GASIFICATION OF OIL PALM BIOMASS IN HOT COMPRESSED WATER (HCW) FOR PRODUCTION OF SYNTHESIS GAS

by

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I certainly did not expect that of all the chapters in this thesis, writing down this acknowledgement section is going to be toughest of all. However, I would try my very best and for individuals that are inadvertently omitted, I would like to offer my apologies and thank you for everything. As often said, old age comes in hand not only with wisdoms but also forgetfulness.

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LIST OF ABBREVIATIONS

3-D	Three-dimensional
5-HMF	5-hydroxymethylfurfuraldehyde
ANOVA	Analysis of variance
BCSE	Australian Business Council for Sustainable Energy
BOD	Biochemical oxygen demand
BP	British Petroleum
C_2H_4	Ethylene
C_2H_6	Ethane
$CaCO_3$	Calcium carbonate
CCRD	Central composite rotatable design
CeO_2	Cesium oxide
CH_4	Methane
CIA	Central Intelligence Agency
CO	Carbon monoxide
CO_2	Carbon dioxide
CrNiMoTi	Chromium, Nickel, Molybdenum, and Titanium
C.V	Coefficient of variation
DF	Degrees of freedom
DOE	Design of experiments
EFB	Empty fruit bunch
EIA	Energy Information Administration
F-value	Fisher’s F value
FAO	Food and Agriculture Organization

FFB	Fresh fruit bunch
FRIM	Forest Research Institute Malaysia
FT	Fisher- Tropsch
GC	Gas chromatography
GHG	Greenhouse gases
H_2	Hydrogen gas
HCOOK	Potassium formate
HCOONa	Sodium formate
HCW	Hot compressed water
HHV	Higher heating value
HNEI	Hawaii Natural Energy Institute
IEA	International Energy Agency
JANAF	Joint Army-Navy-Air Force
K_2CO_3	Potassium carbonate
$KHCO_3$	Potassium bicarbonate
KOH	Potassium hydroxide
LHV	Lower heating value
$MgCO_3.CaCO_3$	Dolomite
MPOC	Malaysia Palm Oil Council
MW	Molecular weight
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NIST	National Institute of Standards and Technology
NO_x	Nitrogen oxides

NREL	National Renewable Energy Laboratory
OPEC	Organizations of the Petroleum Exporting Countries
P-value	Probability value
PETRONAS	Petroliam Nasional Berhad
PLOT	Porous layer open tubular
PM	Particulate matter
POME	Palm oil mill effluent
PRESS	Prediction error sum of squares
PSA	Pressure swing adsorption
PV	Photovoltaic
PVA	Polyvinyl alcohol
R	Residual
R & D	Research & Development
RSM	Response Surface Methodology
SCW	Supercritical water
SD	Standard deviation
SO_x	Sulphur oxides
SREP	Small renewable energy power programme
TAPPI	Technical Association of the Pulp and Paper Industry
TCD	Thermal conductivity detector
UNDP	United Nations Development Programme
VOC	Volatile organic compounds
WGS	Water-gas shift
wt %	Weight percent
ZrO_2	Zirconium oxide

LIST OF SYMBOLS

		Units
α	Constant	Dimensionless
β	Ratio of the chemical exergy to the LHV of the organic fraction of biomass	
β_0	Intercept coefficient	
β_i	Linear term coefficient	
β_{ii}	Squared term coefficient	
β_{ij}	Interaction term coefficient	
ε	Dielectric constant	
ε_a	Standard errors	
ΔH^o_{298}	Standard enthalpy change of reaction at 298.15 K	kJ/mol
λ_i	Lagrange multiplier for atom i	
ρ	Density	kg/m^3
ρc	Critical density	kg/m^3
µm	micron meter	
a	Number of different elements (atom types) present in the system	
D	Overall desirability	
d	Individual desirability function	
E	Exergy of a material stream	kJ
E_{ch}	Chemical exergy	kJ
E_{ph}	Physical exergy	kJ
$E^Q_{utility}$	Electrical exergy of heat input at reaction temperature	kJ

F	Number of points in cube portion of the design	
G	Specific Gibbs energy	
$\bar{g}_j$	Partial molar Gibbs function of pure j species	
H	Specific enthalpy of compound at reaction temperature, T	kJ/mol
H_o	Specific enthalpy of compound at reference temperature, T_o	kJ/mol
I	Irreversibility	
Kw	Ionic product of water	mol^2/l^2
LHV_i	LHV of species i in the component gas	MJ/Nm^3
$LHV_{mixture}$	Total LHV of the mixture	MJ/Nm^3
m	Number of responses	
N	Total number of design points for CCRD	
N_j	Number of moles in species j	mole
n	Number of variables	
n_{ij}	Number of atom i atom in j molecule	
P	Pressure	atm, MPa
Pc	Critical pressure	atm, MPa
P_o	Reference pressure	atm
$Q_{utilities}$	Heat input at reaction temperature, T	kJ
R	Universal gas constant	kJ/K.mol
s	Total number of species in the system	
S	Specific entropy of compound at reaction temperature, T	kJ/mol.K
S_o	Specific entropy of compound at reference temperature, T_o	kJ/mol.K

t	Distribution t = 2.920 at 95% confidence	
T	Temperature	^{o}C, K
T_{105}	Percent total solids on a 105 ^{o}C dry weight basis	wt%
Tc	Critical temperature	^{o}C, K
T_o	Environmental/reference temperature	^{o}C, K
wt	Weight field	
X	Independent process variables	
x_i	Mole fraction of species i in the component	
x_j	Mole fraction of species j in its phase	
Y	Predicted response of the process	
Z_O	Weight fractions of oxygen	
Z_C	Weight fractions of carbon	
Z_H	Weight fractions of hydrogen	
Z_N	Weight fractions of nitrogen	

PENGGASAN BIOJISIM KELAPA SAWIT DI DALAM AIR PANAS TERMAMPAT UNTUK PENGHASILAN GAS SINTESIS

ABSTRAK

Kaedah penggasan gentian tandan buah kosong kelapa sawit dalam air panas termampat dikaji secara berkelompok menggunakan reaktor autoklaf bertekanan tinggi. Parameter tindak balas yang dikaji adalah saiz partikel pepejal, kandungan pepejal, masa tindak balas dan suhu. Keadaan optimum untuk tindak balas tersebut adalah 380.0 °C, 5.0 g pepejal/300.0 g air, 30.0 minit, dan saiz partikel ialah $250 < X < 500$ µm dengan penghasilan produk gas terdiri daripada CO_2, CO, H_2, dan CH_4 dengan kecekapan penggasan sebanyak 32.15% dan kadar hasil hidrogen sebanyak 7.22%. Kajian ini juga ditumpukan kepada 2 jenis mangkin homogen, NaOH dan K_2CO_3 serta kesannya terhadap tindak balas. Kandungan optimum mangkin adalah sebanyak 3.0 wt% (K_2CO_3) dan 6.0 wt% (NaOH) dengan kecekapan penggasan sebanyak 39.04% dan 31.68% dan kadar hasil hidrogen sebanyak 19.03% dan 12.15%. Nilai haba rendah bagi campuran produk gas untuk tindakbalas tanpa mangkin dan dengan menggunakan 3.0 wt% K_2CO_3 berada dalam julat pertengahan (7.32 and 8.86 MJ/Nm^3). Walaubagaimanapun, tindak balas dengan penambahan 6.0 wt% NaOH telah menghasilkan komposisi produk yang mempunyai nilai haba yang tinggi iaitu sebanyak 14.25 MJ/Nm^3.

