten sub-processes. First, biomass consists of oil palm shell enters subsequently into the drier section where it is comprised of the hopper, the dry-reactor and the dry-flash with flow rate 166,67 t/h wet basis (with 50% moisture) with an outcome of 88,4 t/h dry biomass (with 5.7% moisture).

Note that in Fig. 7.5 as it can be seen dashed lined parts (the feed handling and tar reformer) are not included into system simulation, second note is that gasifier part of this system is also modeled exactly the same with system 2 which is described previous section, the details can be seen in Fig.7.6. This process also starts with the drier. The drier reduces the amount of water in the biomass from 50% to 5.7%. After the drier process the biomass become the desired dried biomass, it goes sequence order into gasification section which consists of the decomposition, the BCL (gasifier used in this analysis is a low-pressure indirectly-heated entrained flow gasifier), the cyc-1 and the comb-1. The gasification medium is steam. Generally, after the gasification process, the syngas goes through the tar reformer and scrubber to remove tar, left over sand from cyc-1 and any impurities. However in this simulation, in order to make the thermodynamic calculation easier it is assumed that at the end of the gasification process there is no tar and there is no circulation medium sand between the comb-1 and the gasifier. The tar is a complex mixture of heavy and aromatic-rich hydrocarbons. Even though there are some assumptions for tar thermodynamic properties in the literature still the thermodynamic information about tar and its content are so complex and complicated. From this reason tar is not considered due to lack of its thermodynamic properties. In addition there is a gasification simulation study by Elbaccouch *et al.* (2004) where tar was not considered as an outlet in the process. Furthermore, other point must be highlighted that in Aspen Plus simulation; since heat transfer between reactors is accomplished by circulating sand between the gasifier and combustor (Spath *et al.*, 2005) heat stream was used instead of circulation medium sand. In other words, circulation sand was represented as a heat stream in Aspen Plus simulation.

As it can be seen in Fig. 7.5 with dashed lined processes which the feed preparation and the tar reformer energy and exergy calculations were not included in the overall system design in this simulation. Also, the scrubber is designed as a condenser since there is no tar in syngas, normally a scrubber is used for the tar cleaning purposes by using water condensation while in this simulation it is assumed there is no tar in the syngas therefore, the scrubber was designed to eliminate the just vapour content in the syngas

Produced gas from the gasification section travels into the compressor section in order to increase the syngas pressure from approximately 1 to 31 bars. Before the steam reformer process, H_2S (hydrogen sulphide) must be removed from the syngas since H_2S makes the steam reformer reactor inactive. For this reason, after leaving the compressor the syngas enters the sulphur cleaning section mainly consisting of the lo-cat oxidizer vessel, the cyc-200 and the ZNO-200 sulphur removal bed. The H_2S -free syngas moves into the steam reformer section where the main reactors which are the reformer (REFOR-300) and the combustor (COMB-300). These reactors conduct reforming processes to increase the hydrogen yield. Please note that detailed explanations for the components are available in the sub-processes sections.

Steam reformed syngas reaches the shift reaction section that consists mainly of the high-temperature shift reactor (HTS-500) and the low-temperature shift reactor (LTS-500), to produce more hydrogen yield. After the syngas passes through the shift section hydrogen reaches the highest point of yield. In other words, after the shift reaction section there is no other process where hydrogen yield will be increased. In addition to that, this system needs more attributes to run this simulation properly, such as the pressure swing adsorption section (600) where syngas is cleaned and separated. The deaerator section (700) is where the water system treatments happen, the power system section (800) where electricity is produced by steam which is extracted in the turbine. In the steam system section (400) where steam is collected and distributed where it needs to go, the hydrogen liquefaction section (900) where 99.9% purified hydrogen is liquefied by using the Linda-Hampson cycle in order to make it easier for transporting. There are nine sub-processes in System 3 to accomplish the production of hydrogen which will be explained in the following sections.

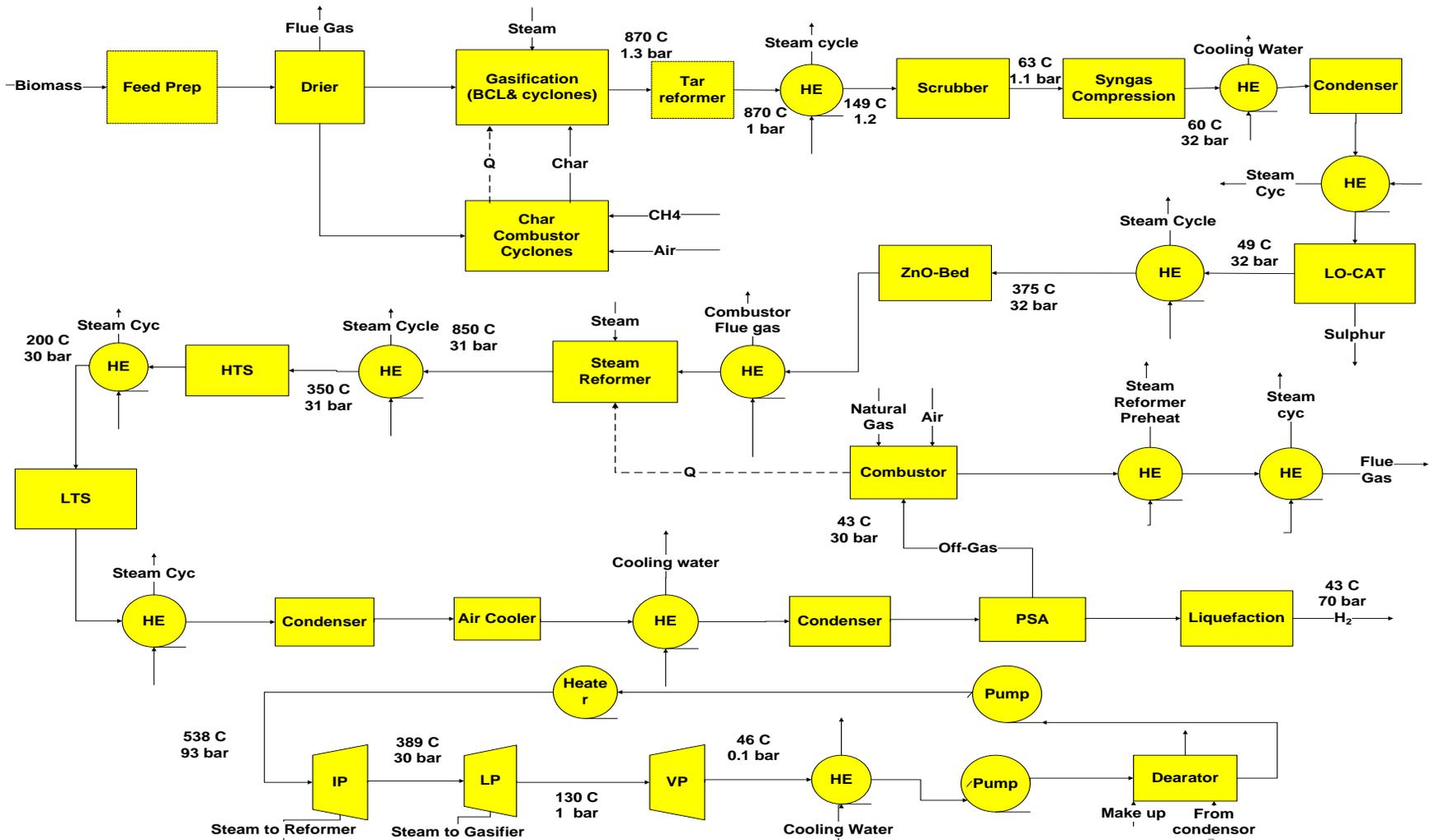


Fig. 7.5: Block flow diagram of simulated system 3.

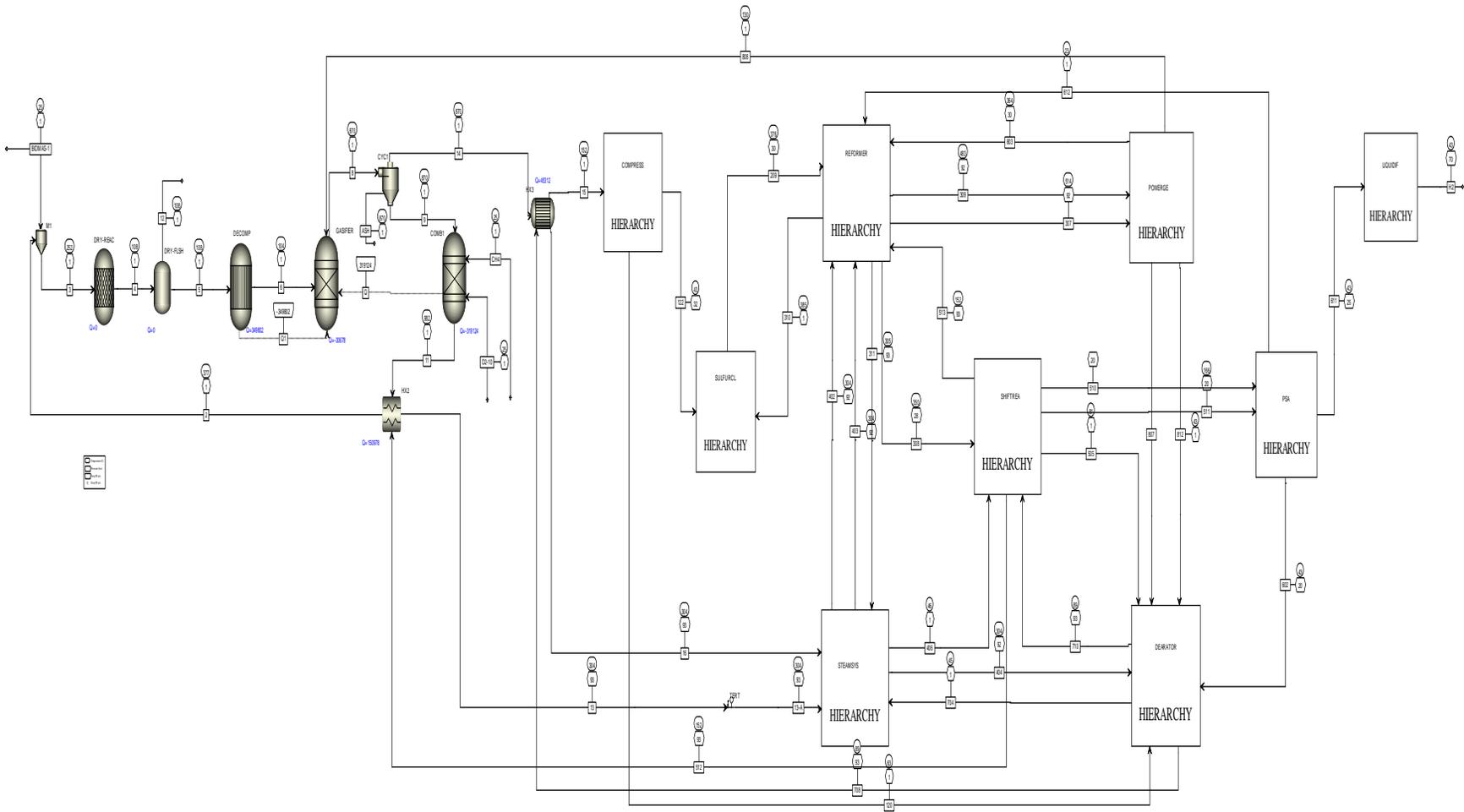


Fig. 7.6: Gasifier section with sub-processes diagram of system 3.

7.4.1 Compressor and Cooling

As can be seen in Figure 7.7, the compressor schematic consists of six condensers, five compressors, five air-coolers and one electric cooler. Gasified syngas enters the five-stage compressor through the first condenser (S-100) where vapour is separated from the syngas, vapour-free syngas goes through the first compressor to increase the syngas pressure (C-100). Simulation temperature and pressure values can be seen in Fig.7.7 for the compressor section, while during the compression not only the pressure increases but also the temperature gradually increases although escalating the temperature is not desired for two reasons: first, after compression, the syngas needs to pass to the sulphur cleaning section where the LO-CAT operates low temperatures, and second when the syngas cooled, the excess water can be extracted easily due to condensation. the syngas cool down where the air-cooler (A-100) is replaced in the compressor section with the aim of cooling which the process basically provides keeping the syngas temperature stable, at the end of the condenser, the compressor and the air-cooler processes; the high pressure syngas with a low temperature will be occurred. As will be mentioned later these three processes repeat five times and finally the syngas pressure becomes 1 bar, 152°C to 32 bars, 43°C.

7.4.2 Sulphur Cleaning

The sulphur cleaning section consists of the lo-cat oxidizer vessel, the ZNO (Zinc-oxide) sulphur removal beds, the cyc-300, the HX4 and HX5 and can be seen in Figure 7.8. Before entering the reformer process the syngas needs to have hydrogen sulphide particles removed from it. Due to presence of hydrogen sulphide in the syngas it can cause inactivation of the steam reformer. The Lo-cat operation includes absorber reactions and oxidizer reactions. At the end of these reactions, the overall reaction can be written as follows: $\text{H}_2\text{S}_{(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{S}_{(s)}$. After the lo-cat operation the syngas goes through to the cyc-300 to separate solid sulphur. The second operation for the sulphur cleaning is the ZNO sulphur cleaning bed, which operates at approximately 650K and 30 bars, to dispose of left over H_2S by purging in the ZNO bed where the following overall reaction takes place: $\text{ZNO} + \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{ZNS}$.

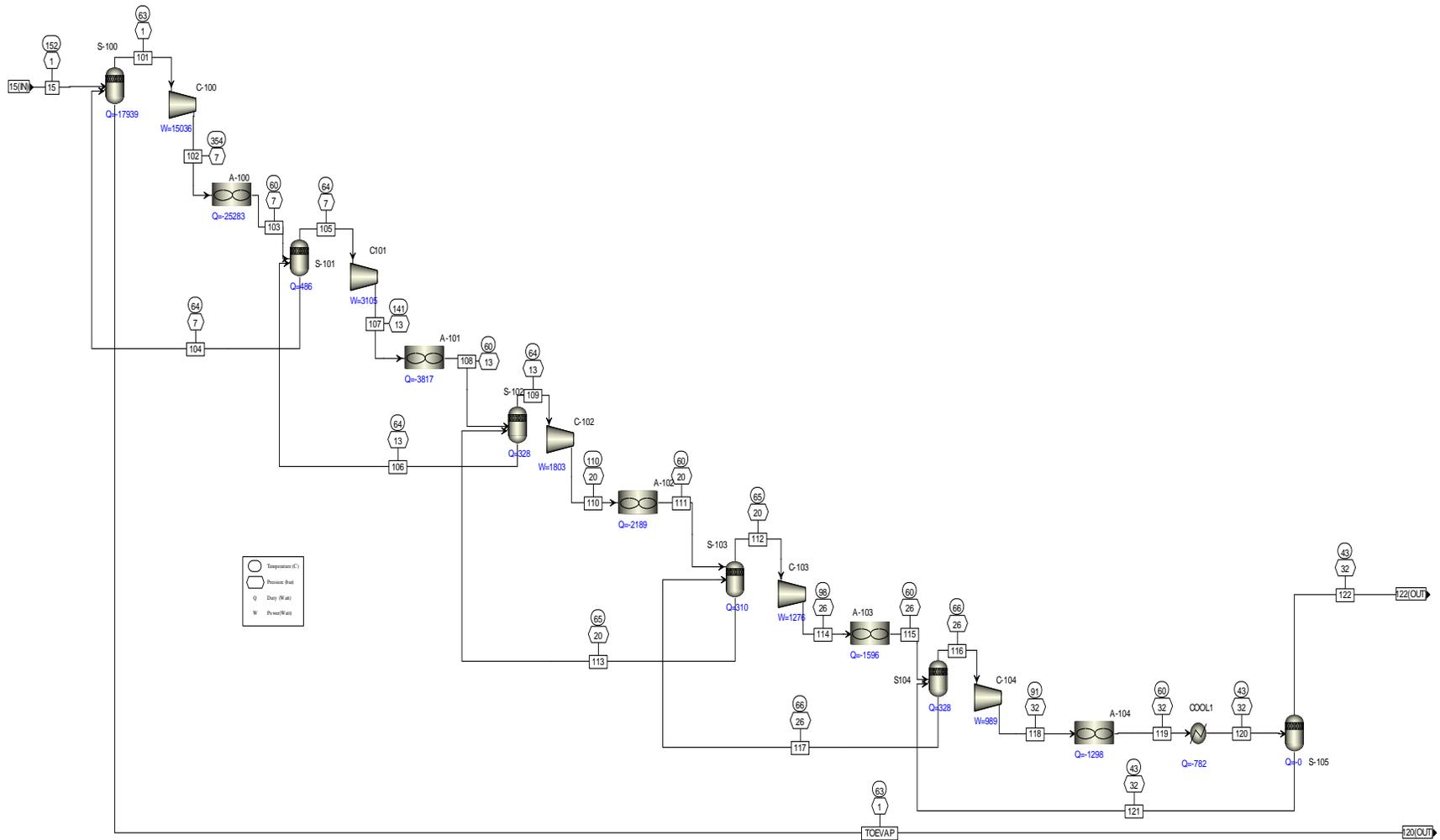


Fig. 7.7: Sub-process compressor and cooling flow diagram of system 3.

