PRODUCTION OF BIOFUEL FROM OIL PALM BIOMASS USING SUBCRITICAL AND SUPERCRITICAL LIQUEFACTION

by

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Thesis submitted in fulfillment of the requirements
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This Thesis is dedicated to my beloved
Wife (Anahita), Kids (Yasaman& Mehrasa),
Mother, Brothers, Sisters,
and to the memory of my late Father.

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LIST OF ABBREVIATIONS

AI	Acetone Insoluble
ANOVA	Analysis Of Variance
AS	Acetone Soluble
BS	Benzene Soluble
CCRD	Central Composite Rotatable Design
DES	Diethyl Ether Soluble
DOE	Design Of Experiments
DP	Degree of Polymerization
EFB	Empty Fruit Bunch
EIA	Energy Information Administration
F-value	Fisher‟s F value
FFB	Fresh Fruit Bunch
FPF	Oil Palm Fruit Press Fiber
FTS	Fischer–Tropsch Synthesis
GC/MS	Gas Chromatography / Mass Spectroscopy
GNP	Gross National Product per Capita
GP	Gaseous Product
HCW	Hot compressed water
HMF	Hydroxyl Methyl Furfural
HTFT	High Temperatures Fischer–Tropsch
HTU	Hydrothermal Upgrading
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change

K_2CO_3	potassium carbonate
LCC	Lignin-Carbohydrates Complex
LCM	Lignocelluloses Materials
LP	Liquid Product
LTFT	Low Temperatures Fischer–Tropsch
NREL	National Renewable Energy Laboratory
MPOC	Malaysia Palm Oil Council
MPOB	Malaysia Palm oil Board
MSW	Municipal Solid Wastes
Mtoe	Million tonnes of oil equivalent
Na_2CO_3,	Sodium Carbonate
NaOH	Sodium Hydroxide
NREL	National Renewable Energy Laboratory, USA
OPEC	Organization of the Petroleum Exporting Countries
OPS	Oil Palm Shell
P-value	Probability value
Pd	Particle size
PRESS	Prediction error sum of squares
RSM	Response Surface Methodology
SCW	Subcritical /Supercritical Water
SCF.	Supercritical Fluid
SD	Standard Deviation
SOx	Sulfur Oxides
SR	Solid Residue
TAPPI	Technical Association of the Pulp and Paper Industry

TCC	Thermochemical Conversion
TCD	Thermal Conductivity Detector
TACD	Trends in Atmospheric Carbon Dioxide
TPEFS	Total Primary World Energy Supply
UNDP	United Nation Development Program
WS	Water-Soluble
$ZnCl_2$,	Zinc Chloride

LIST OF SYMBOLS

Symbol		**Units**
β0	Intercept coefficient	Dimensionless
βi	Linear term coefficient	
βii	Squared term coefficient	
βij	Interaction term coefficient	
εa	Standard errors	
Xi, and Xj	Uncoded independent process variables	
ρ	Density	Kg/m^3
ρc	Critical density	Kg/m^3
μm	Micron meter	
D	Overall desirability	
n	Number of variable	
P	Pressure	MPa
P_c	Critical pressure	MPa
T	Temperature	K
T_c	Critical temperature	K
T_b	Boiling temperature	K
X	Independent process variables	
Y	Predicted response of the processes	

PENGHASILAN BAHANAPI-BIO DARIPADA BIOJISIM KELAPA SAWIT MENGGUNAKAN PENCECAIRAN SUBGENTING DAN GENTING LAMPAU

ABSTRAK

Projek penyelidikan ini memfokus terhadap kajian penguraian bermangkin dan tak bermangkin biojisim kelapa sawit dalam pelarut subgenting dan pelarut supergenting kepada pelbagai produk cecair dengan menggunakan reaktor autoklaf bertekanan tinggi. Kajian meliputi penguraian biojisim kelapa sawit (tempurung kelapa sawit, tandan buah kelapa sawit kosong dan gentian tekan buah kelapa sawit) dalam pelarut sub/genting lampau (air, metanol, etanol, aseton dan 1,4-dioksana) pada julat suhu 483-603 K. Produk cecair yang diperolehi dipisahkan kepada produk larut air dan biominyak (biomentah) melalui penyarian dengan air, benzena, dietil eter, etil asetat dan aseton.

Hasil produk cecair penguraian tempurung kelapa sawit (OPS) dengan menggunakan pencecairan sub/genting lampau ialah masing-masing 22.0, 24.4, 33.1, 25.6 dan 40.5 % untuk air, metanol, etanol, aseton dan 1,4-dioksana pada 523 K. Hasil produk cecair penguraian tandan buah kelapa sawit kosong (EFB) ialah masing-masing 39.6, 49.4 dan 54.2 % untuk air, etanol dan 1,4-dioksana pada 563 K sementara hasil ialah masing-masing 34.6 dan 52.2 % untuk metanol dan aseton pada 603 K. Hasil produk cecair pencecairan gentian tekan buah kelapa sawit (FPF) di bawah rawatan sub-supergenting ialah masing-masing 49.0, 38.0, 32.5, 38.5 dan 50.5 % untuk air, metanol, etanol, aseton dan 1,4 dioksana pada 563 K. Hasil produk cecair pada masa mastautin malar bergantung kuat kepada suhu tindakbalas, jenis pelarut dan jenis biojisim kelapa sawit. Suhu optimum untuk pengeluaran hasil produk cecair yang ditemui ialah sekitar 563 K sementara air ditemui sebagai pelarut terbaik untuk hasil

produk cecair yang lebih tinggi. Maka, pencecairan air subgenting sebagai teknik hijau yang mesra alam telah digunakan dengan jayanya bagi rawatan biojisim kelapa sawit dan pengeluaran produk cecair atau jenis bahan api yang lain.