Kemampuan kaedah respons permukaan (RSM) bersama dengan rekabentuk stastistik komposit tengah berputar (CCRD) telah digunakan bagi menentukan hubungan berfungsi di antara 3 parameter tindak balas iaitu masa tindak balas, kandungan pepejal, dan suhu bertujuan untuk mengoptimumkan 2 reaksi iaitu kecekapan penggasan dan kadar hasil hidrogen. Disamping kajian terhadap reaksi tunggal, pengoptimuman berbilang reaksi juga dijalankan bagi menentukan parameter proses yang optimum supaya kedua-dua reaksi boleh dioptimumkan secara serentak. Kecekapan penggasan maksimum yang dijangka daripada pengoptimuman respons tunggal adalah sebanyak 29.55% (372.7 ^oC, 5.5 g kandungan pepejal, dan 47.7 min) dan kadar hasil hidrogen sebanyak 6.01% (380.0 ^oC, 5.0 g kandungan pepejal, dan 29.5 min). Pengotimuman berbilang respons yang diperolehi menunjukkan terdapat beberapa set penyelesaian yang memberikan nilai maksimum bagi kedua-dua respon dengan kecekapan penggasan yang dihasilkan dalam julat 31.22-32.28% dan julat kadar hasil hidrogen sebanyak 7.09-7.34%. Keadaaan tindak balas optimum yang sama telah digunakan untuk kajian eksperimen selanjutnya dengan tambahan mangkin K_2CO_3 dan NaOH untuk tujuan perbandingan. Kecekapan penggasan didapati meningkat dengan ketara daripada 33.38% (tanpa mangkin) kepada 61.56% (6.0 wt% NaOH) dan 78.43% (3.0 wt% of K_2CO_3). Bagi kadar hasil hidrogen, ia meningkat daripada 7.77% (tanpa mangkin) kepada 32.54% (6.0 wt% NaOH) dan 48.32% (3.0 wt% of K_2CO_3).

Analisis kecekapan eksergi telah dijalankan untuk tindak balas tersebut bagi sistem berkelompok dengan bertujuan untuk menentukan pencapaiannya daripada aspek termodinamik. Kecekapan eksergi tertinggi yang dicapai daripada kajian eksperimen adalah hanya sebanyak 8.37% berbanding dengan 25.32% yang dicapai daripada pengiraan teori. Pengiraan teori ini dibuat dengan menjangkakan kadar hasil keseimbangan maksimum berdasarkan sistem tenaga bebas Gibbs dengan anggapan bahawa semua pepejal telah ditukarkan kepada singas (kecekapan penggasan 100%).

GASIFICATION OF OIL PALM BIOMASS IN HOT COMPRESSED WATER (HCW) FOR PRODUCTION OF SYNTHESIS GAS

ABSTRACT

The study on the HCW gasification of the oil palm empty fruit bunch (EFB) fibers was investigated in a batch system using a high-pressure autoclave reactor. The reaction parameters investigated were solid particle size, solid loading, reaction time, and temperature. The optimum reaction conditions were 380.0 ^{o}C, 5.0g solid/300.0 g water, 30.0 min reaction time, and particle size of $250 < X < 500$ µm which produced gases mainly of CO_2, CO, $H_{2,}$ and CH_4 with gasification efficiency of 32.15% and H_2 yield of 7.22%. The study also focused on 2 types of homogenous catalyst, NaOH and K_2CO_3 and their effects towards the reaction. The optimal amounts identified were 3.0 wt% (K_2CO_3) and 6.0 wt% (NaOH) with gasification efficiency achieved of 39.04% and 31.68% respectively and H_2 yield of 19.03% and 12.15%. The lower heating value for the product gases mixture, $LHV_{mixture}$ for reaction without catalyst and with 3.0 wt% of K_2CO_3 were in the middle range (7.32 and 8.86 MJ/Nm^3). However, reactions with the addition of 6.0 wt% of NaOH gave product compositions with high quality heating value of 14.25 MJ/Nm^3.

The reliability of response surface methodology (RSM) in conjunction with central composite rotatable design, CCRD were used to determine the functional relationships between the 3 operating parameter i.e. reaction time, solid loading, and temperature with the aim of optimizing 2 responses i.e. gasification efficiency and hydrogen yield. Apart from single response, the multi- responses optimization was also performed to find the optimal process parameters such that both responses were

maximized simultaneously. The maximum gasification efficiency predicted from the single response optimization was 29.55% (372.7 ^{o}C, 5.5 g solid loading, and 47.7 min) and the maximum H_2 yield predicted was 6.01% (380.0 ^{o}C, 5.0 g solid loading, and 29.5 min). The multi response optimization indicated sets of solutions, which gave the maximum desirability for both responses with predicted gasification efficiency range of 31.22-32.28% and H_2 yield of 7.09-7.34%. The same optimum conditions were used for additional experimental run with addition of K_2CO_3 and NaOH for comparison purposes. The efficiency of the gasification increased significantly from 33.38% (without catalyst) to 61.56% (6.0 wt% NaOH) and 78.43% (3.0 wt% of K_2CO_3). For H_2 yield, the increase was from 7.77% (without catalyst) to 32.54% (6.0 wt% NaOH) and 48.32% (3.0 wt% of K_2CO_3).

The exergetic efficiency analysis was applied to the reaction in a batch system in order to provide a true measure of the performance of the reaction from the thermodynamic point of view. The highest exergetic efficiency obtained from experimental work was 8.37% compared to 25.32% as obtained from the theoretical calculations, which predicted the maximum equilibrium yield based on the Gibbs free energy of the system based on the assumption that all solids were converted into synthesis gases (100% gasification efficiency).

CHAPTER ONE

INTRODUCTION

1.1 World Energy: History and Chronology

Energy has become a necessity in ensuring the survival of humanity. Therefore, it is vital to study its history and chronology to understand the magnitude of its influence and importance in human life. Energy is aptly described as similar to life where it goes in circular motion, a continuous process of conversion and transformation. The establishment of man on earth thousands years ago and its continuing survival on earth was largely dependent on the ability to harness energy for its usage. From the beginning of evolution to the establishment of civilization, the ability to tap into human mental capability, exploitation of knowledge and learning from experiences had been the contributing factors to the success of human survival. However, no matter how much success we achieved in this golden era, the importance of god given natural resources both renewable and non-renewable such as coal, oil, natural gas, wind, biomass etc. for energy generation cannot be denied.

Although the initial period of human exploration into energy generation was not successfully established, it was believed that it originated about 400,000 years ago in China, when prehistoric man made one of the most important discoveries on how to control fire by using wood (Oracle Think Quest, 2008). Since then, wood became major source of heat, light in the form of fire for purpose of food preparation, drinking water, temperature control and even as weapons in warfare. As the centuries roll in, people learned that burning fossil fuels was more efficient than wood therefore started to use oil to fuel their lamps and coal to feed the fire.

Ironically, in the beginning era of energy exploitation for large-scale application, renewable sources were used dominantly (Oracle Think Quest, 2008). For example, the energy that powered the economy of the world in the 1700s ran largely on wood (for heating), oats (for horses), wind (for sailing ships), and river (for water wheels) (Cobb, 2007). These pioneer renewable technologies were simple and basic in its construction, application and did not require high-energy input.