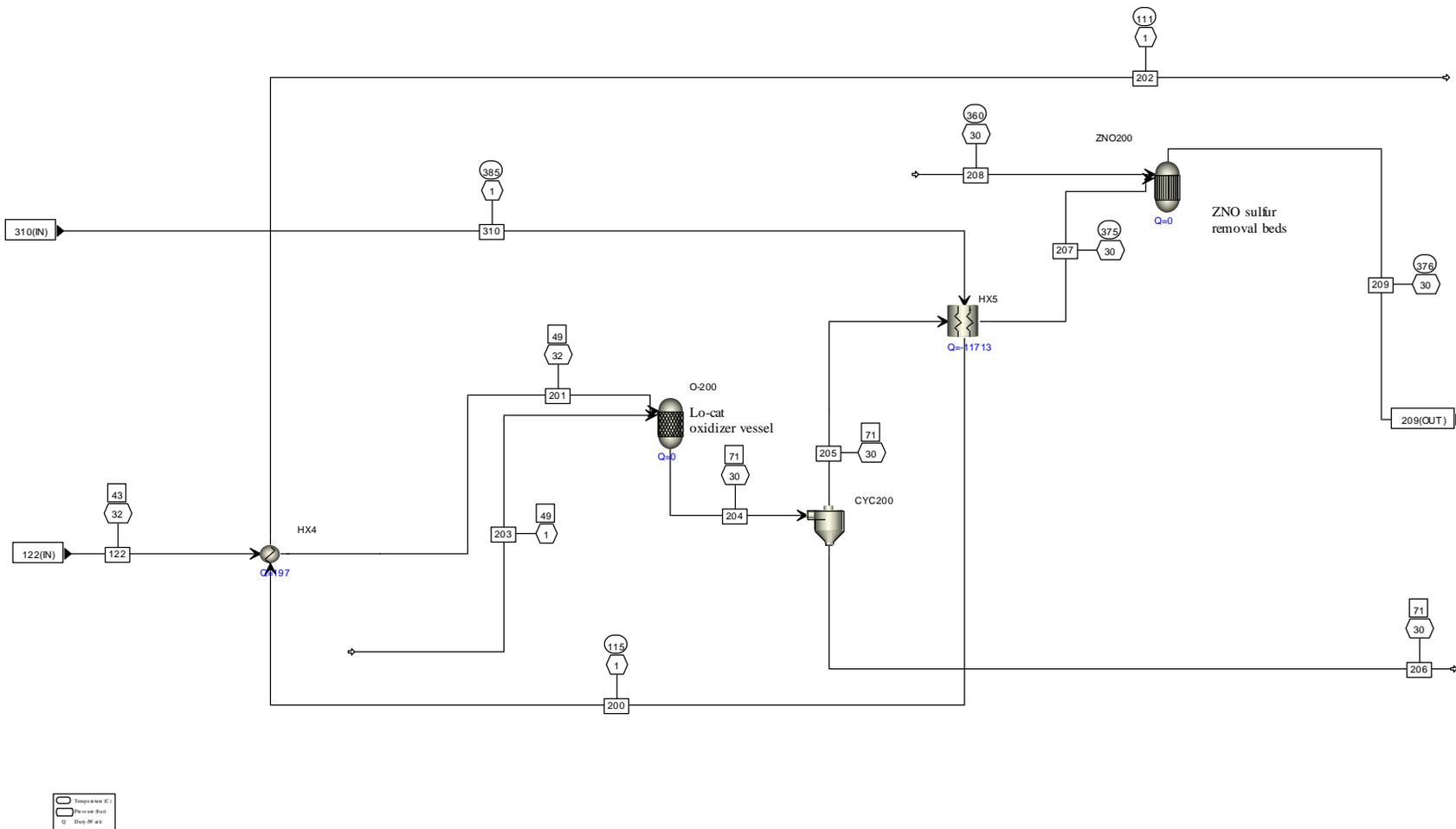


Fig. 7.8: Sub-process sulphur cleaning flow diagram of system 3

7.4.3 Reformer

This reformer section has two main components, the reformer (REFOR-300), and the combustor (COMB-300) in addition to that six contributory components M-301, M-300, PRE1, HX6, SYNCOOL-1, and HX7. The hydrogen sulphide (H_2S) free syngas mixing with the steam (803) in M-301 passes through PRE1 to reach the reformer (it is described earlier which reactions are happening in the reformer). In order to operate the reformer properly; the temperature is at $850^\circ C$ and the pressure is at 28 bars; the energy needs are supplied by the combustion (COMB-300) to meet the reformer's energy requirements. The combustion combusts methane from an outside supply and extra gases which are coming from the gas cleaning section to provide just enough energy for the reformer. As can be seen in Fig. 7.9, the syngas reformer outlet temperature is very high ($850^\circ C$) and it needs to be reduced to approximately $350^\circ C$ by using the SYNCOOL and the HX7 for the shift reactions.

7.4.4 Shift Reactors

This shift reactor section has two shift reactors due to produce more hydrogen, the high temperature shift reactor (HTS500), the low temperature shift reactor (LTS500), three heat exchangers (HX7, HX8, HX9) and one condenser (KNOCK500) in Figure 7.10. The steam-reformed syngas (308) enters to the HTS500 where high temperature shift reaction occurs in the operating temperature at $481^\circ C$ and the pressure at 27 bars, as is mentioned earlier, in the first reactor CO can not fully convert to CO_2 due to the effects of the pressure and the temperature on the equilibrium, for this reason, we need a second shift reactor to produce more hydrogen. Hence, the syngas from the HTS500 goes through HX7 and HX8 to meet the inlet of the LTS500 where the low temperature shift reactor happens at $240^\circ C$ and at 27 bars. The outlet of the LTS500 in which the hydrogen yield in the syngas reaches the maximum level, other words there is no such a process in this simulation where more hydrogen will be produced. The steam-reformed-shifted syngas passes through the HX9 to the KNOCK500 to condense the water in the syngas.

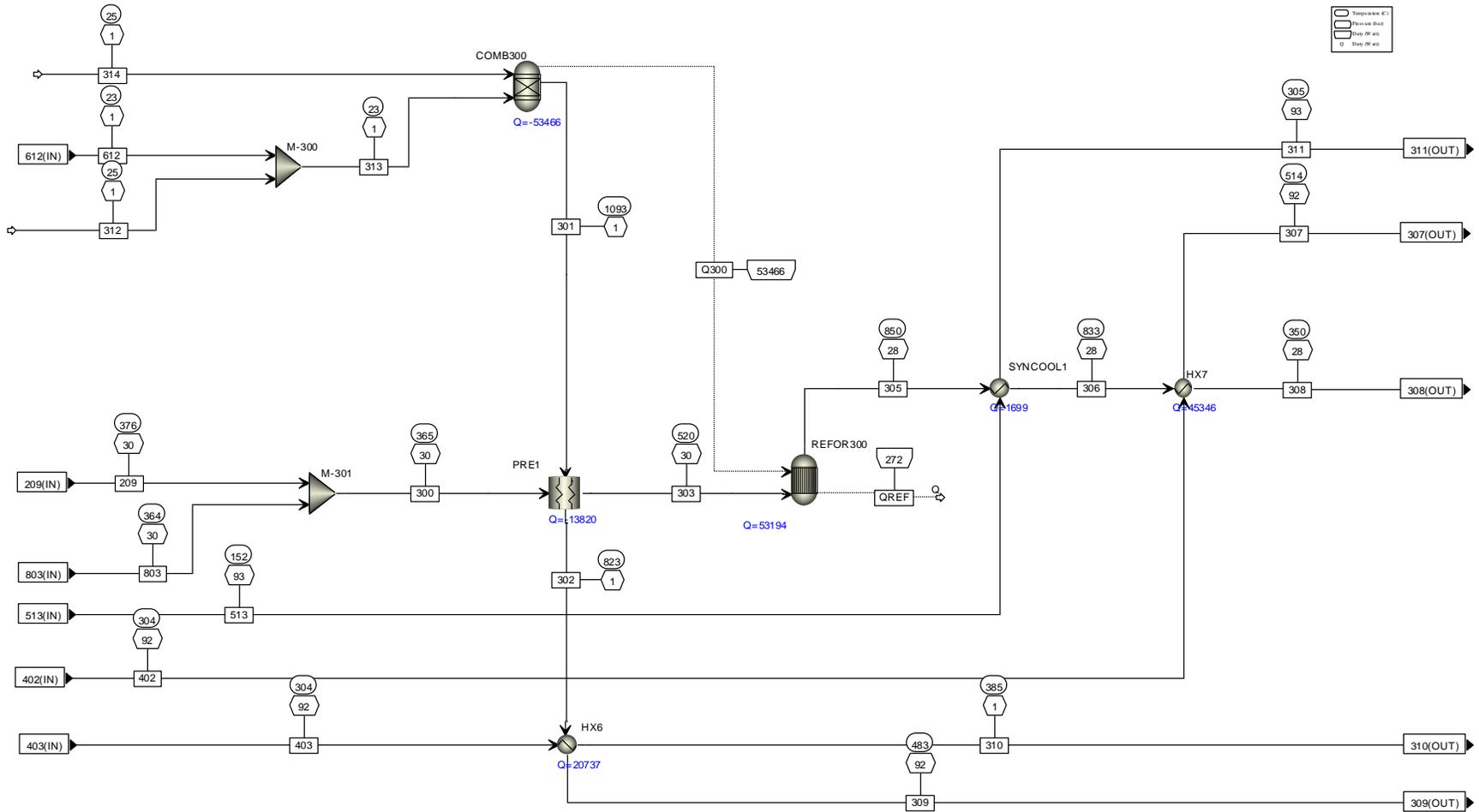


Fig. 7.9: Sub-process reformer flow diagram of system 3.

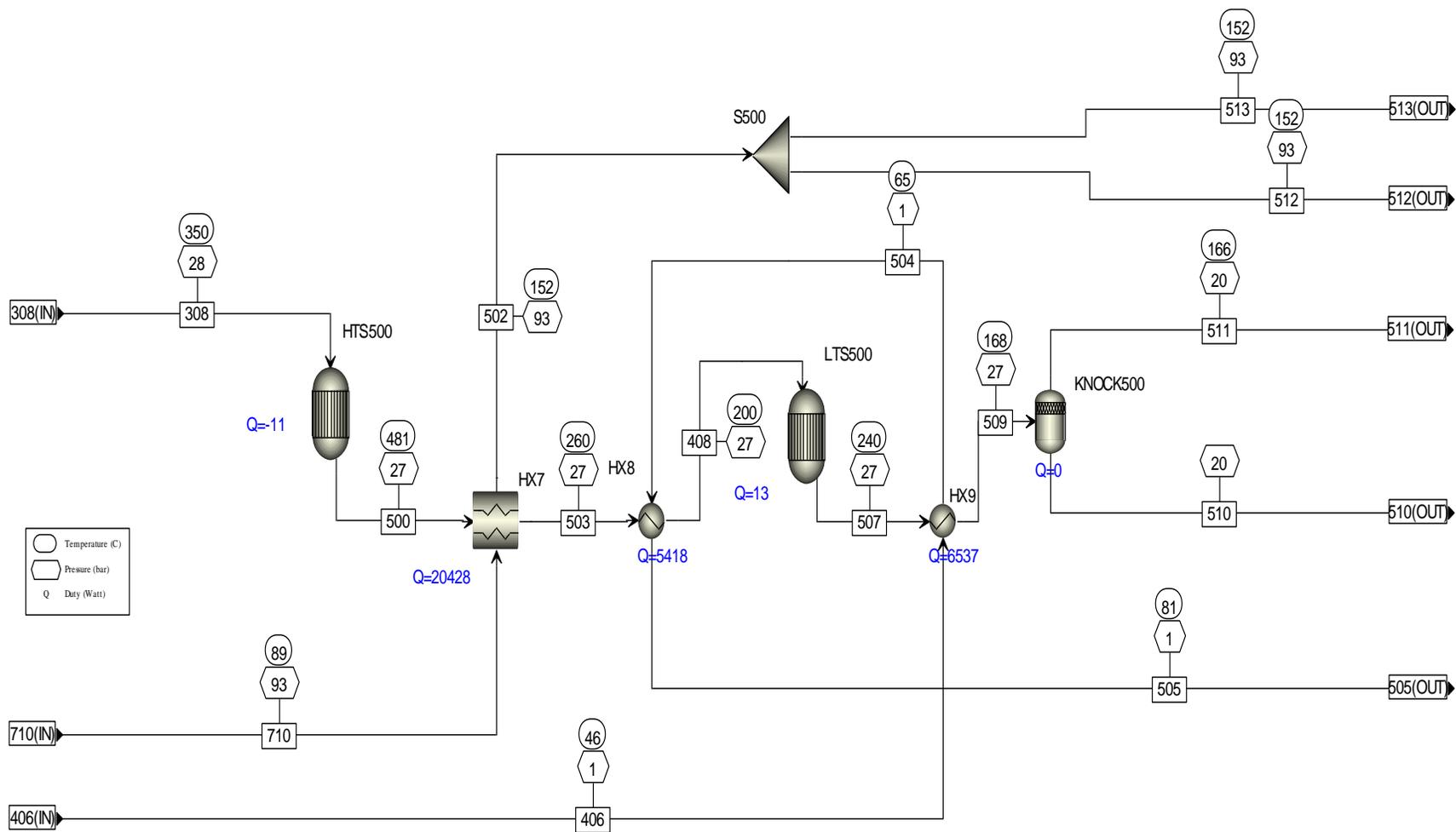


Fig. 7.10: Sub-process shift reactor flow diagram of system 3.

7.4.5 Pressure Swing Adsorption (PSA)

As it can be seen in Figure 7.11, the pressure swing adsorption (PSA) system consists of four main separator reactors (PSA- CO₂, PSA-NH₃, PSA- N₂, PSA-CH₄-CO), one air cooler (A-600), one cooler (COOL600), one condenser (KO-600) and one mixer (MIXER). The steam- reformed and shifted syngas (511) moves through the A-600 and the COOL600 to reduce the temperature of the syngas where it passes through KO-600 to leave the water from the syngas, and enters the PSA- CO₂ where CO₂ is separated, the same way PSA-NH₃ and the PSA-N₂ have occurred in separate reactors. Finally, in the PSA-CH₄-CO reactor where the syngas is purged from CH₄, CO flows into the combustor in the reformer section. At the end of this process, the hydrogen is 99.9% purified, and is produced with the temperature of 43°C with the pressure being 25 bars.

7.4.6 Steam System

This steam system has one steam drum (ST400), one mixer (S400), one condenser (FLSHD400) and one heat exchanger (HX6) and can be seen in Figure 7.12. All the steam which produced several heat exchangers and boilers enter into this section for collection and they have distributed into the areas where steam is necessary, such as the turbine, the reformer and the gasifier. Also extra steam is used for electricity production in the turbines for more heat recovery.

7.4.7 Deaerator

The deaerator section has two storage tanks (T-700, SDRUM700), three pumps (P700, P702, P703), two mixers (M700, S700), and one deaerator (Deara700) and can be seen in Figure 7.13. The aim of this process is to collect the water for treatment and if necessary to add some ammonia and hydrazine or water softener to the deaerator which would be beneficial for the system in order to prevent abrasion in the pipes and other components. Although in this simulation the deaerator is designed as a water tank only, and there are no additions. Another reason for having this system is to control and to collect the water

in the system and to deploy it to the place where water is required, and with the desired pressure.