Oleh yang demikian, kesan garam logam ($ZnCl_2$) dan mangkin alkali (K_2CO_3, Na_2CO_3 dan NaOH) ke atas penguraian biojisim kelapa sawit (OPS, EFB dan FPF) dengan menggunakan pencecairan air subgenting pada keadaan malar telah dikaji. Hasil produk cecair penguraian OPS dengan menggunakan pencecairan air subgenting ialah masing-masing 47.9, 47.0 dan 53.4 % bagi kehadiran mangkin alkali K_2CO_3, Na_2CO_3 dan NaOH pada 563 K. Hasil produk cecair penguraian EFB ialah masing-masing 61.5, 58.3 dan 67.2 % bagi kehadiran K_2CO_3, Na_2CO_3 dan NaOH pada keadaan yang sama. Hasil produk cecair pencecairan FPF di bawah rawatan air subgenting ialah 35.9 % untuk mangkin $ZnCl_2$ serta 71.4 % bagi kehadiran Na_2CO_3 dan NaOH pada 563 K. Hasil produk cecair pada masa mastautin malar bergantung kuat kepada suhu tindakbalas, jenis mangkin dan jenis biojisim kelapa sawit. Suhu optimum untuk pengeluaran hasil produk cecair yang ditemui ialah sekitar 563 K sementara FPF dan sodium hidroksida ditemui sebagai bahan suapan dan mangkin terbaik untuk hasil produk cecair yang lebih tinggi. Maka, air dan sodium hidroksida telah diterima sebagai pelarut dan mangkin untuk pencecairan FPF melalui rawatan subgenting.

Hubungan fungsi antara masa mastautin, suhu, saiz zarah, muatan sampel dan muatan mangkin berdasarkan kebolehpercayaan Metodologi Permukaan Sambutan (RSM) telah ditentukan bagi tujuan mengoptimumkan dua sambutan iaitu penukaran FPF dan hasil produk cecair. Selain daripada sambutan tunggal, pengoptimuman sambutan berbilang turut dilaksanakan untuk mencari parameter proses optimum. Penukaran maksimum FPF yang diramal oleh pengoptimuman sambutan tunggal

ialah 581 K, muatan sampel 10 g, muatan mangkin 9 %, masa mastautin 37 minit dan saiz zarah 710<pd<1000. Hasil produk cecair tertinggi yang diramal oleh pengoptimuman sambutan tunggal pula ialah 551 K, muatan sampel 5 g, muatan mangkin 9 %, masa mastautin 40 minit dan saiz zarah 710<pd<1000. Set penyelesaian yang ditunjukkan oleh pengoptimuman sambutan berbilang memberikan kebolehinginan maksimum bagi kedua-dua sambutan dengan penukaran FPF yang diramal ialah 93 % dan hasil produk cecair 76 %.

PRODUCTION OF BIOFUEL FROM OIL PALM BIOMASS USING SUBCRITICAL AND SUPERCRITICAL LIQUEFACTION

ABSTRACT

This research project focused on the study of oil palm biomass decomposition to various liquid products in subcritical and supercritical solvents by using a high-pressure autoclave reactor with and without the presence of catalysts. The study which comprised of the decomposition process of oil palm biomass (Empty Fruit Bunch, Fruit Press Fiber, and Oil Palm Shell) in sub/supercritical solvents (water, methanol, ethanol, acetone and 1,4-dioxane) was investigated at the temperature range of 483 - 603K. The liquid products were separated into water soluble and bio-oil (as bio-crude) through extraction with water, benzene, diethyl ether, ethyl acetate, and acetone.

The liquid product yield of Oil Palm Shell (OPS) decomposition using sub/supercritical liquefaction was 22%, 24.4%, 33.1%, 25.6%, and 40.5% for water, methanol, ethanol, acetone and 1,4-dioxan at 523 K, respectively. The liquid product yield of Empty Fruit Bunch (EFB) decomposition was 39.6%, 49.4% and 54.2% at 563K for water, ethanol and 1,4-dioxan whereby for methanol and acetone, it was 34.6% and 52.2% at 603K, respectively. The liquid product yield of Fruit Press Fiber (FPF) liquefaction under sub/supercritical treatment was 49%, 38%, 32.5%, 38.5% and 50.5% for water, methanol, ethanol, acetone and 1,4-dioxan at 563K respectively, depending strongly on the reaction temperature, solvent and oil palm biomass type at the constant residence time. The optimum temperature for the production of liquid product yield was found to be at around 563 K, while water was found to be best solvent for higher liquid product yield. Therefore, subcritical water

liquefaction as green and environmentally friendly technique has been successfully applied for oil palm biomass treatment and production of liquid product or other types of fuels.

Consequently, the influences of metal salt ($ZnCl_2$) and alkali catalysts (K_2CO_3, Na_2CO_3, and NaOH) on the decomposition of oil palm biomass (OPS, EFB, and FPF) using subcritical water liquefaction at the constant conditions were investigated. The liquid product yield of OPS decomposition using subcritical water liquefaction in the presence of alkali catalysts such as K_2CO_3, Na_2CO_3, and NaOH was 47.9%, 47.0%, and 53.4% at 563K, respectively. The liquid product yield of EFB decomposition was 61.5%, 58.3% and 67.2% in the presence of K_2CO_3, Na_2CO_3, and NaOH in the same condition, respectively. The liquid product yield of FPF liquefaction under subcritical water treatment was 35.9%, with $ZnCl_2$ as the catalyst and 71.4%, in the presence of Na_2CO_3, and NaOH at 563K respectively, depending strongly on the reaction temperature, catalyst and oil palm biomass type at the constant residence time. The optimum temperature for the production of liquid product yield was found to be at around 563K, while FPF and sodium hydroxide were found to be the best feedstock and catalyst for producing the high liquid product yield. Therefore, water and sodium hydroxide were accepted as solvent and catalyst for liquefaction of FPF by subcritical treatment.