As often said, the beginning of something also signified the ending of another. The era known as the Industrial Revolution (dated from 1760-1850) changed the primary energy use from renewable sources to sources with a much higher energetic value such as coal and oil (Edinger and Kaul, 2000). Advances and fundamental changes in the agriculture sector resulted in the increase of food supply and raw materials while the recent developed new technology and transformation of industrial organization and practice contributed to increased production, efficiency and profits (Montagna, 2008). During that period, the acceleration of industrialization was at a higher rate, which demanded a large amount of energy then the capacity of the renewable sources. In addition, fossil fuels, which were cheaper with benefits of availability at any place, non-dependent from the availability of wind or water, were perceived as the better alternatives of source. Both of these factors were certainly the trigger factors to the emergence of crude oil domination as the major energy provider for decades that ultimately became the main cause of significant political events around the world.

1.2 Non-Renewable Energy Resource and Use

1.2.1 World Non-Renewable Energy Profile

The recent madness dominating headlines everywhere were due to the rapid increase of oil price in the span of 3 decades causing chaotic situations. These unforeseeable circumstances were attributed to serials of significant events such as the Yom-Kippur war, 1979-1980 Iranian Revolution, political complications in Middle Eastern countries such as Iraq – Kuwait War, and Iraq Invasion (Wirl, 2007). Although the events mentioned above had past, the projected future of oil, remain bleak. Currently the world oil supply is controlled by the members of Organizations of the Petroleum Exporting Countries (OPEC). Formed in 1960 with initial 5 founding members, Iran, Iraq, Kuwait, Saudi Arabia, and Venezuela, this powerful organization holds the upper hand in controlling the price and to certain extent the quantity of oil released to the market, which caused the erratic situations (Wirl, 2007 and Williams, 2007). Economically, the price of oil/barrel had grown exponentially from about USD$28.83/barrel in 2003 to USD$147.27/barrel in July 2008 (Kennedy, 2008), an increase of more then 400% in a span of 5 years.

Putting aside the price issue, the existing world oil capacity itself is a major issue. It was commented by Bentley, (2002) that world oil supply will soon be at physical risk due to sum of supply from all countries except for the 5 main Middle-East suppliers was near the maximum set by physical resource limits. It was predicted, if the current trend continues, peaking of the conventional oil production is likely to be around 2010 to 2030. Another issue that needs to be addressed is the unequal distribution of the reserves for mineral oil and natural gas in the world. More than 70% of these reserves were found within the ”strategic ellipse” of countries which extends from Saudi Arabia to the south, Iraq, Iran, and Russia (Muller-Steinhagen and Nitsch, 2005). This uneven concentration of source within a small group of countries caused the increase in market dominance and the power to control the market price. Both of these factors substantially contributed to the world energy crisis, which is on the verge of its explosive period.

The world consumption of crude oil in comparison with production from 1996 - 2006 is shown below in Figure 1.1 as obtained from BP (British Petroleum) (2007). The total consumption was consistently higher then the production yearly despite the increasing trend of production, which demonstrated the urgency in demand of energy worldwide. Muller-Steinhagen and Nitsch, (2005) established that whereas the world population has quadrupled since 1870, to 6.0 billion at present, the worldwide energy consumption of fossil resources in the form of coal, oil and natural gas had in fact increased by factor of 60 to the present level of 99.96 quadrillion Btu.

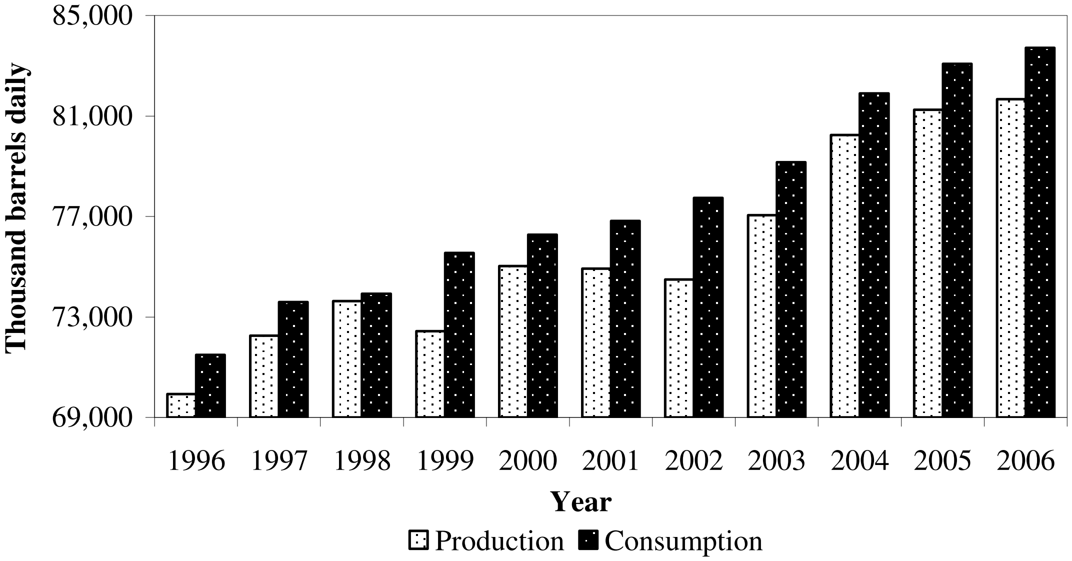

Figure 1.1: World crude oil production and consumption from 1996-2006 (BP, 2007).

1.2.2 Malaysia Energy Profile

For a better understanding of the current energy situation in Malaysia, it is therefore necessary to study its energy profile. Malaysia with total population of 25.27 million as for July 2008 and land area of 329,750 km^2 (CIA, 2008) is blessed with a plentiful and relatively cheap supply of conventional energy resources such as oil, natural gas and coal. The country economy was accelerated with its involvement in information technology and electronic, both identified as the main significant driver. With the rapid economic growth enhanced by the country structural transformation from agricultural-based economy to industrially orientated nation, therefore the burden on providing adequate energy supply especially electricity has never been this crucial.

The crucial role of energy in this country's survival and development has long been acknowledged and identified with the formation of various policies concerning this matter. The early venture into the this foray started with the establishment in 1974 of Petroliam Nasional Berhad (PETRONAS) as the national oil company responsible for the exploration, development, refining and marketing of Malaysia's petroleum products (UNDP, 2007). This was followed by the National Petroleum Policy in 1975, introduced to ensure optimal use of petroleum resources, regulation of ownership and management of the industry, and economic, social, and environmental safeguards in the exploitation of this valuable resource (UNDP, 2007). The country total primary energy production in 2005 was 3.90 quadrillion Btu while the total energy consumption was 2.55 quadrillion Btu as obtained from EIA (Energy Information Administration), (2007a). The primary energy source for Malaysia came from fossil fuels with both crude oil and natural gas held the lion share of 96.09% of the total production. Interestingly enough, the energy from renewables such as hydroelectricity and combustible wastes account to only 0.53% for the former and 2.99% for latter (EIA, 2007a).

The total primary energy consumption from 1980 to 2005 is shown below in Figure 1.2 in conjunction with the total energy production. As shown in the figure, the energy consumption in Malaysia had increased over five fold in the span of 25 years from 0.42 (1980) to 2.55 quadrillion Btu (2005) while the production increased from 0.66 in 1980 to 3.90 quadrillion Btu in 2005. In general, transportation sector was the largest consumer of energy in Malaysia followed industrial, residential and commercial sector in which all are expected to increase the demand by over 6% during the year 2006-2010 (UNDP, 2007).