7.4.8 Power System

As it can be seen in Figure 7.14, the power system has three main sections; high pressure turbine (HPTUR800), low pressure turbine (LPTUR800), vacuum pressure turbine (VPTUR800), two heaters (H800, HEAT800), one cooler (COOL800), five mixers (M800, M801, S800, S801, S802) and one pump (P800). This system produces electricity for a few reasons. First, the plant needs electricity to run. Second, excess electricity could be sold. Furthermore, this system provides steam to the reformer section. In addition, the heat recovery which contains excess heat can transform into electricity.

7.4.9 Liquefaction (Hydrogen compression)

This process has three condensers (KNOCK900, KNOCK901, and KNOCK902), two compressors (C900, C901), two air coolers (A900, A901), and one cooler (COOL900). The hydrogen compression section is the last process in the simulation where hydrogen alters from gas to liquid for easy transportation by using the Linda-Hampson method which can be seen in Fig. 7.15; sequentially this process compresses hydrogen, moves to cooling, on to water condensing and then follows the compressor, etc. Finally, the hydrogen is converted into liquid form at a temperature of 43°C and a pressure of 70 bars.

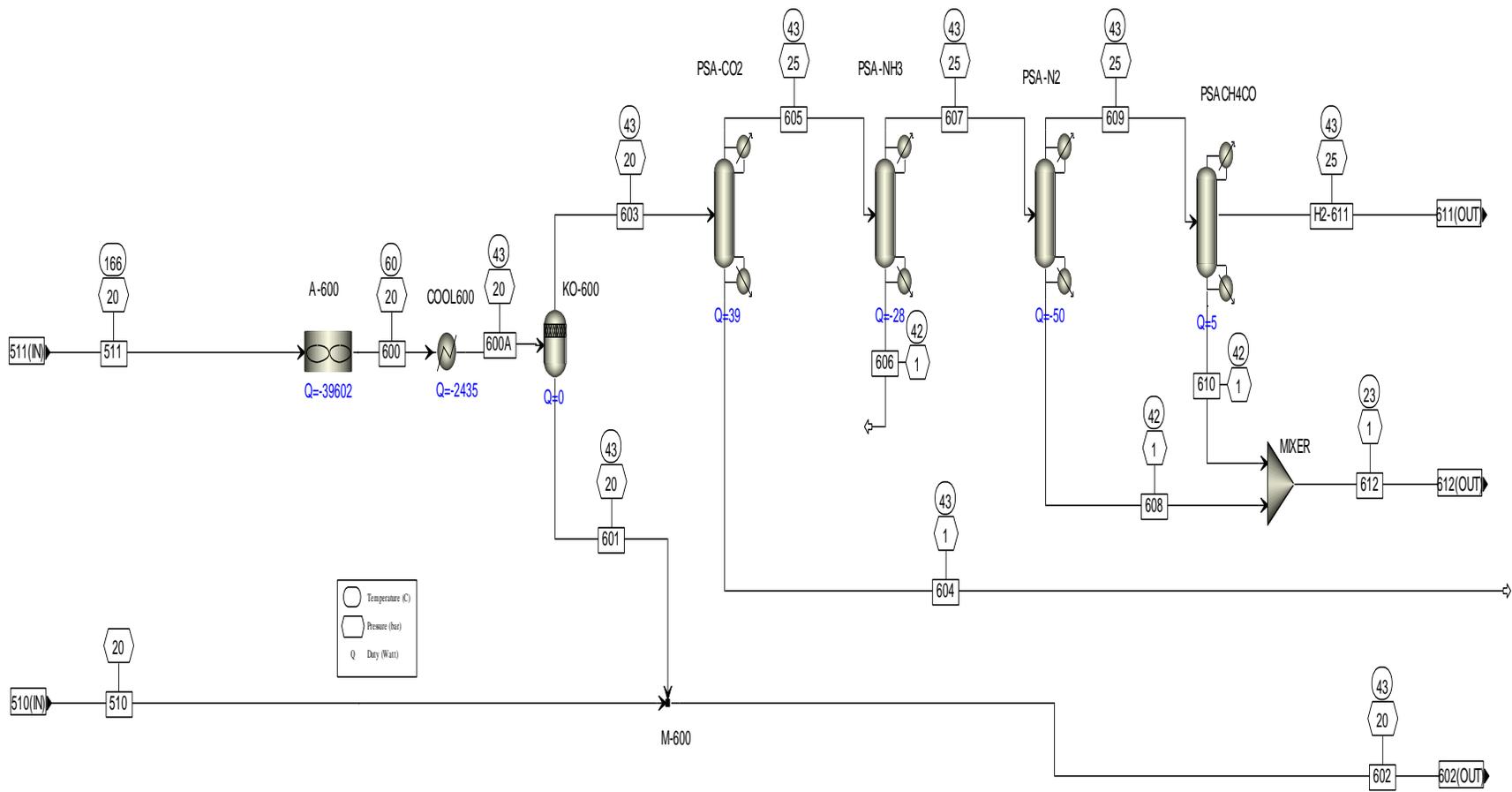


Fig. 7.11: Sub-process PSA flow diagram of system 3.

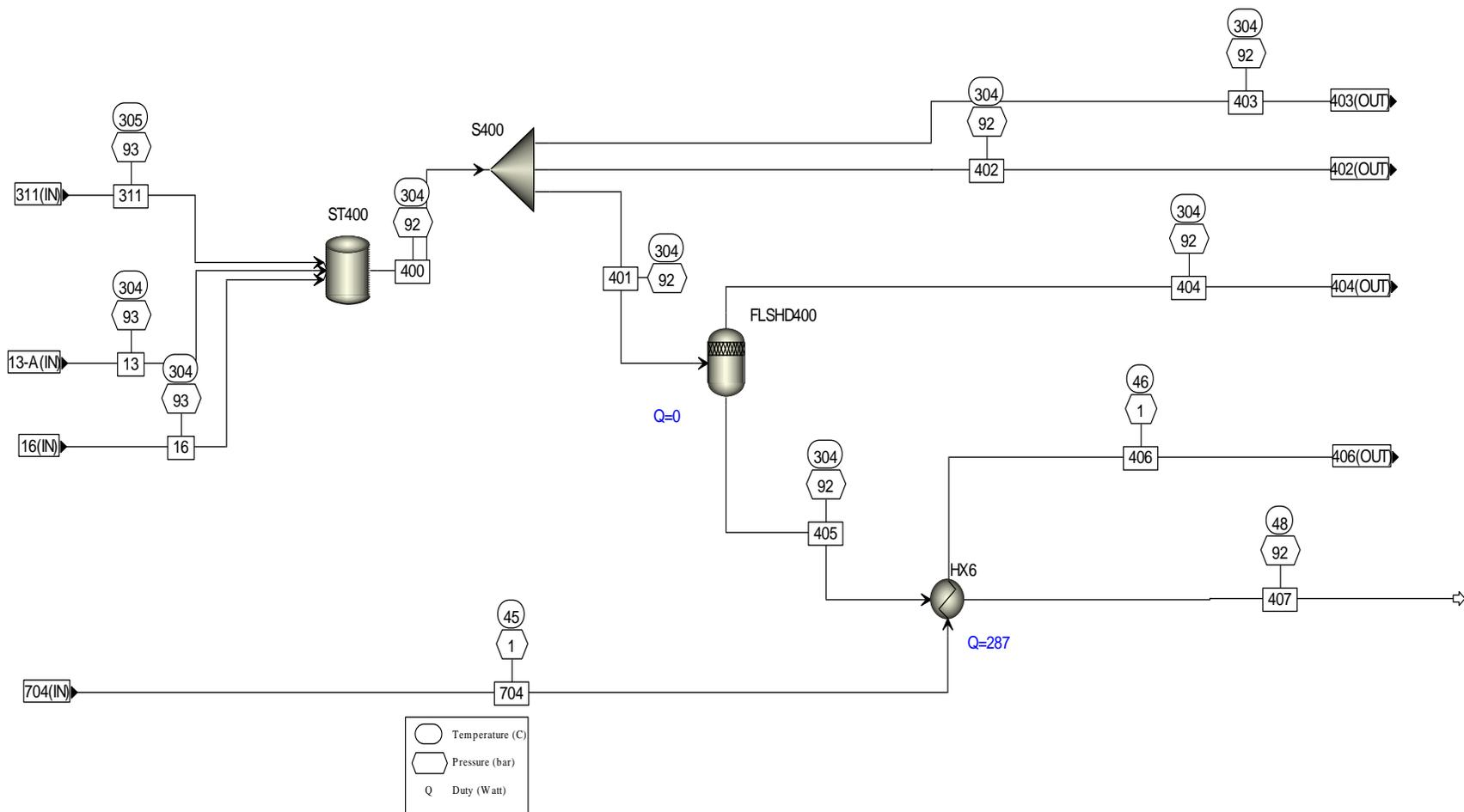


Fig. 7.12: Sub-process steam system flow diagram of system 3.

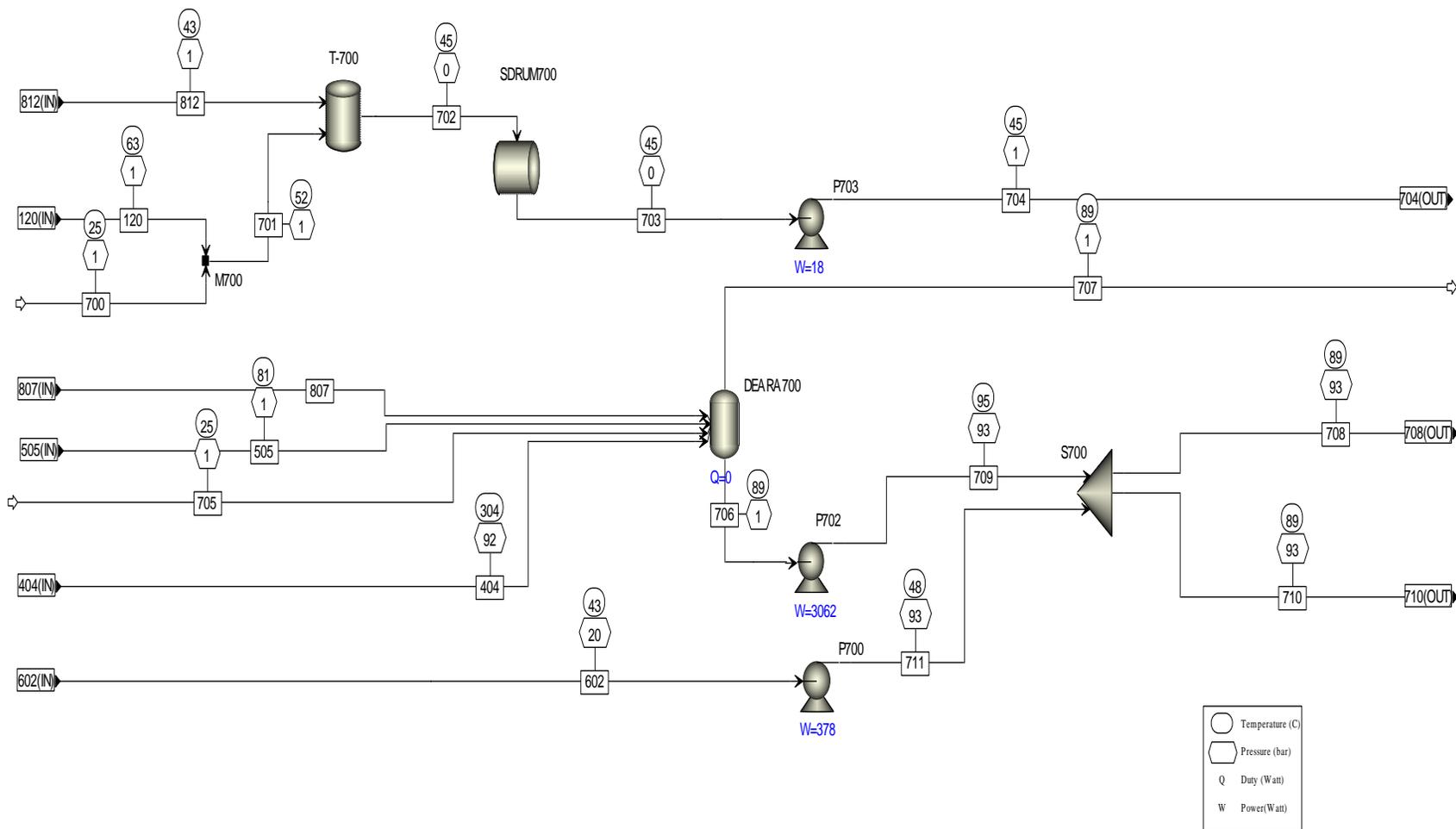


Fig. 7.13: Sub-process deaerator flow diagram of system 3.

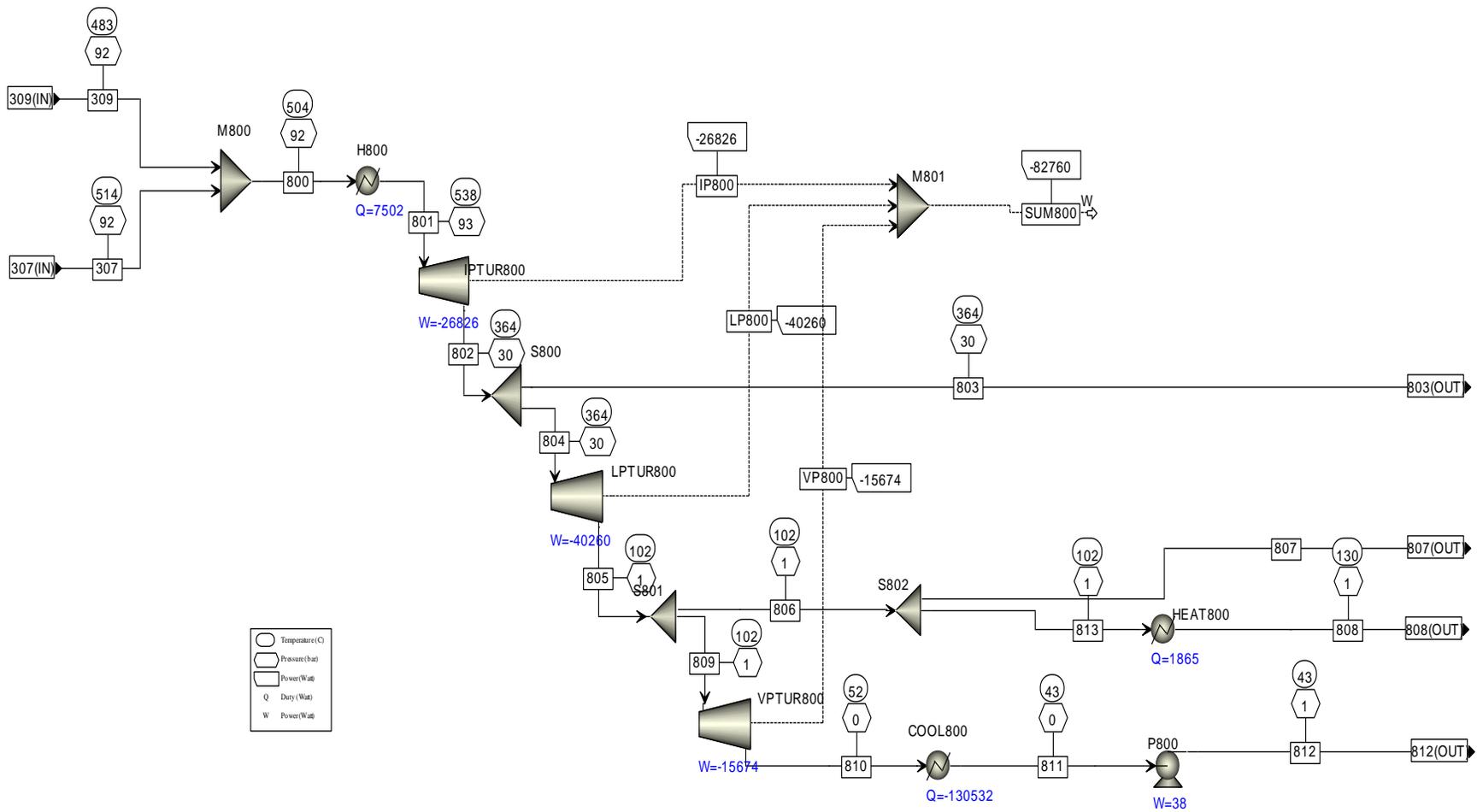


Fig. 7.14: Sub-process power system flow diagram of system 3.