The functional relationships between residence time, temperature, particle size, sample and catalyst loading based on the reliability of Response Surface Methodology (RSM) with the aim of optimizing 2 responses i.e. FPF conversion and liquid product yield was determined. Apart from the single response, the multi response optimization was also performed to find the optimal process parameters. The maximum conversion of FPF predicted from the single response optimization

was 581 K, 10 g sample loading, 9% catalyst loading, residence time 37 min and 710<pd<1000 for particle size and the liquid product yield predicted from the single response optimization was selected 551 K, 5 g sample loading, 9% catalyst loading, 40 min and 710<pd<1000 for particle size due to its high prediction of liquid product yield. The multi response optimization indicated sets of solutions, which gave the maximum desirability for both responses with predicated FPF conversion of 93% and liquid product yield of 76%.

CHAPTER ONE - INTRODUCTION

The average price for crude oil (Oil Dated Brent) in year 2007 was at USD 72.39 per barrel, an increase of 11% with respect to 2006. Crude oil prices increased steadily throughout the year, from as low as $50 in mid-January to above $96 by year-end. By 2008 the average price has increased to $97.26 per barrel, an increment of 34%. Price in 2008 began below $100 and rose sharply through the mid-year peaking above $144 in early July 2008. Other benchmark crudes registered similar gains. But by the end of 2008 the world encountered economic stagnation and with strong Organization of the Petroleum Exporting Countries (OPEC) production growth, ending the year with the average price of crude oil in the world fallen to under USD 60 per barrel. Such volatility in pricing is far from reassuring and may in fact be an indication of worldwide approach in peak oil production. Furthermore, the true cost of fossil fuel energy has been masked by unchecked environmental damage.

While energy cost has been fluctuating wildly, atmospheric Carbon Dioxide ($CO_{2)}$ levels continued a relentless climb of about 0.5% per year; from 374.9 ppm in 2003 to 382.7 ppm in 2007(TACD, 2009). Sea levels were rising, ice caps were melting, and hurricanes were causing record damage as storms were striking regularly and were much more intensified. Some or all of these crises have been directly or indirectly attributed to uncontrolled release of carbon dioxide from the combustion of fossil fuels (IPCC, 2007). Thus, increasing demands, rising costs, and supply issues coupled with treatment and disposal problems for large waste sources are creating needs for new and improved biomass energy conversion process.

Biomass refers to living and dead biological material that can be used as fuel for industrial production.

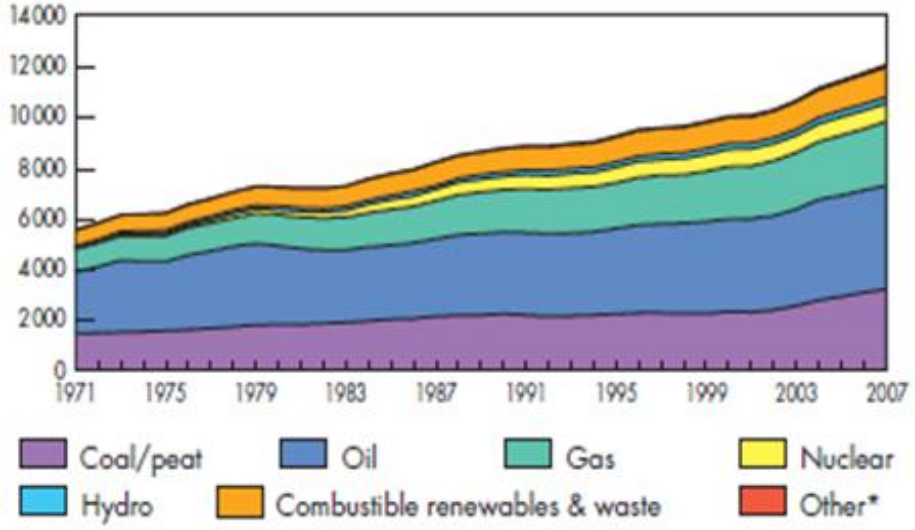
1.1 World Energy & Energy Resources

It is well known that industrialized and developed nations consume energy per capita more than the third world or developing countries. So there is a correlation between a country's living standard and energy consumption. In fact rapid increase in the consumption and demand of various kinds of energy worldwide (mostly by industrialized countries) depleted fuel fossil energy reserves. It means that limitation in fossil fuel resources and the existing world oil capacity is a major issue (Bentley, 2002).

In addition, the world population has quadrupled since 1870 to 6.6 billions at the present. The worldwide energy consumption of fossil resources in the form of coal, oil and natural gas has in fact increased by a factor of 60 to the present level of 99.96 quadrillion Btu (Müller-Steinhagen, et al., 2005; Trieb, et al., 2008).