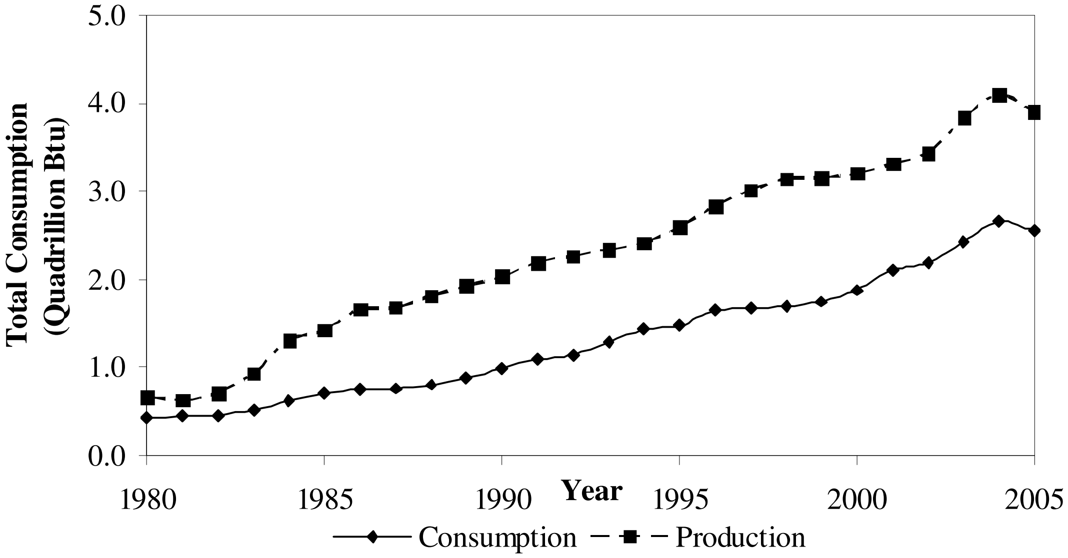

Figure 1.2: Total primary energy consumption and production for Malaysia from year 1980-2005 (IEA, 2007a).

The impact of world oil crisis in recent years especially in 2006 affected Malaysia significantly with the move by the government to trim its subsidies for petrol and diesel by raising its pump prices to 40%. The increases in oil demand but limited reserves certainly caused great concern on its impact to the country future, hence forcing the re-evaluation of the country strategies and existing policy towards embracing new renewable sources to countermeasure these global issues.

Apart from economy and supply complications, the utilization of fossil fuels also caused environment degradation. In fact, fossil fuels were identified as the main cause of various environmental catastrophes at local, regional, and global level (Goldemberg, 2006). The combustion of fossil fuels to generate energy for the industries and commercial vehicles released various harmful pollutants, including Sulphur oxides (SO_x), Nitrogen oxides (NO_x), Carbon monoxide (CO), Carbon dioxide (CO_2), particulate matter (PM) and volatile organic compounds (VOC). The releases of GHG (greenhouse gases) such as CO_2 to the atmosphere caused greenhouse effects and altered the composition and function of entire ecosystems (Goldemberg, 2006). In 2005, it was determined by EIA, (2007b) that the total world CO_2 emissions from fossil fuels were 28,193 million metric tons with Malaysia contributed 155.51 million metric tons itself, making it the world ranked number 28 in terms of total emissions.

Ultimately, the urgent need to curb growth in the demand of the fossil fuels, increasing the geographic and fuel supply diversity, and to mitigate climate-destabilizing emissions such as greenhouses gases pushes the need to find and develop renewable energy resources.

1.3 Renewable and Green Energy for Sustainable Development

1.3.1 Introduction

As mentioned in previous section, the exponential development in industrial sectors catalyzed by the expansion of human population caused the persistent increase in annual energy use per capita. In order to sustain the needs, it required the increase use of all sources of energy. There is a significant correlation between energy and sustainable development. Energy is very crucial to sustainable development as it plays an important role in almost every field of human activities i.e. social, economic, and even politics. The controversial soaring prices of energy and the destabilizing geopolitical events were certainly a serious reminder of the essential role of affordable energy plays in economic growth and human development and of the vulnerability of the global energy system to supply disruption (UNDP, 2007). Therefore, there is an urgent need to find and develop new green energy strategies for the sustainable development of the future with minimum impact on the environment. In regards to the environment, this new energy source should able to reduce the negative effects of fossil fuels and the overall emissions from electricity generations, decreases the greenhouse gases, and meets the clean energy demand for both industrial and non-industrial applications (Midilli *et al.,* 2005).

1.3.2 World Renewable Energy Profile

Renewable energies such as hydroelectric power, solar thermal, solar photovoltaic, geothermal, wind, and biomass energy had in fact been utilized by several industries although the share of its production and consumption was still at miniscule level at best due to certain complications. An observation of the past 200 years showed a relationship between the level of industrialization and its dependence of fossil fuels. Many countries have thus realized the need to harness local resources to increase the security of energy supply and reverse fossil fuel dependency. As a result, there is a general trend to search for alternative energy involving locally renewable resources. Various countries have chosen different paths to move towards sustainable energy systems. For example, the United Kingdom (UK) Government has set out its ambition of securing 20% of electricity from renewable sources by 2020 (Gross, 2004), while Ministry of Economic Affairs of Netherlands stated its goal of 10% renewable energy by 2020 (Agterbosch *et al.,* 2004). Figure 1.3 shows the total consumption of renewable energy in the world from year 2003-2007.

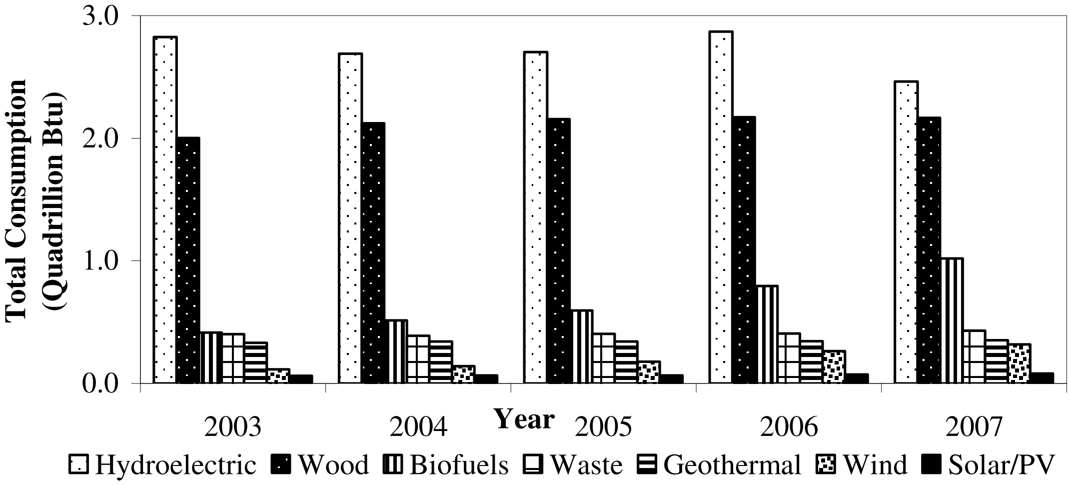

Figure 1.3: Total consumption of renewable energy in the world from 2003-2007 (EIA, 2007c).