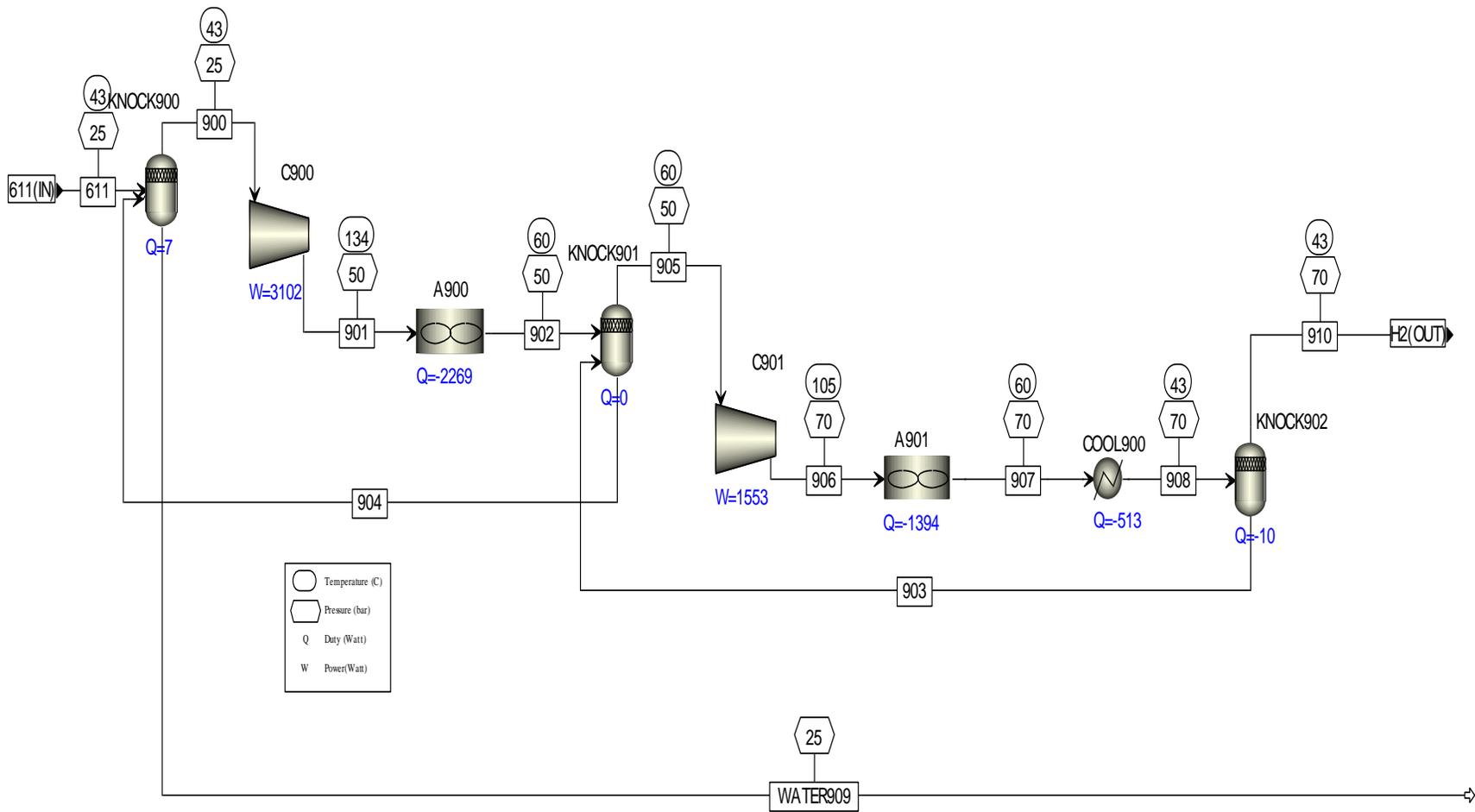


Fig. 7.15: Sub-process liquefaction flow diagram of system 3.

Chapter 8

RESULTS AND DISCUSSION

This chapter deals with the main findings and applications of the simulated results. Three systems were simulated in this study which covers the gasification plant and the hydrogen plant, related energy and exergy efficiency, and an economic analysis.

On a broader scale, the results of this study support the contention by many that biomass may contribute to a future hydrogen economy. Although biomass has the advantage of being renewable if managed properly, challenges exist; large quantities of biomass need to be grown and transported to produce a small amount of hydrogen. Transportation concerns may be alleviated by using pyrolysis of biomass to produce bio-oil, as opposed to direct gasification. The simulated systems results can be seen in the following section.

We now report the results of the energy and exergy analysis, including the energy and exergy efficiencies, and exergy destructions for each component. The results are reported for these three systems in the following sections. It is demonstrated that the inlet and outlet exergy flows for the hydrogen plant are mainly attributed to the energy and exergy inlet with the biomass and the methane gas. The electricity produced also contributes to the system products and efficiency, on an energy and exergy basis. Further, the exergy losses are observed to be due to emissions and internal consumptions associated with chemical reactions, particularly those related to combustion and gasification. Note that inlet exergy values are evaluated for fuel on an LHV basis. Hydrogen production and exergy losses are considered as the main criteria for the system selection in this study.

As mentioned earlier, in this thesis there are three different gasification processes considered for hydrogen generation. The three processes are the basis for a hydrogen production plant that produces 99.99% pure hydrogen.

Based on the costs and availability of hydrogen production processes, it is likely that hydrogen will be produced by steam methane reforming or coal gasification during a

transition to a hydrogen economy. Future advances in water-splitting processes may allow them to replace fossil fuel processes as cleaner, long-term energy solutions. Many predictions of how a hydrogen economy will unfold have been published. For instance, a roadmap is created that provides an overview of a possible evolution of hydrogen production technologies in the future (Miller *et al.*, 2004). The timing of each step in this evolution towards a hydrogen economy depends on how quickly technology advances among other factors.

8.1 Results for System 1

Some key results from the simulations for system 1 are presented and compared in Table 8.1. It can be seen that the major energy and exergy flow supplied to the system is biomass and CH₄. Energy and exergy balances for the overall hydrogen plant for system 1 were calculated and it should be apparent that the overall system energy efficiency is at 22% which is the sum of hydrogen and net electricity outputs, while system exergy efficiency is just 19% respectively. There is a big part of energy losses from the exhaust in system 1 and some other components such as the syngas compressor which constitute 60% of the total energy inlet. It should also be noted that total exergy destruction from each component is 66.4%, while some components destruction cannot be included in the calculation. For instance; splitters, cyclone and pumps exergy losses are ignored and some component's exergy destruction cannot be calculated since enough results are unavailable. These components are to be included in the "others" category in Table 8.1

The main results of this process can be seen in Table 8.2. The starting biomass flow rate is 166.67 t/h (wet basis). The hydrogen production final rate is 2,98 t/h with a purity of 99.9%, as seen in Table 8.4. The most important component in the system in terms of the hydrogen production step is the gasifier. Table 8.3 illustrates the (RGIBBS) gasifier reactor outlet conditions of system 1, where there is a negligible amount of carbon and CH₄ in the outlet of the syngas. In contrast, there is a large amount of CO which will be utilized through the shift reactor to increase the hydrogen yield. Table 8.4 also identifies the outlet conditions of the main streams in the plant.

Table 8.1: Energy and exergy balances for system 1.

| | Energy Flow Rate (MJ/h) | Percentage of Total Energy Inlet Rate (%) | Exergy Flow Rate (MJ/h) | Percentage of Total Exergy Inlet Rate (%) |
|--------------------------------------------------------------|--------------------------------|--------------------------------------------------------------|--------------------------------|--------------------------------------------------|
| Inputs | | | | |
| Dry Biomass | 1,957 | 77 | 2,197 | 79 |
| Water | 3.0 | 0.0 | 0.2 | 0.0 |
| Air | 0.2 | 0.0 | 7.0 | 0.0 |
| Methane (CH ₄) | 453 | 18 | 471 | 17 |
| Electricity | 96 | 4.0 | 96 | 3.0 |
| Total | 2,509 | 100 | 2,771 | 100 |
| Outputs and Destructions | | | | |
| Hydrogen | 450 | 18 | 439 | 16 |
| Electricity | 1,650 | 7.0 | 46 | 6.0 |
| Exhaust | 238 | 1.0 | 123 | 4.0 |
| Wastewater | 0.3 | 0.0 | 2.0 | 0.0 |
| Exergy Output | | | 729 | 26 |
| Exergy Destruction | | | 1,926 | 70 |
| Others | 1,655 | 66 | 117 | 4.0 |
| Total | 2,509 | 100 | 2,771 | 100 |
| System Energy Efficiency, η_{sys} (%) | 22 | System Exergy Efficiency, ψ_{sys} (%) | | 19 |
| Cold Gas Efficiency, η_{cg} (%) | 22 | | | |

The benefit of having this system mainly categorized is for three reasons. First, in order to meet the energy demand of the system, splitting biomass for combustion purposes is a good way to reduce the amount of added-CH₄ to the system. When in this simulation biomass source is lacking enough energy to provide to the gasifier; therefore CH₄ was added to the system. Reducing added-CH₄ will decrease the outlet of the green gas

emission while increasing sustainability in the system. Second, as can be noticed in Table 8.4 the amount of outlet CH₄ is very low, so even though syngas passes through the reformer the hydrogen yield is staying almost stable until the HTS process occurs where the hydrogen yield is drastically increased by the high temperature shift reaction in Fig.8.1. In this system there is no low temperature shift reactor, which means there is no more hydrogen production after the HTS, even though there is still some CO in the produced gas outlet of the HTS.

Table 8.2: Assumptions for system 1.

| Quantity | Value |
|-------------------------------------------|--------|
| Biomass flow rate (wet) (t/h) | 166.67 |
| Biomass flow rate (dry) (t/h) | 88.40 |
| Split Ratio: Biomass to combustors | 0.47 |
| Biomass to COMB1 flow rate (dry) (t/h) | 41.5 |
| Biomass to COMB2 flow rate(dry) (t/h) | 19.5 |
| Biomass to Gasifier flow rate (dry) (t/h) | 24.8 |
| Steam input to Gasifier (t/h) | 14.9 |
| CH ₄ input to COMB1 (t/h) | 8.96 |
| Steam-biomass ratio (STBR) | 0.60 |

Table 8.3: Conditions at the gasifier outlet for system 1.

| Quantity | | | Value |
|-------------------------------------|------|------------------|-------|
| Gasifier outlet temperature (°C) | | | 870 |
| Combustor 1 outlet temperature (°C) | | | 1000 |
| Combustor 2 outlet temperature (°C) | | | 1000 |
| Gasifier outlet composition(t/h) | | | |
| H ₂ O | 4.6 | NH ₃ | 0.08 |
| H ₂ | 2.98 | H ₂ S | 0.13 |
| CO | 25.5 | C (solid) | 0.001 |
| CH ₄ | 0.03 | Ash | 1.14 |
| CO ₂ | 5.97 | | |

Table 8.4: Properties and composition of the main streams for system 1.

| Streams | | | | | | |
|--------------------------------|---------------|----------------|---------------|--------------|--------------------------|------------|
| Quantity | SMR Outlet | COMP Outlet | HTS Outlet | PSA Inlet | H ₂ Outlet | Off Gas |
| <i>T</i> (°C) | 820 | 950 | 450 | 120 | 120 | 40 |
| <i>P</i> (bar) | 1 | 29 | 28 | 28 | 25 | 1 |
| Flow rate (t/h) | 39.21 | 39.21 | 66.43 | 51.7 | 3.7 | 48 |
| Dry gas composition (% vol) | | | | | | |
| H ₂ O | 3.0 | 3.0 | 10 | 3 | 0 | 9.9 |
| H ₂ | 56 | 56 | 60 | 65 | 99.9 | 1.5 |
| CO | 35 | 35 | 6 | 7 | 0 | 12.7 |
| CO ₂ | 5 | 5 | 23 | 25 | 0 | 75.6 |
| CH ₄ | 0.0 | 0.0 | 0.0 | 0.0 | 0 | 0.0 |

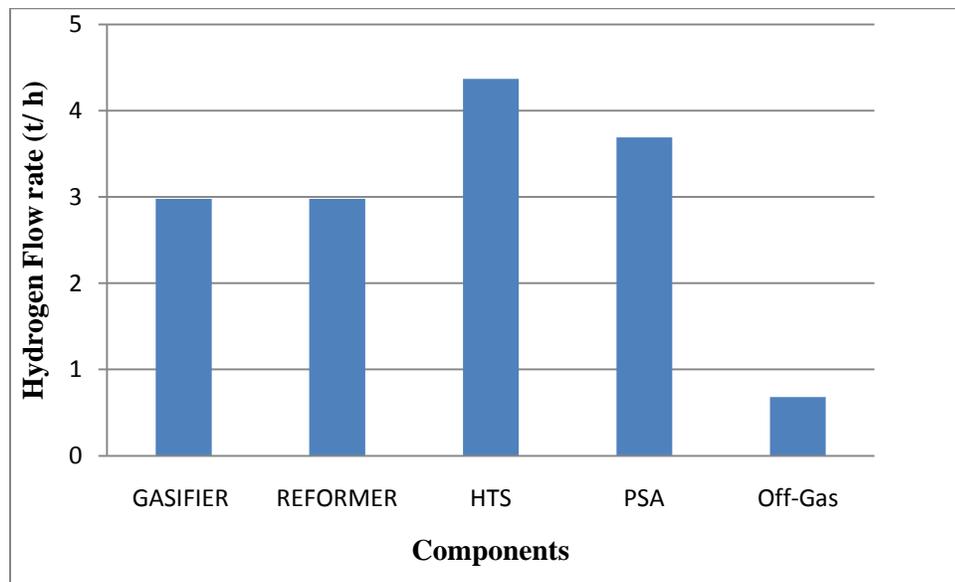


Fig. 8.1: Hydrogen flow rates for system 1.

In Fig. 8.1, the hydrogen production route identifies a better understanding of the main components' outlet. The outlet of the HTS where the hydrogen level is at the maximum level slightly reducing outlet of the PSA since is not available to purify the hydrogen with 100% quality which means some of the hydrogen escapes in the off-gas during the PSA process.

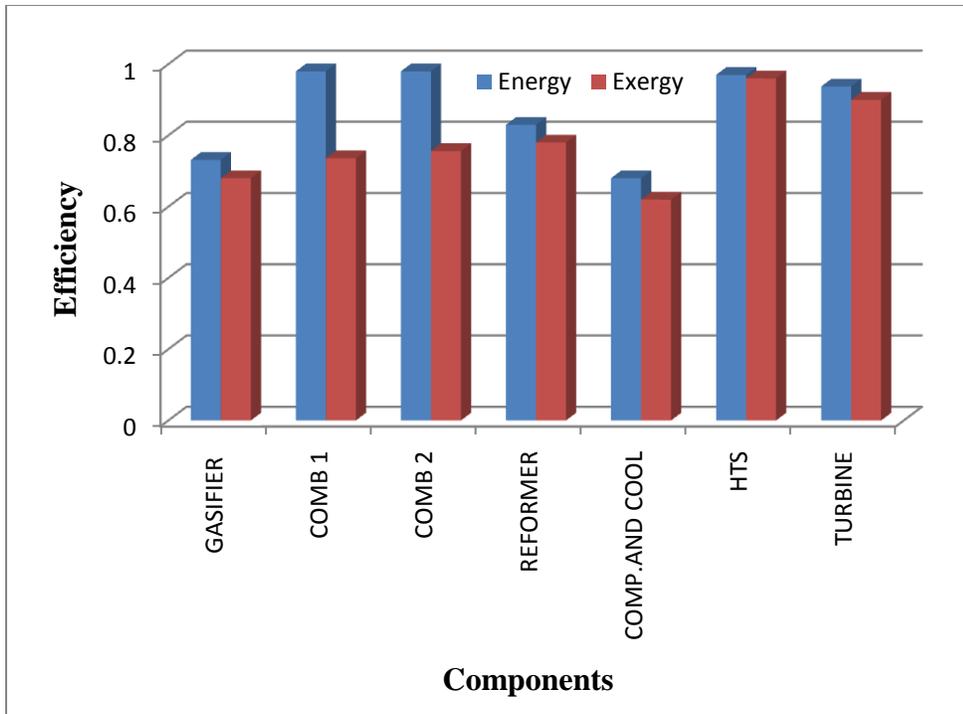


Fig. 8.2: Energy and exergy efficiencies for main components of system 1.