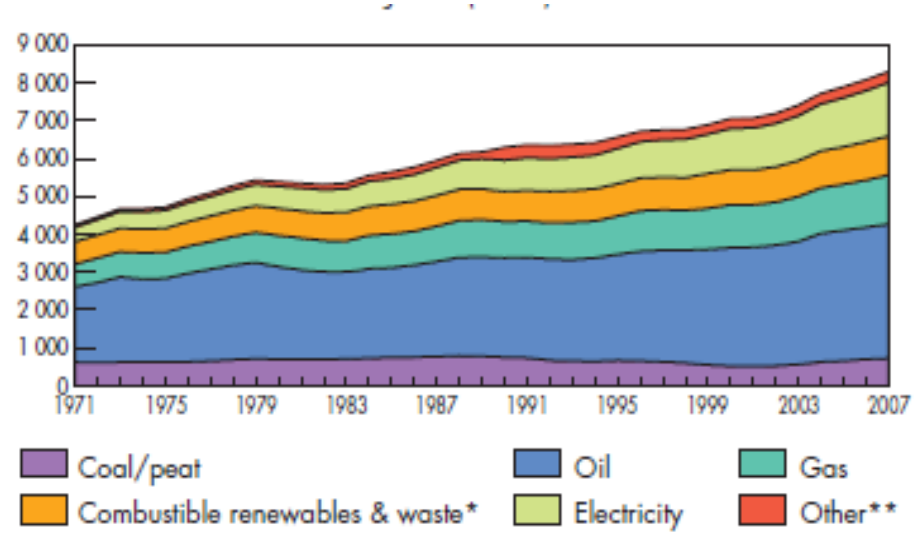
Overall primary energy supply and total final energy consumption of world evolution from 1971 to 2007 shown in Figure 1.1 as obtained from IEA (International Energy Agency, 2009). In 2006 world primary energy consumption grew slowly but the growth remained just about 10-years average. Oil was the slowest growing fuel while coal was the fastest growing. Although oil remained the world‟s leading energy source, it has lost market share to coal and natural gas in the past decade.

Therefore, damages rising from using the fossil fuel, and the increment of crude oil price day by day on one part, and limitation in fuel fossil resources on the other part, has made it important to look for a new energy resource.



**other includes geothermal, solar, wind, heat, etc

(a) Total primary energy supply



**other includes geothermal, solar, wind, heat, etc

(b) Total final consumption

Figure 1.1 Overall primary energy supply and final energy consumption of world evolution from 1971-2007 by fuel (Mtoe) (IEA)

1.2 Renewable and Green Energy in Malaysia

There is a significant correlation for most countries with status of economic and technological development to the gross national product per capita (GNP) and energy consumption per capita. In fact there is a good correlation between the

magnitude of annual energy consumption per capita and the corresponding gross national product per capita for the developing and also already developed countries.

Energy plays an important role in almost every field of human activities i.e. social, economic, and even politics. Malaysia with a whole population of 25.27 million (as at July 2008) and land area of 329,750 km^2 is blessed with plenty and relatively cheap supply of conventional energy resources such as oil, natural gas and coal. 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 fuel with both crude oil and natural gas held the lion share of 96.09% of the total production.

Interestingly enough, the energy from renewable materials such as hydroelectricity and combustible waste account to only 0.53% and 2.99% respectively (EIA, 2007a). Malaysia‟s total primary energy consumption in comparison with the total energy production from 1980 to 2005 is shown in Figure 1.2. As shown in the figure, the energy consumption in Malaysia has increased over five fold in the extent 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, the transportation sector was the largest consumer of energy in Malaysia followed by industrial, residential and commercial sector (UNDP, 2007).

The increase in oil demand but limited reserves certainly caused great concerns on the impact it brought to the country‟s future, hence forcing the re-evaluation of the country‟s strategies and existing policy towards embracing new renewable sources to countermeasure these global issues. Besides economy and supply complications, the utilization of fossil fuels also caused environmental degradation.

In fact, fossil fuels were identified as the main cause of various environmental catastrophes at the local, regional, and global level (Goldemberg, 2006).

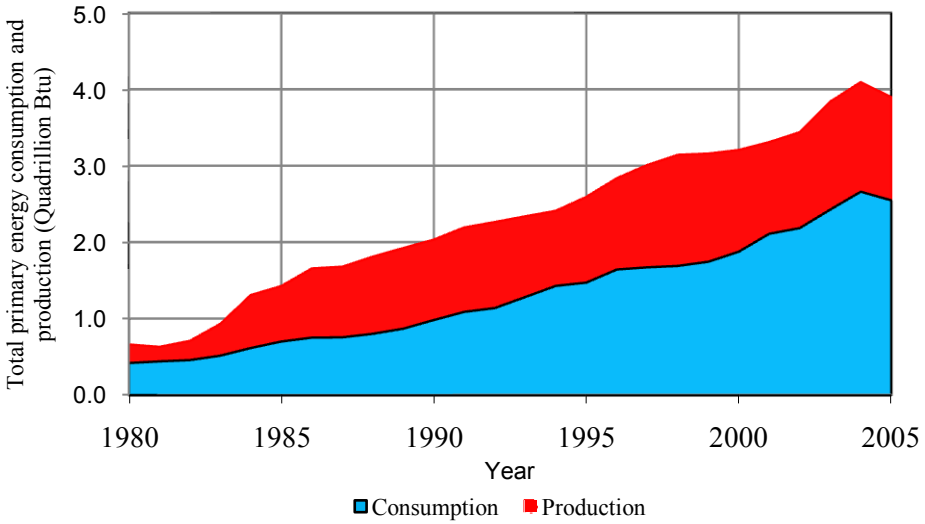


Figure 1.2 Total primary energy consumption and production for Malaysia from year 1980-2005 (IEA, 2007a).