The types of renewable energy shown in this figure constitutes of biomass (wood and wood derived fuels, municipal solid waste, and biofuel such as fuel ethanol and biodiesel), hydroelectric, geothermal, solid, wind. As observed, the consumption percentage for 2003 in comparison to 2007 saw an increase of about 11.05%. The increase though still minimal definitely proved that with proactive efforts from all responsible parties, renewable energy certainly has a promising future. Apart from biofuel that showed an increasing trend for the past 5 years, others had a mixed trend without any significant increase for any of the years discussed here. The increase in biofuel trend were largely contributed by the higher production and consumption of bio-ethanol and biodiesel especially in United States enhanced by the introduction of various policies and incentives such as federal tax laws that provided incentives of 51% per gallon tax credit for each gallon of ethanol blended into gasoline.

The non-consistent trend in other types of renewables indicated the minimum progress achieved so far in the development of those technologies mostly due to various complications associated with each sources. For example although hydropower is one of the only mature technology developed worldwide and has long been used for economic generation of electricity, but its high initial construction cost and the destructions to the ecological, had halted its charted progress. Biomass such as wood and plant wastes has the potential as ideal renewable sources since the input materials were essentially zero value and can be converted into valuable heat and energy source. However, the existing combustion technology for biomass is still far from perfect especially with its very low efficiency thus its non-competitive production price in comparison with other fossil fuels.

1.3.3 Malaysia Renewable Energy Profile

The urgent demand for fossil fuels in various sectors despite its steadily declining reserve in the recent years posed a major challenge to the country. Realizing this possible catastrophe, the government had introduced various reforms to its energy sector in order to make it become more competitive at lower cost of production. One of the significant decisions was the introduction of the 1981 Four Fuel diversification policy, which emphasized on the fuel diversification designed to avoid dependence on oil while aimed at placing increased emphasis on gas, hydroelectricity, and coal (UNDP, 2007). In 2000, the government realized the importance of biomass to intensify the development of the country renewable energy, therefore the inclusion of renewable energy as the “fifth fuel” policy. The policy was set out with a target of renewable energy providing 5% of the electricity generation by 2005 (500-600 MW) of installed capacity (BCSE, 2005).

In 2001, there was a significant leap towards the utilization of renewable energy in power generation, with the launching of the Small Renewable Energy Power Programme (SREP) with its primary objective was to facilitate the expeditious implementation of grid-connected renewable energy resources-based small power plants (Chuah, *et al.,* 2006). With this programme, private sectors were encouraged to undertake small power generation projects using renewable sources including biomass, biogas, municipal waste, solar, mini-hydroelectricity, and wind energy (UNDP, 2007).

The production of biodiesel as an alternative source of biofuel in Malaysia had received majority share of news this recent years. Biodiesel are produced from oil palm in which the crude palm oil, crude palm stearin, and crude palm kernel oil were converted to methyl esters (Chuah *et al.,* 2006). Biodiesel produced via oil palm possessed similar properties to petroleum diesel and can be used directly as fuels in unmodified diesel engines. The pilot testing of this technology into real vehicles was demonstrated in 2006 with the introduction of B5, a blend of 5% refined olein and 95% diesel, known as Envodiesel in vehicles (Sumathi *et al.,* 2007). With this encouraging development, therefore the next step was towards its commercialization. This was achieved by the construction of 2 biodiesel plants with projected capacity of 60,000 metric tons of production in Port Klang, Selangor and Pasir Gudang, Johor (Chuah *et al.,* 2006).

Currently Malaysia is the second largest producer and exporter of palm oil, producing about 47.0% of the total world supply in 2007. With the projected growth in the cultivation of oil palm, the destination of the huge amount of residues raised concerns. The supply of oil palm biomass and its processing byproducts were found to be 7 times more than the availability of natural timber (Basiron and Chan, 2004). This huge amount of biomass is an ideal energy source, which could be tapped for further utilization. In fact, many of the palm oil mills in Malaysia are using palm fibre and shell as the boiler fuel to generate heat and electricity for the production processes (Chuah *et al.,* 2006). It was estimated in the year 2004 about 1400 million kWh of electricity was generated and consumed by the palm oil mills (Chuah *et al.,* 2006). However, more often than not, the energy requirement for the oil palm mills was much lower in comparison with the amount of biomass produced forcing the excess to be disposed off separately.

Besides solid biomass, palm oil mills also produced large quantities of liquid wastes known as Palm Oil Mill Effluent (POME). Due to its high biochemical oxygen demand (BOD), the substances were treated prior to its discharged into the environment. POME were normally treated by anaerobic process, which in return produces biogas, an important source of energy due to its high heating value. Although the technology is still in development stage, there had been successful examples as demonstrated by a private company, Keck Seng (Malaysia) Berhad (Chuah *et al.,* 2006). The company had developed a closed tank anaerobic digester system for POME biogas capture and utilization, and currently in the progress of commercializing its technology for wider utilization by others.

1.4 Synthesis Gas (Syngas) and Hydrogen: Production and Potential

1.4.1 Synthesis Gas (Syngas)

Synthesis gas or syngas is actually a gaseous mixture consisting of Hydrogen (H_2), Carbon monoxide (CO), Carbon dioxide (CO_2), and Methane (CH_4). Syngas is widely useful either as intermediates or as final product in transportation fuels, electricity and heat generation, chemical production or even for biobased products, which includes organic acids, alcohols, and polyesters (Wang *et al.,* 2008). The routes of syngas utilization for transportation fuels, energy generation, and chemical production are simplified below in Figure 1.4 as shown by Huber *et al.* (2006) in its publication.