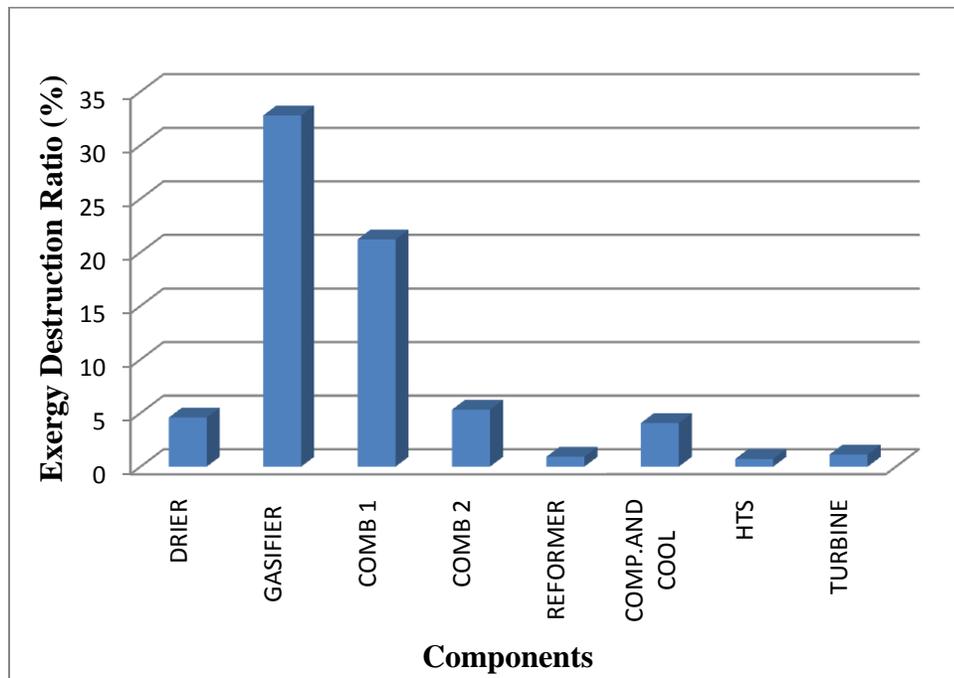


Fig. 8.3: Exergy destruction ratios for main components of system 1.

Exergy destruction ratios help understand the exergy destructions in any system as it identifies where the greatest part of the total inlet exergy is destroyed. When analysing the above Figure 8.3, the drier section which consists of the Dry-React, the HX0, and the flash reactor in the simulation, it is considered that these three components' exergy destruction ratios combined as the drier. As a result, the dry-react, the HX0 and the flash vessel exergy destruction ratios accumulated, reflect the drier exergy destruction ratio which is 4.7%. As it is easy to see that the major exergy destruction ratio which is described in Eq. (5.17) in the thermodynamic analysis section, was found to be 37% which means that the total exergy inlet of the system's 37% is disappearing after the gasifier process. The gasifier system has a large amount of exergy destruction, because in the gasifier, biomass is decomposed and partially oxidized through several reaction chambers. If we include the COMB 1 as a part of gasification system, the exergy destruction ratio will be increasing to 41%. These results correspond with the literature results, in addition the COMB2 and COMP exergy destruction ratios are 3.6% and 4.2% respectively, while the REFORMER, the HTS and the TURBINE have a small amount of exergy destruction ratios.

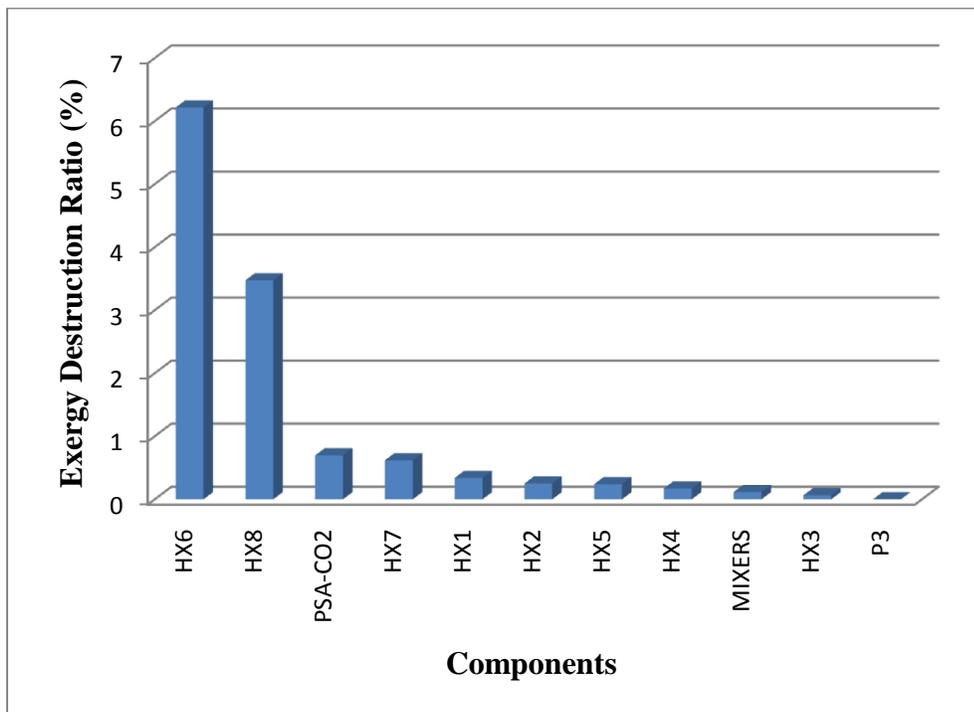


Fig. 8.4: Exergy destruction ratio for auxiliary components of system 1.

Although the main purpose and main goal of using a heat exchanger in system 1 are to obtain an increased heat recovery, some heat exchangers such as the HX6 (6%) and the HX8 (3.2%) in Fig. 8. 4 have a considerable amount of exergy destruction rates. Since both heat exchangers are simulated as waste heat boilers where phase change occurs during this boiler process is increasing the exergy destruction more. Another point is the hot inlet stream temperatures of approximately 1000°C which is much higher than the cold inlet temperatures of approximately 100°C. These huge temperature differences are one of the sources of the high exergy destruction rates. If the hot inlet temperature stream passed through two or three more heat exchangers instead of one boiler process, the exergy destruction rate could be reduced. While this process would increase the equipment cost, it would allow the system to gradually reduce the hot inlet stream's temperature, producing less exergy destruction results and a drastically decreased hot inlet temperature.

In this simulation the results show that the PSA system exergy calculation considers the physical exergy losses from the temperature and pressure differences inlet and outlet gases. The syngas inlet condition is 120°C with 25 bars while the exit conditions are 40°C with 1 bar, identifying that there are physical exergy losses taking place in the PSA where the exergy destruction ratio is approximately 1.8%. During the hydrogen production process other components also produce entropy such as the HX7, HX2, HX5, HX 4 and "MIXERS". The sum of all the mixers in the system of exergy destruction ratios is available in Fig.8.4. This analysis gives a good picture of where the inefficiencies exist, as can be seen in Fig 8.3 and 8.4.

8.2 Results for System 2

For this system, with its feed rate of 4000 tonne per day of wet biomass to the gasification process, the hydrogen production energy efficiency is 31% (see Table 8.5). It is determined with the simulation that 185.3 tonne hydrogen can be produced from 4000 tonne biomass with an energy rate of 6.2 MW.

Table 8.5: Energy and exergy balances for system 2.

| | Energy Flow Rate MJ/h) | Percentage of Total Energy Inlet (%) | Exergy Flow Rate (MJ/h) | Percentage of Total Exergy Inlet (%) |
|------------------------------------------------------------|-------------------------------|-----------------------------------------------------------|--------------------------------|---------------------------------------------|
| Inputs | | | | |
| Dry Biomass | 1,957 | 61 | 2,197 | 62 |
| Water | 1.7 | 0.0 | 15 | 0.4 |
| Air | 0.4 | 0.0 | 3 | 0.0 |
| Methane (CH ₄) | 1,190 | 37 | 1,237 | 35 |
| Electricity | 73 | 2.0 | 73 | 2.0 |
| Total | 3,222 | 100 | 3,526 | 100 |
| Outputs and Destructions | | | | |
| Hydrogen | 937 | 29 | 922 | 26 |
| Electricity | 115 | 4.0 | 115 | 3.0 |
| Exhaust | 171 | 5.0 | 132 | 4.0 |
| Wastewater | 51 | 2.0 | 69 | 2.0 |
| Exergy Output | | | 1,239 | 35.0 |
| Exergy Destruction | | | 2,170 | 61.0 |
| Others | 1,978 | 60 | 117 | 3.0 |
| Total | 3,222 | 100 | 3,526 | 100 |
| Energy Efficiency η_{sys} (%) | 31 | Exergy Efficiency, ψ_{sys} (%) | | 28 |
| Cold Gas Efficiency, η_{cg} (%) | 30 | | | |

As it can be observed in Table 8.5, products from this process are hydrogen and electricity, but other energy streams also exit. There are two sources of flue gas: the char combustor and the second combustor (SMR-COMB). Together, their energy contents account for about 5% of the total energy inlet.

Table 8.6: Properties and composition of the main streams in system 2.

| Streams | | | | | | | |
|-----------------------------|-------------|------------|------------|------------|-----------|---------|-----------------------|
| Quantity | COMP Outlet | SMR Outlet | HTS Outlet | LTS Outlet | PSA Inlet | Off Gas | H ₂ Outlet |
| <i>T</i> (°C) | 43 | 850 | 483 | 241 | 43 | 40 | 43 |
| <i>P</i> (bar) | 30 | 28 | 27 | 26.5 | 25.2 | 1 | 25 |
| Flow rate (t/h) | 61.55 | 146.53 | 146.53 | 146.53 | 94.86 | 87.14 | 7.72 |
| Dry gas composition (% vol) | | | | | | | |
| H ₂ O | 0.0 | 23.0 | 15.0 | 13.0 | 0.0 | 0.0 | 0 |
| H ₂ | 48.0 | 46.0 | 57.0 | 60.0 | 69.0 | 25.65 | 99.9 |
| CO | 29.0 | 23.0 | 5.00 | 0.0 | 0.0 | 0.0 | 0 |
| CO ₂ | 9.0 | 5.0 | 21.0 | 25.0 | 28.0 | 69.4 | 0 |
| CH ₄ | 13.0 | 2 | 2.00 | 2.0 | 2.0 | 5 | 0 |

Properties and composition of the main streams in system 2 can be seen in Table 3. This table shows the maximum produced hydrogen to be 7.72 t/h. It also demonstrates the dry gas composition outlet for the main components. Notice that the off gas has some CH₄

Table 8.7 Assumptions for system 2.

| Quantity | Value |
|-----------------------------------------|--------|
| Biomass flow rate (wet) (t/h) | 166.67 |
| Biomass flow rate (dry) (t/h) | 88.40 |
| Steam input to gasifier (t/h) | 33.17 |
| Syngas fraction to SMR-COMB | 0.0 |
| CH ₄ input to COMB1 (t/h) | 23.5 |
| CH ₄ input to SMR-COMB (t/h) | 7.6 |
| Steam-biomass ratio (STBR) | 0.38 |

Table 8.7 gives the some assumptions for the system 2 such as biomass flow rate or steam input to the gasifier.

Table 8.8: Conditions at the gasifier outlet for system 2.

| Quantity | | Value | |
|-------------------------------------|-------|------------------|-------|
| Gasifier outlet temperature (°C) | | 890 | |
| Combustor 1 outlet temperature (°C) | | 982 | |
| Gasifier outlet composition (t/h) | | | |
| H ₂ O | 38.23 | NH ₃ | 0.08 |
| H ₂ | 3.52 | H ₂ S | 0.08 |
| CO | 31.87 | N ₂ | 0.70 |
| CH ₄ | 5.93 | C (solid) | 18.02 |
| CO ₂ | 22.98 | Ash | 0.77 |

The simulated hydrogen production flow rates for system 2 are shown in Fig. 8.5. It is seen there that hydrogen flow rate maximized the LTS outlet which is around 9.1 t/h. It is also observed that some of the hydrogen will be lost during the PSA process for which as previously mentioned a hydrogen recovery rate of 85% is typical with a product purity of 99.9% by volume (Mann, 1995).

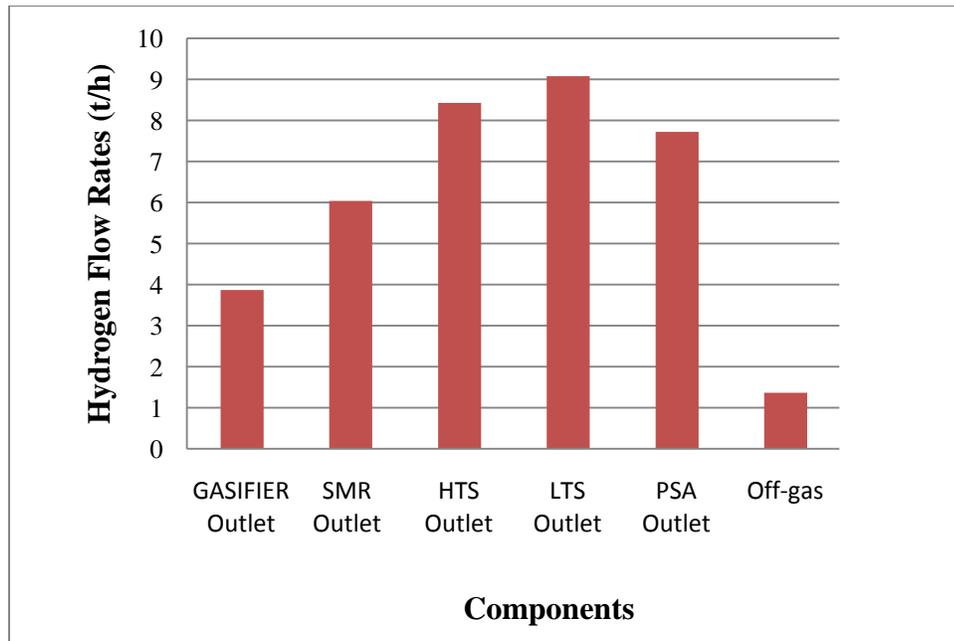


Fig. 8.5: Hydrogen flow rates for system 2.

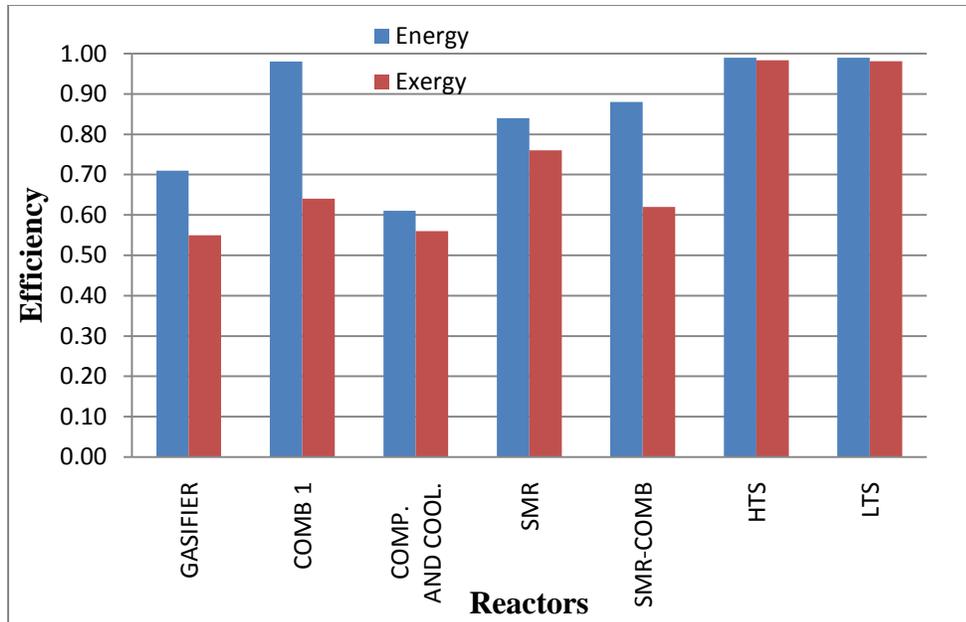


Fig. 8.6: Energy and exergy efficiencies for main system components of system 2.