The release of greenhouse gases such as CO_2 to the atmosphere caused greenhouse effects and altered the composition and function of the entire ecosystem (Goldemberg, 2006). It was determined that in year 2005 the total world CO_2 emissions from fossil fuels were 28,193 million metric tons which Malaysia, ranked at number 28, contributed 155.51 million metric tons (EIA, 2007b).

1.3 Biomass

Biomass is predicated to all earth‟s living organic materials consist of carbon, hydrogen, oxygen, nitrogen and some small portion quantities of other components. As late as the mid 1800s, biomass supplied the vast majority of the world's energy and fuel needs and only started to be phased out in industrialized countries as the fossil fuel era began slowly at first and then at a rapid rate. Biomass was replaced by coal, petroleum crude oil, and natural gas, which became the raw materials of choice

for manufacturing and producing a host of derived products and energy as heat, steam, and electric power, as well as solid, liquid, and gaseous fuels. But with the onset of the first oil shock in the mid 1970s, biomass was again realized by many governments and policy makers to be a viable, domestic, energy resource that has the potential of reducing oil consumption and imports and improving the balance of payments and deficit problems caused by dependency on imported oil. Biomass is one of the few renewable, indigenous, widely dispersed, natural resources that can be utilized to reduce both the amount of fossil fuels burned and several greenhouse gases emitted by or formed during fossil fuel combustion process.

The fossil fuel era has indeed left a large impact on civilization and industrial development. However, since the fossil fuel reserve depleted as they are consumed, and environmental issues that came together, mainly those concerned with air quality problems (perceived by many scientists to be directly related to fossil fuel consumption), biomass is expected to exhibit increasing usage as an energy resource and feedstock for the production of organic fuels and commodity chemicals. Carbon dioxide, for example, is one of the primary products of fossil fuel combustion which is a greenhouse gas and it is widely believed to be associated with global warming. Carbon dioxide is removed from the atmosphere via carbon fixation by photosynthesis of plants.

1.3.1 Oil Palm Biomass

The oil palm tree (Elaeis guineensis jacq.) originates from Africa where it grows in the wild and later was developed into an agricultural crop. It was introduced in Malaysia, in the early 1870ʿs by the British. The first commercial planting took place in 1917, in Selangor (Tennamaran Estate), laying the foundations for the vast oil palm plantations and the palm oil industry in Malaysia. The cultivation of oil

palm increased rapidly in the early 1960s under the government‟s agricultural diversification program, which was introduced to reduce the country‟s economic dependence on rubber and tin. 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 the edible oil used for cooking, while those extracted from the kernel is used mainly in the soap manufacturing industry. Oil palm is Malaysia‟s golden crop in the agricultural sector. Oil palm is the top 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). At present, oil palm is one of the major economic crops in a large number of countries, which triggered the expansion of plantation area around the world (Yusoff, 2006).

Nowadays, 4.49 million hectares of land in Malaysia is used for oil palm cultivation; producing 17.73 million tonnes of palm oil and 2.13 tonnes of palm kernel oil. The total mature areas of oil palm plantation represent 56% of the total agricultural land and 11.75% of the country‟s total land area (MPOC, May 2009).In year 2008, 4.88 million hectares of land in Malaysia is covered by oil palm cultivation. The amount of oil palm biomass produced by these oil palm plantations in year 2008 is estimated to be about 37.0 million tonnes, consisting of 22% empty fruit bunch (EFB), 13.5% fruit press fiber (FPF) and 5.5% shell (MPOC, 2004) and Malaysia Palm oil Board (MPOB January, 2009). Figure 1.3 shows the general mass balance of various products generated from a palm oil mill. As shown in Figure 1.3, Fresh Fruit Bunch (FFB) contains only 21-22% of palm oil while the rest, 6-7% palm kernel, 5-6%, shell 12-13.5% fiber and 22% empty fruit bunch (EFB) are left as biomass (MPOC, 2007; Umikalsom, et al., 1997).