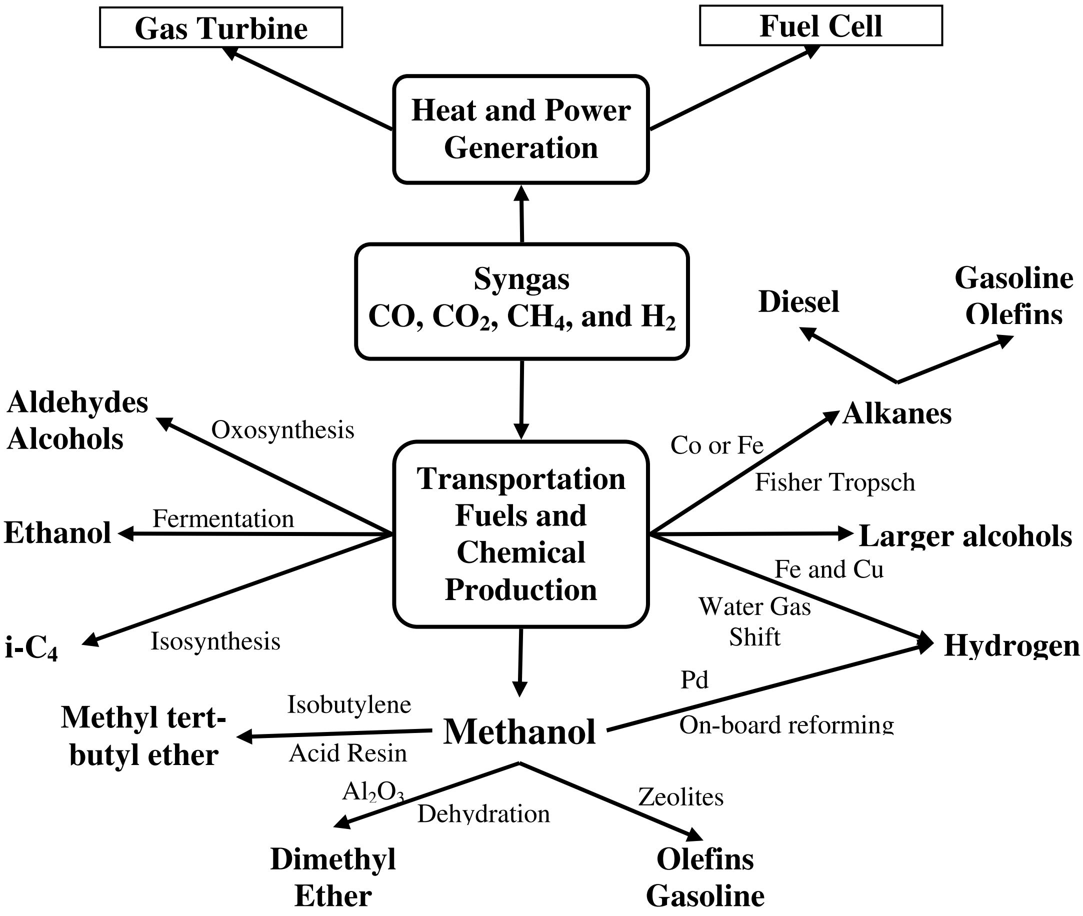

Figure 1.4: The routes of syngas utilization for transportation fuels, energy generation, and chemical production (Huber *et al.,* 2006).

In general, the fuels produced from syngas included hydrogen (water-gas shift reaction), methanol (by methanol synthesis), alkanes (by Fisher-Tropsch synthesis), isobutene (by isosynthesis), ethanol (by fermentation), and aldehydes or alcohols (by oxosynthesis) (Huber *et al.,* 2006). Fisher- Tropsch (FT) synthesis is one of the widely preferred conversion method in which syngas are converted into liquid hydrocarbon fuels. FT liquids are free of sulphur and contain very few aromatics compared to gasoline and diesel (Tijmensen *et al.,* 2002). The low number of aromatics in the compositions resulted in lower emissions levels when applied to the normal combustion engine. This process is currently operated commercially at Sasol South Africa and Shell Malaysia with utilization of coal for the former and natural gas for the latter as the feedstock (Tijmensen *et al.,* 2002).

In addition, syngas is widely used as intermediates for production of valuable chemicals such as ammonia, olefins, acetic acid, acrylates, etc. Syngas is also particularly important in the generation of heat and power. High quality syngas with zero tar, dust, and high heating value can be fed to gas engines directly or gas turbines for power generation (Wang *et al.,* 2008). Another alternative is by converting the CH_4 and CO into more H_2 through further water reforming and water gas shift reactions and subsequently utilized with O_2 in fuel cell to produce electricity

Currently, syngas production is mainly from fossil fuels such as natural gas, naphtha, residual oil, petroleum coke, and coal through steam reforming method or gasification (Wilhelm *et al.,* 2001). Steam reforming is the conventional method used to produce syngas. The main disadvantages of this method is its highly endothermic and requires very high reaction temperature (>850 ^{o}C) in addition to the risk of catalyst deactivation due to the formation of carbon onto the catalyst surface (Song and Guo, 2005). Coal gasification is another method widely used in the synthesis of syngas. However, due to partial coal combustion with O_2 and air in order to supply the necessary energy during reaction will result in access CO_2 being released to the environment.

Production of syngas through biomass conversion is another prospective method as a replacement for fossil fuels. Figure 1.5 below shows the various routes for the conversion of biomass to syngas. Currently there are 3 established conversion routes for the production of syngas from biomass i.e. biomass derived oil, biomass derived char and biomass gasification. The conversion of biomass to syngas via gasification can be further divided into 4 different processes (pyrolysis, combustion, steam, direct solar and HCW (>300 ^{o}C) gasification) depending on the medium of reaction and reaction conditions.

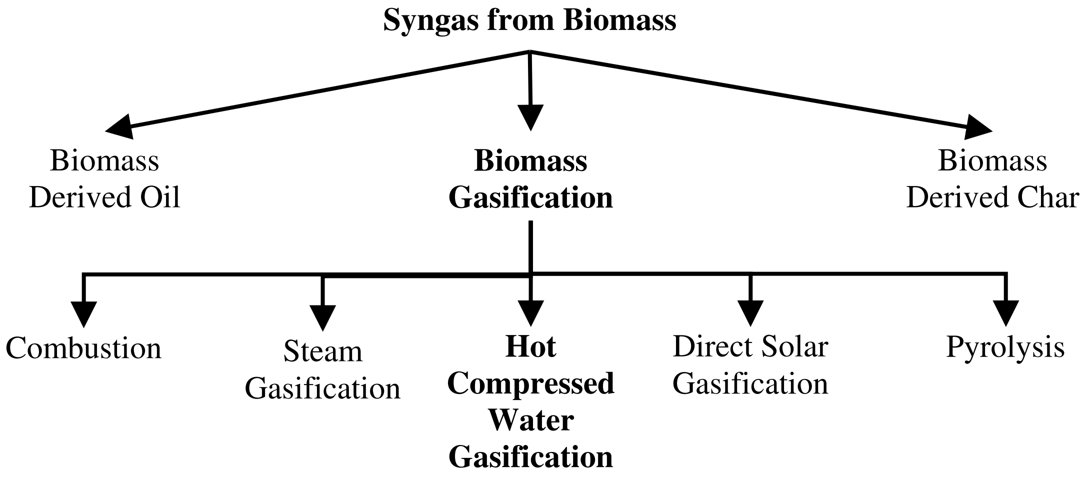

Figure 1.5: The various routes for the conversion of biomass to syngas.

Among the 5 different processes, HCW gasification is a newly developed process. Comparison of this method with others are shown in Table 1.1. Established method for biomass conversion into syngas such as combustion has a low net efficiency ranging from 20% to 40% (Wang *et al.,* 2008). Dinjus and Kruse, (2004) in its study review stated that for biomass with water content of more than 40%, the thermal efficiency of the traditional steam gasification plant decreased drastically from 80% to 10%. Solar gasification method depended heavily on the consistent supply of sunlight, which forced its limitations to certain regions only.

Although the prime disadvantage of HCW gasification is its high-energy requirement for the heating up process, however the components of syngas especially H_2 and CH_4 are substantially high in energy content ultimately producing higher thermal output. With a comprehensive energy recovery system, it will result in high-energy conversion efficiency of the reaction. In addition, heteroatom constituents in biomass such as Sulfur and Nitrogen will leave the process with the aqueous effluent hence avoiding expensive preliminary cleaning gas process.

Table 1.1: Comparison of different methods for biomass conversion to syngas (Huber *et al.,* 2006).