The energy and exergy efficiencies of the main components involving chemical reactions are shown in Fig. 8.6. The energy efficiency of the gasifier is approximately 72% while the corresponding exergy efficiency is 66% based on Eqs. (5.18) and (5.19). Normally the energy efficiency at these conditions may be expected to be around 80%; the value here is lower since the system assessed has unconverted solid carbon as char and catalysis is not used to promote the gasifier reactions. In addition, the fuels are over-oxidized in the gasifier in order to attain the required gasification temperature (Babu, 2002), and this process may reduce the gasifier efficiency. The gasifier exergy efficiency is lower than the energy efficiency, mainly due to chemical reactions and oxidization. Both combustion reactors operate with high energy and low exergy efficiencies. The latter are associated primarily with internal irreversibilities. For the steam methane reformer, the energy efficiency is found to be 83% and the exergy efficiency 77%. These values are consistent with this reported in the literature (Rosen, 1992). Note that in the HTS and LTS units, the shift reactions occur but there is no combustion. Therefore internal exergy destructions are very low, leading to high exergy efficiencies for these devices. It is observed that significant heat is transferred to water to produce steam in heat exchangers, boilers and economizers. The results suggest that the low-pressure indirectly heated gasifier requires improvements in terms of energy recovery.

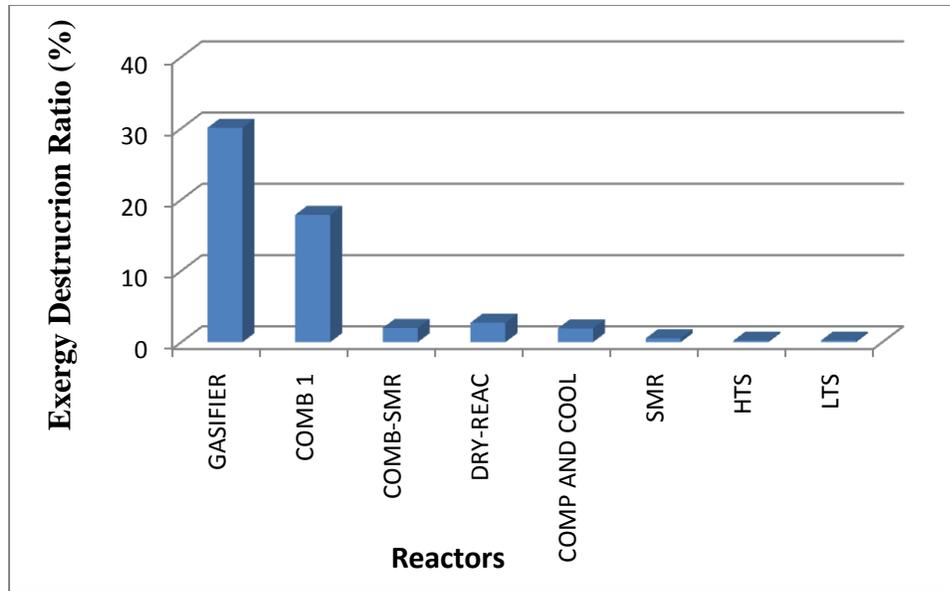


Fig. 8.7: Exergy destruction ratios for the main components of system 2.

It can be seen in Fig. 8.7 that the reactors with the highest exergy destruction rates based on Eq. (5.21) are the gasifier (RGIBBS), in which 30% of the total exergy inlet is destroyed. This observation implies that the gasifier is an important component for efficiency system improvement, especially since the biomass can be gas, solid and liquid. The combustion reactors are also responsible for large exergy destructions, mainly due to irreversibilities associated with the combustion reactions. These exergy losses mainly relate to chemical exergy destructions, and for both combustion 1 and 2 are around 20%. It is also interesting that the dry reactor has a high exergy destruction rate, which is approximately 4.5% due to the 50% moisture content of the inlet biomass. Thus, the heat demand is high for this process, resulting in high exergy destruction rates. It might be better to use dry biomass or to use sun light to dry the biomass before engaging in the process.

Some waste heat boilers in Fig. 8. 8 have a considerable amount of exergy destruction rates. Since phase change occurs during this boiler process is increasing the exergy destruction more. Another point is the hot inlet stream temperatures of approximately 982°C for the WHB which is much higher than the cold inlet temperatures of

approximately 51°C. It is also noticeable that the scrubber has a considerable amount of exergy destruction rate since the condensation happens.

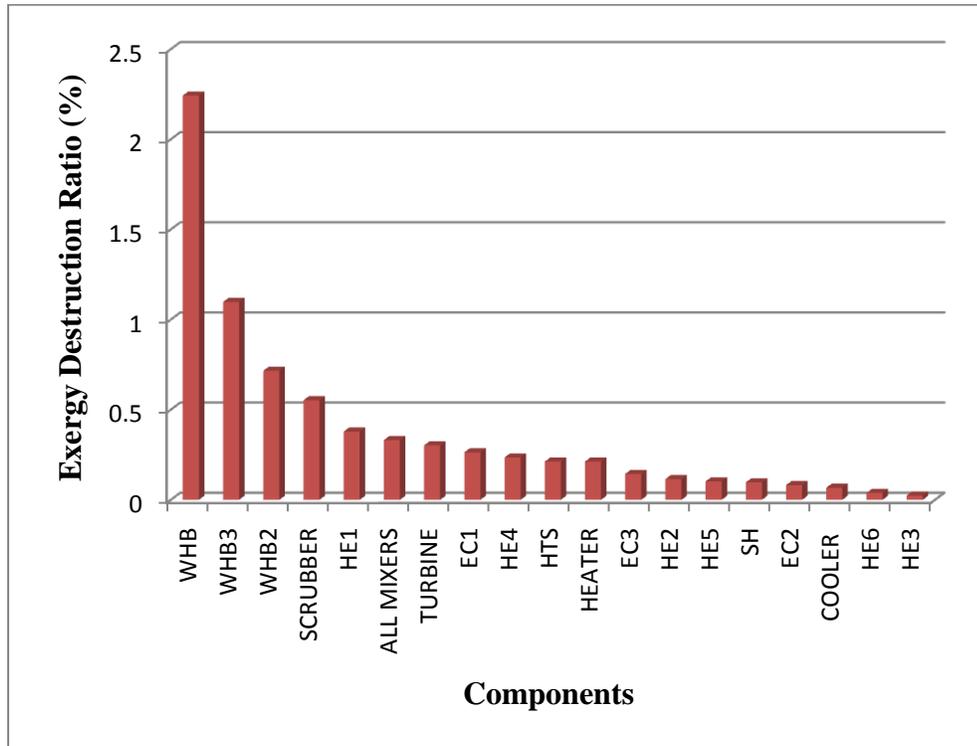


Fig. 8.8: Exergy destruction ratio for auxiliary components of system 2.

8.3 Results for System 3

A similar hydrogen plant to the one here has been studied by Spath *et al.* (2005) as a technical report from National Renewable Energy Laboratory. In this study, the process of hydrogen production through low pressure indirectly heated Battelle Columbus Laboratory (BCL) gasifier. The economic utilization was observed in detail and at the end of this report the minimum hydrogen production cost is calculated at 1.38 \$/kg. It should be noted that when system 3 configurations are set up in the simulation the approach in this study by Spath *et al.* (2005) should be followed. Also in this simulation study for system 3, energy and exergy assessments with an economic analysis are performed.

Table 8.9: Energy and exergy balances for system 3.

| | Energy Flow Rate (MJ/h) | Percentage of total energy inlet (%) | Exergy Flow Rate (MJ/h) | Percentage of total exergy inlet (%) |
|--------------------------------------------------------|--------------------------------|---------------------------------------------------|--------------------------------|---------------------------------------------|
| Inputs | | | | |
| Dry Biomass | 1,957 | 57 | 2,197 | 60 |
| Water | 3.0 | 0.0 | 1.0 | 0.0 |
| Air | 2.0 | 0.0 | 3.5 | 0.0 |
| Methane (CH ₄) | 1,345 | 39 | 1,393 | 37 |
| Electricity | 129 | 4.0 | 129 | 3.0 |
| Total | 3,436 | | 3,724 | 100 |
| Outputs and Destructions | | | | |
| Hydrogen | 924 | 27 | 901 | 24 |
| Electricity | 298 | 9.0 | 298 | 8.0 |
| Exhaust | 358 | 10 | 94 | 3.0 |
| Wastewater | 0.3 | 0.0 | 0.7 | 0.0 |
| Produced Exergy | | | 1,294 | 35 |
| Exergy Destruction | | | 2,326 | 62 |
| Others | 1,784 | 54 | 105 | 3.0 |
| Total | 3,436 | 100 | 3,724 | 100 |
| Energy Efficiency, η_{sys} (%) | 33 | | | 29 |
| | | Exergy Efficiency, ψ_{sys} | | |
| Cold Gas Efficiency, η_{cg} (%) | 25 | | | |

As it can be seen in Table 8.9, the overall energy and exergy balances are ascertained for system 3. Biomass (oil palm shell), water, air and CH₄ enter the system while hydrogen, electricity, exhausts and wastewaters exit the system. When we look carefully at Table 8.9, it's easy to realize the energy and exergy efficiencies to be 33% and 29% respectively; this result is reflected at the end of this simulation as the hydrogen production rate is 7.633 t/h as outlined in Table 8.10.

Another interesting aspect of Table 8.9 is the exhaust gas energy and exergy values 10% and 3.0 % respectively, the exhaust gas is identified to have high energy intensity because of the temperature, but with a low availability which identifies the necessity of a second

law investigation. It seems that the exergy perspective can give us accurate answers in terms of a thermodynamic point of view.

Table 8.10: Properties and composition of the main streams in system 3.

| Streams | | | | | | | |
|--------------------------------|------------------------|-----------------------|-----------------------|-----------------------|----------------------|--------------------|---------------------------------|
| Quantity | COMP Outlet | SMR Outlet | HTS Outlet | LTS Outlet | PSA Inlet | Off Gas | H₂ Outlet |
| <i>T</i> (°C) | 43 | 850 | 481 | 240 | 166 | 27 | 27 |
| <i>P</i> (bar) | 32 | 28 | 27 | 26.5 | 20 | 1 | 70 |
| Flow rate (t/h) | 61.54 | 145.12 | 145.12 | 145.12 | 98.69 | 91.06 | 7.63 |
| Dry gas composition (% vol) | | | | | | | |
| H ₂ O | 0.0 | 21.0 | 14.0 | 12.0 | 0.0 | 0.0 | 0 |
| H ₂ | 48.0 | 45.0 | 56.0 | 59.0 | 69.0 | 24.5 | 99.9 |
| CO | 29.0 | 23.0 | 5.0 | 0 | 0.0 | 0.0 | 0 |
| CO ₂ | 9.0 | 5.0 | 21.0 | 25.0 | 28 | 68.2 | 0 |
| CH ₄ | 13.0 | 3.0 | 2.00 | 2.0 | 3 | 7.3 | 0 |

As can be seen properties and composition of the main streams in system 3 in Table 8.10. Notice that H₂ outlet flow rate is 7.63 t/h which is the amount of produced hydrogen at the end of system 3.

Table 8.11: Assumptions for system 3.

| Quantity | Value |
|---------------------------------------------|--------------|
| Biomass flow rate (wet) (t/h) | 166.67 |
| Biomass flow rate (dry) (t/h) | 88.40 |
| Steam input to the gasifier (t/h) | 33.17 |
| CH ₄ input to the COMB 1 (t/h) | 25.5 |
| CH ₄ input to the SMR-COMB (t/h) | 7.6 |
| Steam-Biomass Ratio (STBR) | 0.38 |

Table 8.11 shows the assumptions for the system 3. It displays the how much CH₄ added to the system 3. This table also shows the amount of steam input to the indirectly heated steam gasifier

Table 8.12: Gasifier performance and syngas composition for system 3.

| Quantity | | Value | |
|-------------------------------------|-------|------------------|-------|
| Gasifier outlet temperature (°C) | | 870 | |
| Combustor 1 outlet temperature (°C) | | 983 | |
| Gasifier outlet composition (t/h) | | | |
| H ₂ O | 38.23 | CO ₂ | 15.81 |
| H ₂ | 3.87 | NH ₃ | 0.08 |
| CO | 32.84 | H ₂ S | 0.45 |
| CH ₄ | 8.35 | C (solid) | 20.17 |

Table 8.12 demonstrates conditions at the gasifier outlet; the produced hydrogen yield is 3.87 t/h.

As it can be seen below in Fig. 8.9, hydrogen production rates will be increased following the gasifier, SMR, HTS and LTS processes. The maximum hydrogen level can be observed outlet of the LTS which is around 8,8 t/h.

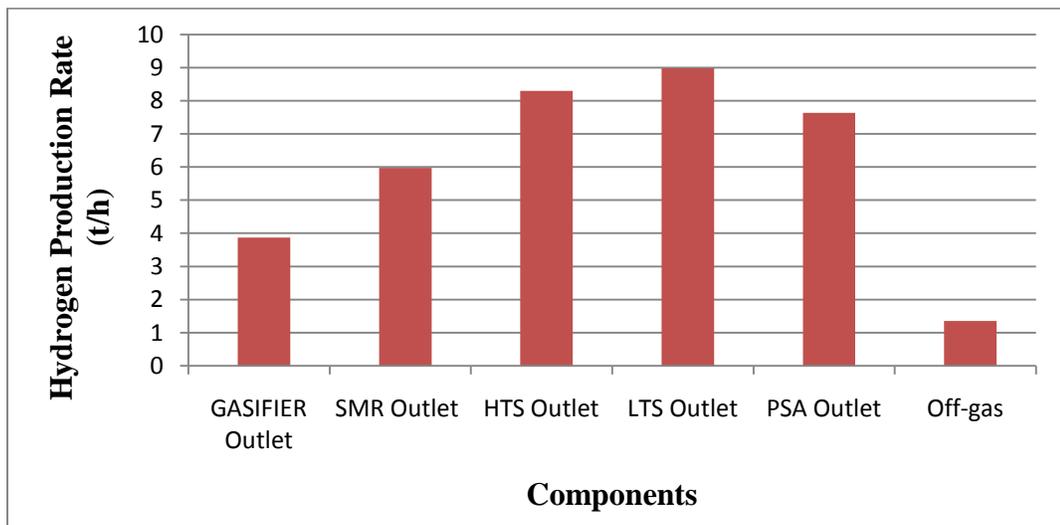


Fig. 8.9: Hydrogen flow rates for system 3.

One thing must be highlighted in Fig. 8.10. The gasifier section has the highest exergy destruction rate which is almost 47%. This number is partially very high because in this case gasifier section consists of the DECOMP, COMB1, GASIFIER, HX2 and HX3 means these five reactors' exergy destruction rates are summarized as a "Gasifier System" exergy destruction rate while other system for instance, reformer system consists of the SMR-Comb, Reformer and five heat exchangers which they have already been explained previous chapter, has how many components in each sub-system can be seen from their figures in chapter 7.

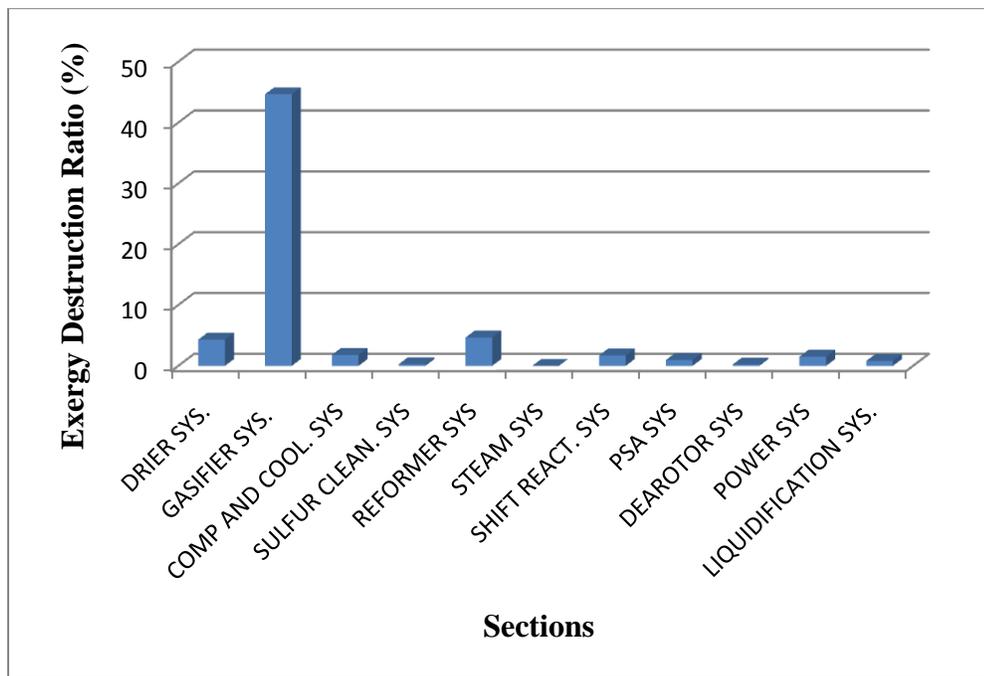


Fig. 8.10: Exergy destruction ratios for the sub-systems of system 3.