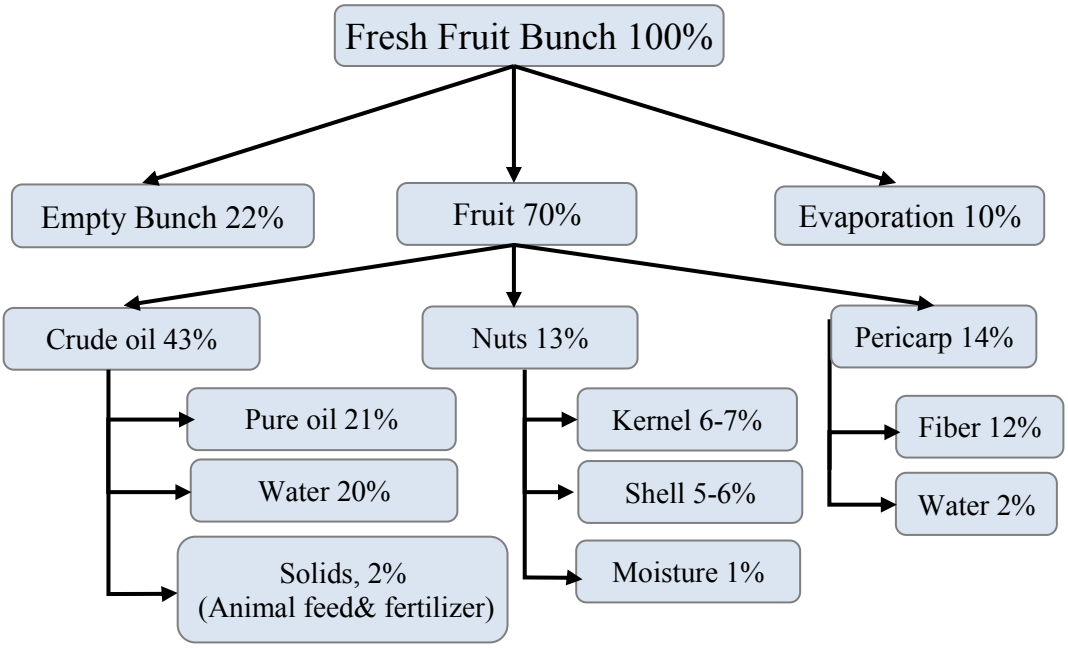


Figure 1.3 Palm oil fruit and production composition chart (Umikalsom, et al. 1997; MPOC, 2007)

The palm oil industry provides more than half a million job for the people and with the projected growth in the oil palm cultivation, the concern is on what should be done with the enormous quantities of biomass waste. Every year, oil palm industries produce more than a hundred million tonnes of biomass waste worldwide. 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 are used to make mattresses, seats, insulations etc. (Kelly-Yong, et al., 2007). Paper making industry utilizes paper pulp from oil palm biomass for its various end usage purposes.

Fruit Press Fiber (FPF), Oil Palm Shells (OPS), and Empty Fruit Bunch (EFB) were generally dumped in open areas or disposed by open burning generating pollutant gases harmful to the environment. In some other cases, these fiber and shells were used as sources of energy in the processing mill itself to generate heat and electricity via the combustion reaction. 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. Therefore, there is an urgent need of transforming these wastes into more valuable products. A promising option is by converting them into biofuel (liquid and gaseous products) via thermochemical conversion. Oil palm biomass is the perfect choice as feedstock for the subcritical or supercritical water liquefaction processes. It has high energy and moisture content (>50%), both integral requirements for this particular reaction and for generation of renewable energy. In other words, however, since a large portion of biomass wastes is wet biomass that could contain up to 90% of water, thus making the current thermochemical process requires additional drying process. Removing the water of wet biomass by drying before processing increases the energy requirements and cost needed to convert biomass to gas or liquid fuels. However, recently, it is found that supercritical water liquefaction present a promising method for converting biomass into higher value fuels without the need to dry the biomass.

1.4 Utilization of Biomass

The technology which has brought the western civilization into the industrial age and beyond has hidden and unintentional costs which demands an immediate attention. The status of present consumption of crude oil is about 79 million barrels per day (IEA, 2007a). The tremendous increasing need of oil, which is predicted to be about 119 million barrels per day by 2020 and the shortage of oil thereafter (after 10-15 years), is predicted based on the total reserves in hand, urgently put forward the emphasis to focus the research in finding alternative means to fulfill the energy

needs worldwide. Therefore, the end of the fossil fuel age necessitates the development of new technologies to replace fossil fuels.

Alternatives to fossil fuels include solar, wind, hydro, and biomass. Solar can be harnessed for direct thermal use, such as heating of water or living space, and as such is an excellent replacement for fossil fuels for these purposes. Solar photovoltaics, like wind and hydro, produce electricity, a very high grade of energy in its own right, but it is indeed impossible to store unless it is converted into another form such as chemical energy in batteries, mechanical energy in rotors or potential energy by pumping water uphill.

Consequently, there is a general trend to search for alternative energy involving local 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 mission of securing 20% of electricity from renewable sources by 2020 (Gross, 2004), while the Ministry of Economic Affairs of Netherlands stated its goal of 10% renewable energy by 2020 (Agterbosch, et al., 2004).

At present, Malaysia is the second largest producer and exporter of palm oil, producing about 47.0% of the total world supply in 2007. Oil palm biomass and its processing byproducts were found to be 7 times more than the availability of natural timber (Basiron, 2007). 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 fiber and shell as the boiler fuel to generate heat and electricity for the production processes (Chuah, et al., 2006). However, the energy requirement for the oil palm mills is much lower in comparison with the amount of biomass produced forcing the excess to be disposed off separately.

1.5 Biomass Conversions Technologies

The industrial age has brought to the developed world spectacular advances in human health and well being. Unfortunately, the burning of fossil fuels has also been concerned in increasing atmospheric CO_2 concentrations and global climate change. Biomass contains a variety of biological materials with distinctive physical and chemical characteristics, such as woody or lignocellulosic materials, especially grass and legumes, and crop residues.

Biomass energy creates thousands of jobs and helps regenerate rural and urban communities. It seems that as industrial activity has increased in many countries, more concentrated and convenient sources of energy have been replaced with biomass. Biomass is able to be converted to various forms of energy by various technical processes, depending on the raw material characteristics and the type of energy desired. Consequently, a wide variety of conversion schemes have been developed to take the best advantage of the properties of the biomass to be processed. Biomass conversion technologies were thoroughly discussed by different authors such as (Demirbas, 2009a; Demirbas, et al., 2006; Demirbas, 2006; Kucuk, et al., 1997). Bio-renewable feedstock can be used as a solid fuel, or converted into liquid or gaseous forms for producing, electric power, heat, chemicals, or gaseous and liquid fuels.

The main biomass conversion processes are direct combustion, thermochemical conversion, biochemical conversion and indirect liquefaction. Figure 1.4 shows the main types and classification of biomass conversion processes. The conversion of biomass materials has the accurate objective to transform a hydro carbonaceous solid material, which is originally difficult to handle, bulky and of low energy concentration, into fuels (liquid and gaseous form) which have physico-

chemical characteristics and allow economic storage and transferability through pumping systems.