Method	**Technical Description**	**Advantages**	**Disadvantages**
Biomass Pyrolysis	Thermal conversion at temperature range of 350-550 °C in the absence of air/oxygen	Produce hydrogen directly.	a. High char abrasion & erosion to equipment b. Catalyst deactivation due to char.
Biomass Combustion	Direct burning of biomass in the presence of air to convert the chemical energy into heat and power i.e. mechanical & electricity	Simple and available technology	a. Feasible only for biomass with low moisture content b. Requires feedstock pretreatment
Steam Gasification	High rate pyrolysis carried out with steam in a fluidized bed gasifier at the temperature of 700-850 °C	Maximum conversion can be obtained.	Thermal efficiency decrease drastically for biomass with high moisture
Direct Solar Gasification	Solar energy concentrated to temperature above 1700 °C to activate chemical reactions.	High hydrogen yield can be obtained.	Efficiency is low due to re-radiation loss.
HCW Gasification	Biomass is gasified in HCW near & in the vicinity of the supercritical temperature and pressure	Suitable for biomass with high moisture content	Complications due to the high energy requirement

1.4.2 Hydrogen Gas from Syngas

Hydrogen is often cited as the unlimited clean energy resources. It is colorless, odorless, and most importantly non-poisonous. It has long been acknowledged of its capability and advantages from environment and economic standpoint to replace the conventional fossil fuels. The use of hydrogen in fuel cells is a promising technology to supply heat and power for various applications. Vehicles powered by hydrogen fuel cell technology are 3 times more efficient than a gasoline powered engine (Momirlan and Veziroglu, 2005). This technology is already used by several major car producers such as BMW, American Honda Company and Toyota Motors. This environmental friendly technology is certainly in line with the Kyoto Protocol, which demanded the industries to reduce its greenhouse gas (GHG) emissions through reduced diesel use (Nath and Das, 2003).

One of the potential sources of hydrogen is from biomass. Biomass can be converted into hydrogen energy via 2 different process routes i.e. thermochemical (pyrolysis, gasification, partial oxidation, and liquefaction), or biological (fermentation, biophotolysis and biological water gas-shift reaction) processes (Nath and Das, 2003). Thermochemical method produced mixture of gases (CO, CO_2, CH_4, and H_2), or syngas but not pure hydrogen. Therefore, the challenge is on converting this mixture into rich H_2 gas for further utilization. The gaseous mixture from biomass thermochemical gasification could be further converted to hydrogen rich gas via water-gas shift (WGS) reaction of CO and water to H_2 and CO_2 with different types of catalyst (both homogenous and heterogeneous). The unwanted CO_2 in the gaseous mixture could be further removed by using adsorbent such as CaO, which can react with CO_2 to produce $CaCO_3$ (Wang *et al.,* 2008).

The WGS reaction to produce higher H_2 content in the product gas was successfully demonstrated by Zhang *et al.* (2004) using commercial CO-shifts catalysts in two fixed bed reactors operated in series. This 2 shift reactors were divided into low and high temperature. The high temperature-shift reactor was for rapid reaction at elevated temperature for faster kinetics to convert about 75% of the CO into H_2. Meanwhile, the lower temperature reactor functioned to shift the thermodynamic equilibrium of the reaction to produce even lower concentration of CO in the mixture (Zhang *et al.,* 2004).

Additional H_2 purification were done by using pressure swing adsorption (PSA) with water as the solvent as suggested by Ji *et al.* (2006). It was established that by using the high-pressure separator followed by low-pressure separator, significant concentrations of CO_2 and other gases were dissolved in the water phase leaving the purified H_2.

As stated previously, one of the concerns regarding the utilization of biomass as a source of renewable energy is on its sustainable, sufficiency of supply in long term without sacrificing other vital issues such as environmental, and the competition for land for food issue. It is therefore vital to identify the types of plantation that are suitable for this purpose while at the same time fulfills all the prerequisite requirements.

1.5 Oil Palm Biomass

Oil palm, Elaeis *guineensis*, is a tree whose fruits are used for extraction of edible oil. Originated from South Africa, it is cultivated in all tropical areas of the world and has become one of the main industrial crops. The reddish in color fruit grows in large bunches, each weighing at about 10-40 kg. Inside each fruit is a single seed also known as the palm kernel surrounded by the soft pulp. The oil extracted from the pulp is edible oil used for cooking, while those extracted from the kernel is used mainly in the soap manufacturing industries.

Oil palm topped the ranking as number 1 fruit crops in terms of production for year 2007 with 36.90 million tonnes produced or 35.90% of the total edible oil in the world (MPOC, 2007). Oil palm is now one of the major economic crops in a large number of countries, which triggered the expansion of plantation area around the world (Yusoff, 2006). Overall, the oil palm account for about 29.04% of the total oil crops production in Asia region and 21.16% for Africa (FAO, 2007).

In Malaysia, total mature areas of oil palm plantation represent 56.00% of the total agricultural land and 11.75% of the country's total land area. The evolution of world plantation area and the total production of oil palm from 1980-2005 is shown in Figure 1.6. It is observed that the production consistently increases each year with total in 2005 amounts to 33.73 million metric tons.

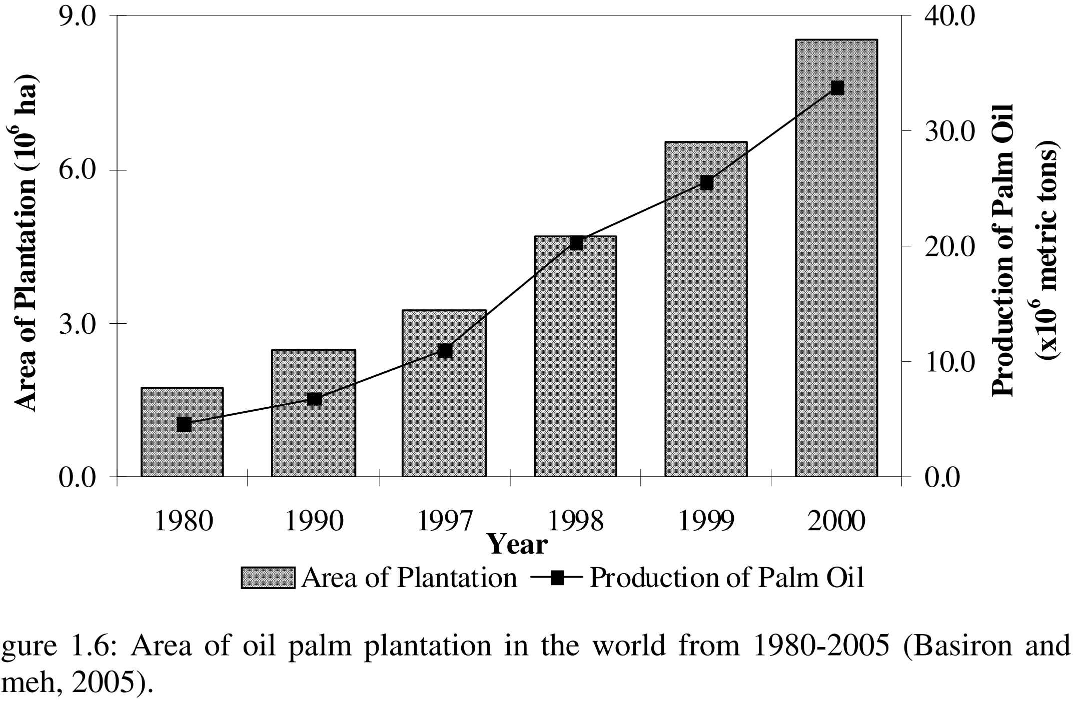

Figure 1.6: Area of oil palm plantation in the world from 1980-2005 (Basiron and Simeh, 2005).