8.4 Thermodynamic Comparison of the Systems Considered

One of the more significant articles to be addressed following the simulation results is the overall energy and exergy efficiencies. This section there will be a comparison among the simulated system's thermodynamic results; in addition to that next section there will be economical assessment and comparison among them. The energy and exergy calculation formulas and assumptions for the simulated systems can be found in chapter 5. In addition, in chapter 6, it is available economic evaluation and detailed explanations with

the assumptions for the studied systems. It can be seen in Table 8.13 the simulated systems have some shared characteristics and differences regarding simulation set-up.

Table 8.13: Comparison of three biomass-based hydrogen plants.

| | System 1 | System 2 | System 3 |
|--------------------------------------------|-----------------|-----------------|-----------------|
| Plant Capacity (t/d) | 2000 | 2000 | 2000 |
| Biomass to Gasifier flow rate (t/h) | 24.8 | 88.4 | 88.4 |
| Consumed CH ₄ (t/h) | 8.96 | 23.52 | 33.6 |
| Produced H ₂ flow rate (t/h) | 3.72 | 7.72 | 7.63 |
| System energy efficiency, η_{sys} (%) | 22 | 31 | 33 |
| System exergy efficiency, ψ_{sys} (%) | 19 | 28 | 29 |
| Cold gas efficiency, η_{cg} (%) | 22 | 30 | 25 |

Table 8.13 demonstrates the differences in exergy efficiencies for the three systems. In all cases, the energy and exergy efficiencies are relatively lower than the SMR or coal gasification energy and exergy results reported in the literature. The desirability of having a biomass based hydrogen production system is because of the environmental concern and sustainability. This can be explained by releasing carbon after any process which must be identified in the carbon cycle.

There are many variables which could affect the whole system energy and exergy efficiencies such as the type of biomass or the amount of moisture in the biomass. In this study, all the simulated systems were planned to follow the same path, for instance, the same kind of biomass is chosen, oil palm shell, or the biomass outlet temperature set up at 870°C for these three systems to figure out the real picture in terms of thermodynamic efficiencies and related for the purposes of comparison. When the simulations were created, it was attempted to keep all the variables and the conditions are similar as much as possible to see clear results for all three systems.

From inspection of the following figures, three main points should be addressed. The first is the exergy efficiencies are once again noticeably lower than the corresponding energy efficiencies. Secondly, it can be observed that system 2 and system 3 have the same

amount biomass flow rate to the gasifier, resulting in almost the same amount of produced hydrogen at the end of processes. Furthermore, the amount of methane gas consumed among the systems are incorporated with the biomass directly affecting the system performance therefore, system 3 has the highest system energy and exergy efficiency identified as 33% and 29 % respectively, while system 1 has the lowest system energy and exergy efficiencies found to be 22% and 19% respectively. The energy and exergy portion of the methane included with the biomass feed can be seen in the thermodynamic evaluation section in Table 8.9 for system 3.

The third main finding is the cold gas efficiency are not related the system energy and exergy efficiency results, it is directly related to the amount of produced gas which is hydrogen in this case.

In system 1, energy and exergy efficiencies are relatively low due to the biomass split; this evokes less biomass entering the gasifier meaning less hydrogen production at the end. An important aspect of this system is that it consumes less CH_4 because the splitting process makes this system more sustainable even though this system's efficiency is the lowest with respect to the amount of the green gas released to the atmosphere is also the lowest, making this system more favourable in an environmental aspect.

An important point should be highlighted that system 2 and system 3 are similar but their energy and exergy efficiencies are different due to the fact that system 3 has more heat recovery implementation than system 2 which directly affects the produced electricity from the turbine. For instance, system 3 has separated water and steam treatment sub-systems while system 2 does not have. Furthermore, system 3 has more heat exchangers than system 2. In addition, system 3 has three stage power systems consist of high pressure turbine low pressure turbine and vacuum turbine while system 2 has just one turbine provides system 2 less work output.

When we compare the three simulated systems; system 3 has a more sophisticated arrangement than systems 1 and 2 making it closer to a functioning hydrogen plant by

implementing water and steam treatment, and a collection unit. This system also has three turbines that lead to the production of more electricity.

It is also important to note that real world systems may have lower energy and exergy values due to the increased heat loss, and lack of heat recovery, however the simulation process enables a deep understanding of these systems. It might be accepted that any system starts with the idea, continues on to research, and generates simulations to comprehend this system.

8.4. Economic Results of the Considered Systems

In this economic results section, detailed economic analyses were investigated to estimate minimum hydrogen production cost. It should be noted that all explanations, assumptions and methods about economic evaluation are explained in previous chapter 6. As it can be observed below tables there are many factors affect minimum hydrogen production cost (MHPC), the intention doing this investigation was to minimize the minimum hydrogen production cost, also this section will touch how we can reduce the MHPC to make it competitive with other fuels.

8.4.1 Economic Results for System 1

In Table 8.14, direct capital cost, indirect capital cost and operating cost for system 1 can be observed. For this case, tar cracking catalyst, olivine (gasifier bed material) and other catalysts cost were not included to the operating cost as it can be seen in Table 8.14, the major parts of operating costs come from feedstock and natural gas, as a result this system with the delivered feedstock cost is 40 \$/tonne, minimum hydrogen production cost founds to be 1.84 \$/kg other words is 15.3 \$/GJ. It is also clear that some produced electricity contribute to reduce MHPC.

Table 8.14: Hydrogen production economic evaluation for system 1.

| Hydrogen Production Economic Analysis System 1 | | | |
|---------------------------------------------------------------------|-----------------|-------------------------------------------------|------------------------------------|
| 2000 Dry Metric Tonnes Biomass per Day, All Values in 2009\$ | | | |
| Minimum Hydrogen Production Cost (\$/kg) | 1.84 | 15.32 | (\$/GJ H ₂ , LHV basis) |
| Hydrogen Production (MM kg / year) | 29.76 | | |
| Delivered Feedstock Cost \$/Dry US Ton | 40 | | |
| Direct Capital Costs (M\$) | | Operating Costs (cents/kg H₂) | |
| Feed Handling & Drying | \$23.170 | Feedstock | 95.05 |
| Gasification | \$9.336 | Natural Gas | 37.05 |
| Compression & Sulfur Removal | \$6.408 | Tar Reforming Catalyst | 0.00 |
| Steam Methane Reforming, Shift, and PSA | \$5.610 | Other Catalysts | 0.00 |
| Hydrogen Compression | \$0.00 | Olivine | 0.00 |
| Steam System and Power Generation | \$5.610 | Other Raw Materials | 1.68 |
| Cooling Water and Other Utilities | \$1.273 | Waste Disposal | 2.35 |
| | | Electricity | -29.96 |
| Total Installed Equipment Cost (TIC) | \$51.408 | Fixed Costs | 19.00 |
| | | Capital Depreciation | 15.45 |
| Indirect Costs (M\$) | | Average Income Tax | 12.36 |
| Engineering (% 13 of TIC) | \$6.683 | Average Return on Investment | 30.90 |
| Costruction (% 14 of TIC) | \$7.197 | Operating Cost(M\$/yr) | |
| Legal and Contractor fees (%9 of TIC) | \$4.626 | Feedstock | \$28.288 |
| Project contingency (% 15 of TIC) | \$7.711 | Natural Gas | \$11.025 |
| | | Tar Cracking Catalyst | \$0.00 |
| Indirect Costs | \$40.558 | Other Catalystss | \$0.00 |
| | | Olivine | \$0.00 |
| | | Other Raw Matl. Costs | \$0.5 |
| | | Waste Disposal | \$0.7 |
| Total Project Investment (TPI) | \$91.965 | Electricity | -\$8.917 |
| | | Fixed Costs | \$5.655 |
| | | Capital Depreciation | \$4.598 |
| Total Plant Electricity Usage (KW) | 26644 | Average Income Tax | \$3.679 |
| Electricity Produced Onsite (KW) | 45861 | Average Return on Investment | \$9.197 |
| Purchased Electricity (KW) | -19217 | Total Operating Cost | \$54.725 |

8.4.2 Economic Results for System 2

In Table 8.15, direct capital cost, indirect capital cost and operating cost for system 2 can be observed. As it can be seen in Table 8.15, also for this system the major parts of operating costs come from feedstock and natural gas. As a result this system with the delivered feedstock cost is 40 \$/tonne, minimum hydrogen production cost founds to be 1.55 \$/kg other words is 12.8 \$/GJ. It is also matter of a fact that this system purchases some electricity affect the MHPC in a negative way.

Table 8.15: Hydrogen production economic evaluation for system 2.

| Hydrogen Production Economic Analysis System 2 | | | |
|----------------------------------------------------------------------|------------------|--------------------------------------------|-----------------------------------------|
| 2000 Dry Metric Tonnes Biomass per Day - All Values in 2009\$ | | | |
| Minimum Hydrogen Production Cost (\$/kg) | 1.55 | 12.89 | (\$/GJ H₂, LHV basis) |
| Hydrogen Production at Operating Capacity (MM kg / year) | 62.48 | | |
| Delivered Feedstock Cost \$/Dry Tonne | 40 | | |
| Direct Capital Costs (M\$) | | Operating Costs (cents/kg hydrogen) | |
| Feed Handling & Drying | \$23.170 | Feedstock | 45.28 |
| Gasification | \$20.160 | Natural Gas | 46.41 |
| Compression & Sulfur Removal | \$12.000 | Tar Reforming Catalyst | 0.00 |
| Steam Methane Reforming, Shift, and PSA | \$20.710 | Other Catalysts | 0.00 |
| Hydrogen Compression | \$0.00 | Olivine | 0.00 |
| Steam System and Power Generation | \$7.536 | Other Raw Materials | 0.80 |
| Cooling Water and Other Utilities | \$5.251 | Waste Disposal | 1.12 |
| | | Electricity | 8.62 |
| Total Installed Equipment Cost (TIC) | \$88.834 | Fixed Costs | 11.75 |
| | | Capital Depreciation | 10.73 |
| Indirect Costs (M\$) | | Average Income Tax | 8.59 |
| Engineering (%13 of TIC) | \$11.548 | Average Return on Investment | 21.47 |
| Costruction (%14 of TIC) | \$12.436 | Operating Cost(M\$/yr) | |
| Legal and Contractor fees (%9 of TIC) | \$7.995 | Feedstock | \$28.288 |
| Project contingency (% 15 of TIC) | \$13.325 | Natural Gas | \$28.998 |
| | | Tar Cracking Catalyst | \$0.00 |
| Indirect Costs | \$45.305 | Other Catalysts | \$0.00 |
| | | Olivine | \$0.00 |
| | | Other Raw Matl. Costs | \$0.5 |
| | | Waste Disposal | \$0.7 |
| Total Project Investment (TPI) | \$134.139 | Electricity | \$5.387 |
| | | Fixed Costs | \$7.341 |
| | | Capital Depreciation | \$6.707 |
| Total Plant Electricity Usage (KW) | 31904 | Average Income Tax | \$5.366 |
| Electricity Produced Onsite (KW) | 20294 | Average Return on Investment | \$13.414 |
| Purchased Electricity (KW) | 11610 | Total Operating Cost | \$96.700 |

8.4.3 Economic Results for System 3

In Table 8.16, direct capital cost, indirect capital cost and operating cost for system 3 can be observed. As it can be seen in Table 8.16, the major parts of operating costs come from feedstock and natural gas, as a result this system with the delivered feedstock cost is 40 \$/tonne, minimum hydrogen production cost founds to be 1.28 \$/kg, other words is 10 \$/GJ. It is interesting fact that this system has a highest produced electricity rate which mean in this system we can sell electricity and hydrogen at the same time to reduce operating cost which is directly linked MHPC. Further discussion will be available next section in terms of economic comparison of these three systems.

Table 8.16: Hydrogen production economic evaluation for system 3.

| Hydrogen Production Economic Analysis for System 3 | | | |
|----------------------------------------------------------------------|------------------|-------------------------------------------------|------------------------------------|
| 2000 Dry Metric Tonnes Biomass per Day - All Values in 2009\$ | | | |
| Minimum Hydrogen Production Cost (\$/kg) | \$1.28 | \$10.03 | (\$/GJ H ₂ , LHV basis) |
| Hydrogen Production at operating capacity (MM kg / year) | 61.1 | | |
| Delivered Feedstock Cost \$/Dry Tonne | \$40 | | |
| Direct Capital Costs (M\$) | | Operating Costs (cents/kg H₂) | |
| Feed Handling & Drying | \$23.170 | Feedstock | 46.30 |
| Gasification | \$20.160 | Natural Gas | 53.68 |
| Compression & Sulfur Removal | \$15.373 | Tar Reforming Catalyst | 0.00 |
| Steam Methane Reforming, Shift, and PSA | \$21.670 | Other Catalysts | 0.00 |
| Hydrogen Compression | \$4.992 | Olivine | 0.00 |
| Steam System and Power Generation | \$12.100 | Other Raw Materials | 0.82 |
| Cooling Water and Other Utilities | \$5.909 | Waste Disposal | 1.15 |
| | | Electricity | -35.66 |
| Total Installed Equipment Cost (TIC) | \$103.373 | Fixed Costs | 13.45 |
| | | Capital Depreciation | 12.77 |
| Indirect Costs (M\$) | | Average Income Tax | 10.22 |
| Engineering (% 13 of TIC) | \$13.439 | Average Return on Investment | 25.55 |
| | | Operating Cost (M\$) | |
| Project contingency (% 15 of TIC) | \$15.506 | Feedstock | \$28.288 |
| | | Natural Gas | \$32.800 |
| Indirect Costs | \$52.720 | Tar Cracking Catalyst | \$0.00 |
| | | Other Catalysts | \$0.00 |
| | | Olivine | \$0.00 |
| | | Other Raw Matl. Costs | \$0.5 |
| Total Project Investment (TPI) | \$156.093 | Waste Disposal | \$0.7 |
| | | Electricity | - |
| | | | \$21.788 |
| | | Fixed Costs | \$8.220 |
| Total Plant Electricity Usage (KW) | 35803 | Capital Depreciation | \$7.805 |
| Electricity Produced Onsite (KW) | 82760 | Average Income Tax | \$6.244 |
| Purchased Electricity (KW) | -46957 | Average Return on Investment | \$15.609 |
| | | Total Operating Cost | \$78.378 |

8.5 Overview of Three Systems Economic Evaluation Results

Table 8.17 gives the TPI results for these three cases with the capacity of 2,000 tonne/day plant. The detailed capital cost explanations for these three systems were made in previous sections. Once the capital and operating costs have been determined, a minimum hydrogen production cost (MHPC) can be determined using a discounted cash flow rate of return analysis. The methodology used by Aden, *et al.*, (2002). The MHPC is the production cost of hydrogen that makes the net present value of the biomass syngas to

hydrogen process equal to zero with a 10% discounted cash flow rate of return over a 20 year plant life.

Table 8.17: Overview of three system's TPI results.

| | System 1 | System 2 | System 3 |
|----------------------------------------------|-----------------|-----------------|-----------------|
| | (M\$) | (M\$) | (M\$) |
| Total Purchased Equipment Cost (TPEC) | 20.8 | 36.0 | 41.7 |
| Purchased equipment installation | 8.1 | 14 | 16.3 |
| Instrumentation and controls | 5.41 | 9.3 | 11 |
| Piping | 6.45 | 11.1 | 12.9 |
| Electrical systems | 2.1 | 3.6 | 4.2 |
| Buildings (including services) | 6.0 | 10.4 | 12 |
| Yard improvements | 2.5 | 4.3 | 5.0 |
| Total Installed Cost (TIC) | 51.4 | 88.8 | 103 |
| Engineering | 6.7 | 11.5 | 13.4 |
| Construction | 7.2 | 12.4 | 14.4 |
| Legal and contractors fees | 4.6 | 8.0 | 9.3 |
| Project contingency | 7.7 | 13.3 | 16 |
| Total Indirect Costs | 40.5 | 45.3 | 53 |
| Total Project Investment (TPI) | 91.9 | 134 | 156 |

Table 8.18 shows the estimated economic analysis results for a minimum hydrogen production cost which varies between \$1.28/kg to \$1.84/kg with plant capacity 2000 dry tonne per day. Since there are differences with each system, the equipment required for all three systems are similar in some ways, however the needs are more basic for system 1, and more complex for system 3. The impact on capital costs is negative, and positive. For example for system 1, the amount of entered biomass to the gasifier is different than these systems 2 and 3. In other words, for system 1, the gasifier size will be smaller than system 2 and system 3 and it will be cheaper than system 2 and system 3. In addition, it is very clear to understand that hydrogen production cost in Tables 8.14, 8.15 and 8.16 depends on many factors such as, feedstock cost, methane cost, electricity cost or tax etc.