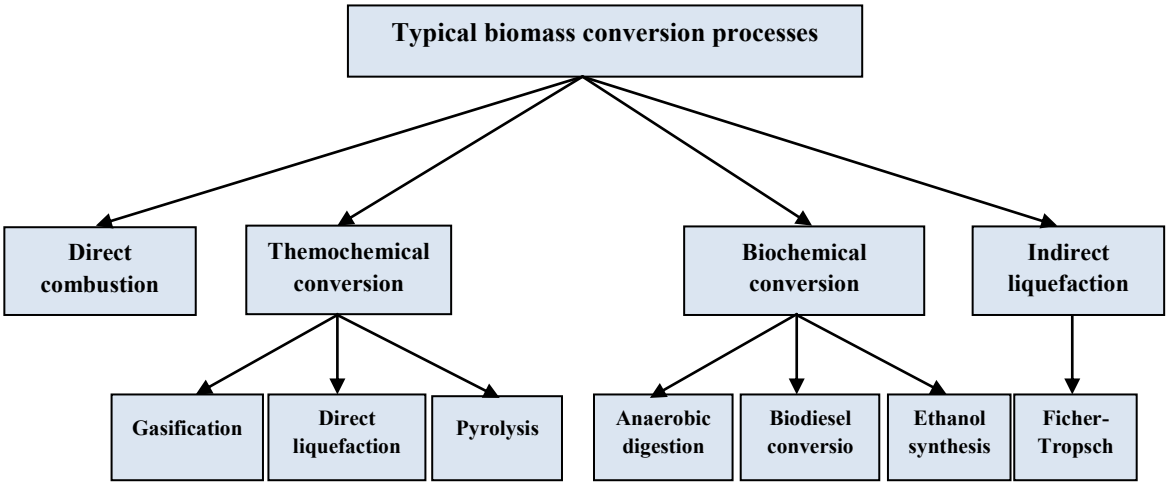


Figure 1.4 The main biomass conversion processes(Demirbas, 2007c)

1.5.1 Direct Combustion

Direct combustion is the most conventional way of using biomass. In general, combustion employs an excess of oxidizer to ensure maximum fuel conversion, but it can also occur under fuel-rich conditions. Combustion is a chemical process which releases energy from a mixture of fuel and air. However, biomass contains relatively high oxygen atom ratios resulting in the lower combustion efficiencies in comparison with other fuels.

During combustion, the combustible part of fuel is divided into volatile and solid residue. The combustion process begins by heating the fuel above its ignition temperature in the presence of oxygen or air. Under the influence of heat, the chemical bonds of the fuel are cleaved. In the complete process of combustion, the combustible elements (i.e. C, H and S) react with the oxygen content in the air to form CO_2, H_2O and SO_2. If there is not enough oxygen present, or the fuel and air

mixture is insufficient, then the burning gases are partially cooled below the ignition temperature and the combustion process stays incomplete. The flue gases also contain combustible components, mainly carbon monoxide (CO), unburned carbon (C), and various hydrocarbons (C_xH_y).

1.5.2 Thermochemical Conversion

Thermochemical Conversion (TCC) technology was studied as early as the 17th century with the first patent issued in 1788 by Robert Gardner for his work in the gasification area. Thermochemical conversion is characterized by higher temperatures and conversion rate is higher than most other processes and include gasification, pyrolysis and direct liquefaction (Surmen, et al., 2002).

1.5.2 (a) Biomass Gasification

Gasification describes the process in which oxygen-absent thermal decomposition of organic matter mainly produces non-condensable fuel or synthesis gases. Gasification generally consists of pyrolysis as well as combustion to provide heat for the endothermic pyrolysis reactions. However, indirectly, gasification is often used to describe the process in which heat is brought from outside the reaction chamber to drive the pyrolysis in the absence of combustion.

The gasification process occurs on between pyrolysis and complete combustion. Gasification compared to combustion has some benefits consist of: more flexibility in terms of energy applications, more economical and thermodynamic efficiency at a small scale, and potentially lower environmental impact when combined with gas cleaning (Demirbas, 2009b). Furthermore, char will participate in a series of endothermic reactions at temperatures above 800°C that upgrades this solid carbon into gaseous fuel constituents. The feedstock for gasification is a dry

matter too. Gasification of biomass for use in internal combustion engines for power generation provides an important alternative renewable energy resource. Gasification is the partial combustion of lignocelluloses materials to produce gas and char at the first stage and subsequent reduction of the produced gases, mainly CO_2 and H_2O, by the charcoal into CO and H_2. In addition, depending on the design and operating conditions of the reactor, some methane and other higher hydrocarbons are also produces (Demirbas, 2002b, 2006).

1.5.2 (b) Biomass Pyrolysis

Thermal decomposition of organic matter is called pyrolysis and it occurs in the absence of air or oxygen. The products of the pyrolytic process can be gaseous, liquid, and/or solid. Pyrolysis of organic materials was studied as early as the 1920's. Pyrolysis can be further divided into conventional pyrolysis and flash pyrolysis (Demirbas, 2007b, 2008b).

Conventional pyrolysis is characterized by a relatively slow heating rate (less than 100°C), compared to that of fast pyrolysis, and long gas and solids residence times. The primary products are tar and char as the secondary choking and polymerization (recombination) reactions.