With the projected growth in the cultivation of oil palm, the concern is on what should be done with the enormous quantities of waste. Every year, oil palm industries produced more then a hundred million tons of waste worldwide. Fresh fruit bunch (FFB) contained only 21% palm oil while the rest, 6-7% palm kernel, 14-15% fibre, 6-7% shell and 23% empty fruit bunch (EFB) were left as biomass (Umikalsom *et al.,* 1997). In total, a hectare of plantation can generate 4.42 (20.43%) tons of EFB, 1.10 (5.09%) tons of palm kernel shells, 2.52 (11.65%) tons of palm kernel trunks, 10.88 (50.30%) tons of fronds and 2.71 (12.53%) tons of mesocarp fibers for a total of 21.63 tons of biomass per hectare each year (Singh *et al.,* 1999).

The world annual palm oil biomass generation from 1980-2005 is shown in Figure 1.7 below (MPOC, 2007). As observed, the percentage of biomass produced from oil palm had increased tremendously since 1980 until 2005 contributed by the expansion of the crop plantation due to the high demand for palm oil. In total, for the year 2005, 184.5 million tons of oil palm biomass was produced worldwide.

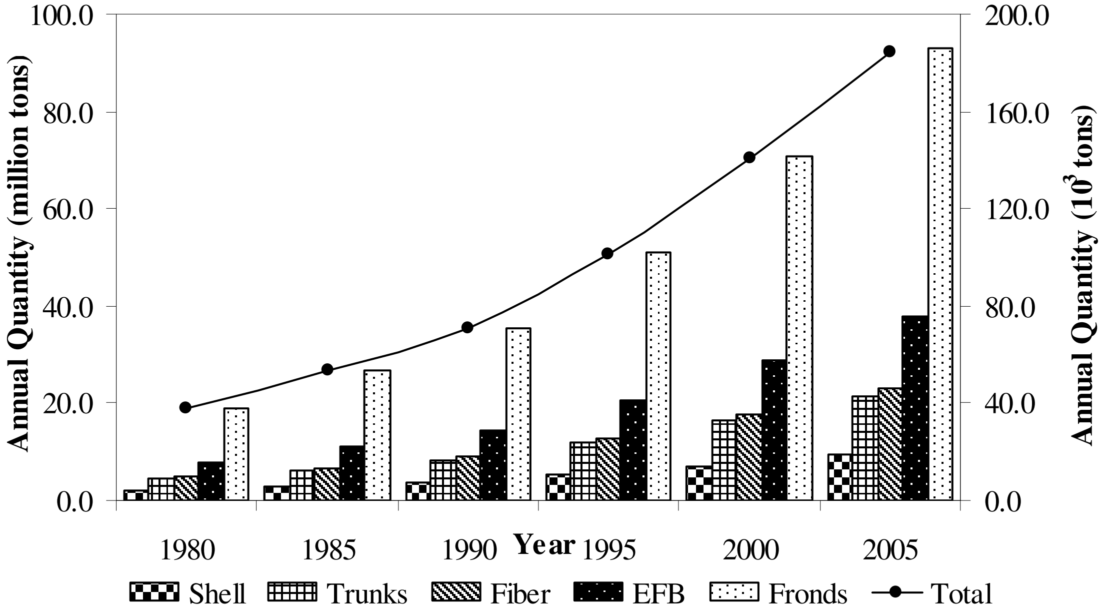

Figure 1.7: World annual oil palm biomass generation from 1980-2005 (MPOC, 2007).

Currently oil palm biomass is converted into various types of value-added products via several conversion technologies that are readily available. For example, fibers from EFB were used to make mattresses, seats, insulations etc (Basiron and

Simeh, 2005). Ashes produced from incineration of EFB were used as fertilizer/ soil conditioner due to its high organic and nutrient content beneficial to crops. Paper making industry utilized paper pulp from oil palm biomass for its various end usage purposes. Nevertheless, it had its limitations since the presence of even a small quantity of oil caused fouling effect to the end product therefore affecting its quality.

On the other hand, the volume of oil palm biomass produced annually were much more compared to the quantity used in these conversion process causing surplus in source and ultimately forced the biomass to be discarded. Fibre, shells, and EFB were generally dumped in open areas or disposed by open burning generating pollutant gases harmful to the environment (Yusoff, 2006). In some other cases, fibre and shells were used as source of energy in the processing mill itself to generate heat and electricity via combustion reaction (Yusoff, 2006). However, this practice was not feasible due to the high moisture content in the biomass and huge amount of energy required for complete combustion thus reducing significantly the energy efficiency in the reaction.

Realizing above complications, there is an urgent need of transforming these wastes into a more valuable end product. A promising option is by converting it into syngas via gasification in HCW. Oil palm biomass is the perfect candidate as feedstock for the gasification process. It has high energy and moisture content (>50%), both integral requirements for this particular reaction and for generation of renewable energy. The insignificant amount of trace minerals in the biomass composition is an added advantage for the reaction.

1.6 Problem Statement

Experts and decision makers widely agree that alleviation of climate change is humanity's greatest threat and challenge for the 21st century and beyond. Approximately 80% of the world primary energy consumption is still dependent on fossil fuel. Progressive emission of greenhouse gases (GHG) especially from power generating plants has been identified as the main cause of global warming. Renewable energy has attracted a large amount of interest with vast emergence of studies and researches produced annually. Far too long dependency on fossil fuels has caused worldwide energy crisis and escalating environmental complications, making it even more necessary to find the new best candidate.

Currently the main method of producing syngas and hydrogen is from fossil fuels i.e. natural gas, naphtha, petroleum coke, and coal through steam reforming method or gasification, which supplies majority of the production in the world. However, apart from its severe dependence on fossil fuels as its feedstocks, this non-environmental friendly production is highly endothermic and requires a very high temperature (>800 ^{o}C). This in turn caused a very low in net energy efficiency (Song and Guo, 2005).

Biomass has the potential as an alternative to be converted into energy via syngas production. Currently, there are numerous established methods of syngas conversion from biomass, including pyrolysis, liquefaction, combustion, pyrolysis, solar and steam gasification. The major complications faced with these technologies are often associated with its very low energy efficiency, for example, biomass combustion has a net efficiency of about 20-40% (Wang *et al.,* 2008). In addition, the current methods of production from biomass are still not economically competitive. This high production cost proves to be the major obstacle in the field or renewable energy although the transition into electricity power has been established for decades.

A large portion of biomass waste is actually wet biomass containing very high percentage of water, which caused high drying costs when classical gasification process is used. Therefore, gasification of biomass in HCW is a promising technology for utilizing high moisture content compounds. Although the prime disadvantage of the HCW (>300 ^{o}C) gasification is its initial energy requirement for the heating up process, however the components of syngas especially H_2 and CH_4, is substantially high in energy content which ultimately produced a much higher thermal output. With a comprehensive energy recovery system, it is believed that it will result in high-energy conversion efficiency of the reaction.

Oil palm biomass is the perfect candidate as the feedstocks for the gasification process. It has high moisture content (>60%), and insignificant amount of trace minerals in its compositions are the 2 integral requirements for reactions in HCW medium. The huge amount of biomass readily available in abundance certainly guarantees its sustainable supply allowing continuous operation of the process yearlong. With this realization, thus the study of new and better method of production is proposed with the title as following: **"Gasification of Oil Palm Biomass in Hot Compressed Water (HCW) For Production of Synthesis Gas"**