Alone feedstock and natural gas cover a large portion of the operating cost. From this perspective the hydrogen production cost will decrease drastically if the natural gas and feedstock costs are reduced.

Those explained correspondent parameters in the previous paragraphs give us minimum hydrogen production cost can be seen in the following below Table 8.18;

Table 8.18: Minimum hydrogen production cost (MHPC).

| Formulas | System 1 | System 2 | System 3 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|-----------------|-----------------|
| $\frac{\text{Total Operating Cost (\$/yr)}}{\text{Total hydrogen production (kg/yr)}} =$ | \$1.84/kg | \$1.55 /kg | \$1.28 /kg |
| $\frac{\text{Total Operating Cost (\$/yr)}}{\text{Total hydrogen production } \left(\frac{\text{kg}}{\text{yr}}\right) \times \text{LHV}\left(\frac{\text{GJ}}{\text{kg}}\right)} =$ | \$15.30/GJ | \$12.90/GJ | \$10.1/GJ |

Another reason that the hydrogen production cost is high for these three systems, is the water in wet biomass (50% moisture) needs to be evaporated in the drier to become dry biomass (5.7 % moisture). This process is very expensive and the direct capital cost will be affected in a negative way because the drier process brings additional cost. If the biomass would already be dry and the need for the drier is not necessary, it could make a huge difference in the hydrogen production cost which is approximately \$0.22, which means the drier process will increase the hydrogen production cost around \$0.22. It is better to use dry biomass or to use sunlight to let the biomass dry first before engaging in the process. For system 1, there is no specified hydrogen production cost available in the literature; however the minimum hydrogen production cost is \$1.84/kg which is quite reasonable. In contrast, even though the operating cost of system 1 is less than system 2 and 3, the hydrogen production cost is the highest because the hydrogen production capacity per year is less than system 2 and system 3. For system 2, and system 3 the hydrogen production capacity are almost the same. System 3 hydrogen production rate is little bit less than system 2 due to the unpredicted losses during system 3 hydrogen production. System 1 and system 3 have some saleable electricity, which impacts on the reduced hydrogen production cost, while system 2 purchases some electricity from

outside sources, increasing the minimum hydrogen production cost. Among these systems, system 1 has the highest hydrogen production cost while it has the lowest purchased methane means of producing hydrogen with the highest cost, and the lowest green gas emission. The same mentality is used for system 3 that having the lowest hydrogen production cost with the highest capacity, but the highest the green gas emission proportional to the one which purchases natural gas.

Chapter 9

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

9.1 Conclusions

For the three simulations, the energy, exergy and economic analyses performed on the biomass-based hydrogen production have yielded energy and exergy efficiencies and an understanding of the impact on performance of several parameters. The feasibility of producing hydrogen from biomass and a better understanding of the potential of biomass as a renewable energy source has been attained by considering three systems: 1) System 1's gasifier is designed as an R-GIBBS reactor splitting the biomass among the combustor and the gasifier. After the gasification process, the hydrogen production path follows the reformer and the high temperature shift reactor. 2) System 2's gasifier is designed as a low pressure indirectly heated BCL gasifier, hydrogen path after the gasifier, follows the reformer, the high temperature (HTS) and the low temperature shift reactor (LTS). 3) System 3's gasifier is designed exactly the same as system 2. In addition, this system is more detailed and it has a better water, steam and power production unit giving a more realistic view of the performance of each process. Oil palm shell is the biomass considered for all three cases.

For the direct gasification reaction, a BCL-type low-temperature indirectly heated steam gasifier is examined. The thermodynamic assessments for the three cases demonstrate that the processes have low efficiencies. The simulation confirms that for system 3 which indicates performance improvements have higher energy and exergy efficiencies than system 1 and system 2. Of all these systems, while studying the energy efficiencies, it was first noticed that the values obtained were quite low; between 22-33% this is as a result of the biomass having a lower fuel density and all three processes operating within high temperatures which cause more heat loss.

While assessing the exergy efficiencies of the system, it was found that the results are relatively lower than its energy counterpart; firstly it was noticed that the exergy efficiencies range from 19-29%. These values are logical due to the inlet biomass and methane gas which go through partial oxidation and combustion processes in high temperatures which increase the amount of exergy destroyed in total since these processes have related chemical reactions.

While appraising the economic investigation for these three systems, it wasn't surprising to note that system 3 which has a maximum energy and exergy efficiency will have the lowest cost for production cost, which is estimated to be \$1,28/kg.

When we look at these three systems from an energy, exergy and economic based analysis, we will discover that system 3 has more energy and exergy efficiency with a lower hydrogen production cost. In referring to system 3, it is identified that this system consumes the highest methane gas. While system 1 consumes the lowest methane gas with lowest energy and exergy efficiency including a higher hydrogen production cost in contrast, when we think of the sustainability of this energy source, System 1 is more favourable than system 2 and system 3 even though it has lowest hydrogen production rate. It can also be concluded that after this study it is observed that the gasifier is the most important component in simulated biomass gasification systems.

To promote the use of biomass conversion in a more profitable way, an interesting strategy seems to be the use of biomass joined with natural gas, in a high efficiency energy conversion system, such as the combined cycle power plants.

9.2 Recommendations for Future Studies

In addition to gas clean-up and conditioning other barrier areas that could reduce the cost of fuel products from thermochemical conversion of biomass includes feed handling and drying, gasification, production of different products and co-products, and process integration. These should be evaluated in detailed studies and compared to the present study to find the most viable hydrogen production method for the given conditions.

Further detailed studies on the effect of catalysts in the different steps in the cycles should be investigated. Better catalysts can be found to maximize the process efficiency. Also, larger scale plants should be studied in detail, the larger the plant capacity the lower the hydrogen production cost is, so increasing the plant size to a certain capacity could lead to a hydrogen price that is competitive to other technologies.

The effect of using a different biomass feedstock should be studied too. Using a different biomass feedstock could lead to better hydrogen production efficiencies and cost. The integration of thermochemical processes and other hydrogen production processes to the studied processes should be examined. It could have great potential and benefits.

Mixing different fuels with biomass can have different outcomes from each process. This issue should be examined well with different fuels and different mixture ratios. The results should be evaluated and compared, then the best fuel-biomass mixture can be found for a specific operating conditions.

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APPENDIX 1: Equipment Design Parameters and Cost References

Parameters and Cost References for System 1

| Key Qty | Tag No | COA Description | Item Description | Cost Basis | Material |
|---------|--------------|-------------------------------|----------------------------------------|-------------|----------|
| 1 | HX0 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | DRY-REAC | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | DRY-FLSH-fla | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| | | | | | |
| 1 | DECOMP | (132) Agitated Vessels | EQUIP & FIELD FABRIC. | Icarus | A285C |
| 1 | SP2 | (134) Mixers | included in overall cost Gasifier | Literature* | CS |
| 1 | COMB1 | (132) Agitated Vessels | EQUIP & FIELD FABRIC. | Icarus | A285C |
| 1 | HX1 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HX8 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | CS |
| | | | | | |
| 1 | COMB2 | (132) Agitated Vessels | EQUIP & FIELD FABRIC. | Icarus | A285C |
| 1 | GASIFIER | (132) Agitated Vessels | EQUIP & FIELD FABRIC. | Icarus | A 214 |
| | CYCLONE | Separator-Gas Cyclone | Included in overall | | CS |
| 1 | HX2 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HX3 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| | | | | | |
| 1 | REFORMER | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HX4 | (252) Waste Heat Boilers | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | SS316 |
| 1 | HX5 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HX9 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | CS |
| 1 | HX6 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | P3 | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | SP1 | (134) Mixers | Including in overall cost Gas clean-up | Literature | A285C |
| 1 | FLASH1-flash | (113) Vertical Vessels | EQUIP & FIELD FABRIC. | Icarus | A285C |
| 1 | SP1 | Separator | Including in overall cost Gas clean-up | Literature | A285C |
| 1 | MIXER | Tank-Vertical Vessel | Including in overall Gas clean-up | Literature | CS |
| 1 | SHIFT | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | HX7 | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | P2 | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | P4 | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | H20FLS-flash | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 214 |
| | | | | | |
| 1 | PSA-CO2 | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA-H2 | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | PSA-N2 | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| | | | | | |
| 1 | TURB | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |

Parameters and Cost References for System 2

| Key Qty | Tag No | Equipment Class | Description | Item Description | Cost Basis | Material |
|---------|--------------|-----------------|-------------------------------|-------------------------------------|------------|----------|
| 1 | HOPPER | Hopper | Tank | Included in overall cost drier | Literature | |
| 1 | DRY-REAC | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | DRY-FLSH-fla | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | DECOMP | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | GASIFIER | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| | CYCLONE | Separator | Gas Cyclone | Included in overall cost drier | Literature | |
| 1 | COMB1 | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| 1 | WHB | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304S |
| 1 | SCRUBBER | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | M44 | Mixer | Tank | Included in overall cost compressor | Literature | |
| 1 | COMP.1-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.2-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.3-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.4-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.5-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.6-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMP.A1 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMP.A2 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMP.A3 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMP.A4 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMP.A5 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMP.C1 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP.C2 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP.C3 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP.C4 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP.C5 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMP.COOLE R | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HEATER | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | ZNO-BED | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |

| | | | | | | |
|---|--------------|-------------------|-------------------------------|---------------------|--------|-------|
| 1 | HE1 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304S |
| 1 | SMR | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| 1 | SMR-COMB | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | HTS | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| 1 | HE6 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304W |
| 1 | SH | Heat Exchangers | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | EC2 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | LTS | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | EC3 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | EC1 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HE5 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | CA443 |
| 1 | HE4 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HE3 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HE2 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304S |
| 1 | P1 | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | P2 | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | PSA | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COOLER-flash | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | TURBINE | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | WHB2 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304S |
| 1 | WHB3 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304S |

Parameters and Cost References for System 3

| Key Qty | Tag No | Equipment Class | COA Description | Item Description | Cost Basis | Material |
|---------|------------------|-----------------|-------------------------------|--------------------------------|------------|----------|
| 1 | Hopper | Hopper | Tank | Included in overall cost drier | Literature | |
| 1 | DRY-REAC | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| 1 | DRY-FLSH | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | SS304 |
| 1 | DECOMP | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | GASIFIER | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | Gasifier Cyclone | Separator | Cyclone | Included in overall cost drier | Literature | |
| 1 | COMB1 | Agitated Tanks | (105) Misc. Item Allowance | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | HX2 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | HX3 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.A-1 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.A-1 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.A-1 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 21 |
| 1 | COMPRESS.A-1 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.A-1 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.C-1 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMPRESS.C10 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMPRESS.C-1 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMPRESS.C-1 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMPRESS.C-1 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | COMPRESS.COOL | Heat Exchangers | Water Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S10 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | COMPRESS.S-1 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | SULFURCL.CYC | Seperator | Cyclone | EQUIPMENT & SETTING | Literature | A 214 |

| | | | | | | |
|---|--------------|-----------------|-------------------------------|---------------------|------------|-------|
| 1 | SULFURCL.HX4 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304W |
| 1 | SULFURCL.HX5 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | SULFURCL.O-2 | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | SULFURCL.ZNO | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| | | | | | | |
| 1 | REFORMER.COM | Agitated Tanks | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | TI50A |
| 1 | REFORMER.HX6 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | TI50A |
| 1 | REFORMER.HX7 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | TI50A |
| 1 | REFORMER.PRE | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | REFORMER.REF | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | TI50A |
| 1 | REFORMER.SYN | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | M-300 | Mixer | Tank | EQUIPMENT & SETTING | Literature | CS |
| 1 | M-301 | Mixer | Tank | EQUIPMENT & SETTING | Literature | CS |
| | | | | | | |
| 1 | SHIFTRIA.HSH | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304W |
| 1 | SHIFTRIA.HX7 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304W |
| 1 | SHIFTRIA.HX8 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | SHIFTRIA.HX9 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | SHIFTRIA.KNO | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | SHIFTRIA.LSH | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | S-500 | Separator | Splitter | EQUIPMENT & SETTING | Literature | |
| | | | | | | |
| 1 | PSA.A-600 | Heat Exchangers | (107) Air Cooler | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | PSA.COOLER | Heat Exchangers | Water Cooler | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA.KNOCKOUT | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA.PSACH4CO | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA.PSA-CO2 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA.PSA-N2 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | PSA.PSA-NH3 | Agitated Tanks | (132) Agitated Vessels | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | MIXER | Mixer | Included in miscellaneous | EQUIPMENT & SETTING | Icarus | CS |
| 1 | M-600 | Mixer | Included in miscellaneous | EQUIPMENT & SETTING | Icarus | CS |
| | | | | | | |
| 1 | LIQUIDIF.A90 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | LIQUIDIF.A90 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | LIQUIDIF.C90 | Gas Compressors | (151) Centrifugal Compressors | EQUIPMENT & SETTING | Icarus | A285C |

| | | | | | | |
|---|--------------|-------------------|--------------------------------|---------------------|------------|-------|
| 1 | LIQUIDIF.C90 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | LIQUIDIF.COO | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | LIQUIDIF.KNO | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | LIQUIDIF.KNO | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | A 516 |
| 1 | LIQUIDIF.KNO | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| | | | | | | |
| 1 | POWERGE.COOL | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | POWERGE.H800 | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| 1 | POWERGE.HEAT | Turbines | (153) Turbo-Expand. Compressor | EQUIPMENT & SETTING | Icarus | |
| 1 | POWERGE.IPTU | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | POWERGE.P800 | Turbines | (153) Turbo-Expand. Compressor | EQUIPMENT & SETTING | Icarus | |
| 1 | POWERGE.VPTU | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | A 214 |
| | | | | | | |
| 1 | STEAMSYS.FLS | Heat Exchangers | (261) Shell & Tube Exchangers | EQUIPMENT & SETTING | Icarus | 304W |
| 1 | STEAMSYS.HX6 | Dust Collectors | (201) Dust Collectors | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | S-400 | Seperator | Splitter | EQUIPMENT & SETTING | Literature | |
| | | | | | | |
| 1 | DEARATOR.DEA | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | CS |
| 1 | DEARATOR.P70 | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | DEARATOR.P70 | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | CS |
| 1 | DEARATOR.P70 | Centrifugal Pumps | (161) Centrifugal Pumps | EQUIPMENT & SETTING | Icarus | A285C |
| 1 | T-700 | Vertical Tanks | (113) Vertical Vessels | EQUIPMENT & SETTING | Icarus | CS |
| 1 | SDRUM-700 | Horizontal Tanks | (114) Horizontal Vessels | EQUIPMENT & SETTING | Icarus | CS |
| 1 | S-700 | Seperator | Splitter | EQUIPMENT & SETTING | Literature | CS |
| 1 | M700 | Mixer | Mixer | EQUIPMENT & SETTING | Literature | CS |

APPENDIX 2: An Overview of Settings and Properties Used with the Aspen-Plus
Simulation Tool

Settings for Aspen Plus

An overview of settings and properties used with the Aspen-Plus Simulation Tool

| | |
|-----------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Software version | Aspen Plus |
| Solver method | Sequential Modular |
| Equation of state property method | The Peng –Robinson equation of state with Boston-Mathias modifications |
| Considered conventional components | H ₂ , O ₂ , H ₂ O, N ₂ , NH ₃ , CH ₄ , CO, CO ₂ , C(s). |
| Trace component convergence setting | “Gradual” |
| Trace component mole fraction threshold | 0.00001 |
| Tear stream convergence tolerance | 0.001 |
| Tear stream convergence variables | Total mole flow Pressure Enthalpy |
| Tear stream convergence criterion: | |

$$-tol \leq \frac{X_{calculated} - X_{assumed}}{X_{assumed}} \leq tol$$