Flash pyrolysis of biomass is also the thermochemical process which converts small dried biomass particles into liquid fuel (bio-crude), and char as well as non-condensable gases by heating the biomass up to 775 K in the absence of oxygen. Char in the vapor phase catalyzes secondary cracking(Demirbas, et al., 2007).

When wood is heated in the absence of oxygen, it decomposes to condensable vapors, char, and light gases. Condensable vapor consist of oxygenated hydrocarbons and water. When heating is rapid ($>100^{o}$ C/s) and residence time in the reaction environment is short (1-2 seconds), the thermochemical process is termed fast

pyrolysis. The oil products are maximized at the expense of char and gas. The feedstock of pyrolysis is usually a dry matter. For well-designed fast pyrolysis processes, the yield of condensable vapors can be as high as 75% on a dry mass basis (Bridgwater, et al., 2002).

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better version of it. Pyrolysis can also be carried out in the presence of a small quantity of oxygen ("gasification"), water ("steam gasification"), or hydrogen ("hydrogenation"). One of the most useful products is methane, which is the suitable fuel for electricity generation using high-efficiency gas turbines (Balat, 2008a; Demirbas, 2008a, 2009a, 2010).

The pyrolysis and direct liquefaction in the presence of water treatments are sometimes confused with each other, and a simplified comparison of the two follows. Both classify in thermochemical processes in which feedstock organic compounds are converted into liquid products. on one hand, in the liquefaction process feedstock, involves macromolecule compounds, are decomposed into fragments of light molecules in the presence of a suitable catalyst (Balat, 2008b). At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Demirbas, 2000b). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase (Balat, 2008c; Demirbas, 2002a).

1.5.2 (c) Biomass Liquefaction

Liquefaction was historically related to hydrogenation and other high-pressure thermal decomposition processes that employed reactive hydrogen or carbon monoxide carrier gases to produce a liquid fuel from organic matter at moderate

temperatures (typically between 300°C and 400°C) . The liquefaction treatment generally used for biomass conversions to bio-oils is grouped under the TCC area of energy conversion methods along with gasification and pyrolysis. Liquefaction can be accomplished directly or indirectly. Direct liquefaction consists of hydrothermal liquefaction and rapid pyrolysis to produce liquid tars and oils and condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products. The liquefaction of biomass has been investigated in the presence of solutions of alkalis, propanol and butanol, and glycerine, or by direct liquefaction (Goto, et al., 2004; Minowa, et al., 1997; Yuan, et al., 2007). In the liquefaction process, the hydrocarbons materials are converted to liquid products through a complex sequence of physical structure and chemical changes (Bhaskar, et al., 2008; Caglar, et al., 2001; Demirbas, 2000a, 2000b; Fang, et al., 2004; Karagoz, et al., 2006).

1.5.3 Subcritical/Supercritical Water Treatment

Lately two biomass conversion processes using water have been studied: hydrothermal upgrading (HTU) under subcritical water and supercritical water treatments. Since the drying process is energy–intensive operation, sub to supercritical water is a promising technology for liquefaction biomass with high moisture content (Kumagai, et al., 2008; Srokol, et al., 2004).

Subcritical water is a promising technology to treat waste streams from various sources and produce valuable bio-products such as biocrude. Subcritical water is a thermochemical process for the conversion of wet biomass material under subcritical to near-critical water conditions and produces a hydrophobic oil layer (biocrude), aqueous liquid products, gasses, and some solid remains. The resulting bio-oil can be used for electricity production, but it can also be upgraded into

transportation fuel. The variety of biomass such as agricultural and civic wastes can be converted, partially, into a heavy oil-like product by reaction with water and carbon monoxide/hydrogen in the presence of sodium carbonate(Demirbas, 2001b).

Previously, the supercritical fluid treatment has been considered to be an attractive alternative in science and technology as a chemical reaction field. The molecules in the supercritical fluid condition such as gas and liquid have high kinetic energy and high density, respectively. In addition, ionic product and dielectric constant of supercritical water are important parameters for chemical reaction. Therefore, the supercritical water can be realized from the ionic reaction field to the radical reaction field. Therefore, it is expected that the chemical reactivity can be high in it. While SCW is a strong solvent for organic compounds, it is a poor solvent for inorganic salts. However, pressure has a negligible effect on hydrogen yield above the critical pressure of water(Ehara, et al., 2005).

The use of SCW for the biomass conversion to liquid fuels and the production of fine chemicals from biomass have been studied by various researchers (Ehara, Saka, et al., 2002; Ishikawa, et al., 2001; Li, et al., 2004; Saka, et al., 1999a). Over the past few years, the interest in the use of renewable resources such as wood, cellulose and lignin as high value products has grown steadily. The components of wood: hemicelluloses, cellulose, lignin and extractives decompose into different organic compounds. Thermal degradation properties of biomass components such as hemicelluloses, celluloses, and lignin can be summarized as follows (Chum, et al., 2001; Demirbas, 1998b, 2000a, 2000b).

hemicelluloses > of cellulose >> of lignin

1.5.4 Fischer–Tropsch Synthesis (FTS)

FTS is a well established process for the production of biofuels (synfuels). The process is used commercially in Malaysia by Shell. FTS can operate at low temperatures (LTFT) to produce a biocrude with a large fraction of heavy, waxy hydrocarbons or it can operate to produce a light biocrude and olefins. At high temperatures (HTFT) process, the primary products can be refined to environmentally friendly gasoline and diesel, solvents, and olefins. In LTFT treatment, heavy hydrocarbons can be refined to specialty waxes. FTS has been widely investigated for more than 70 years. The FTS process produces a variety of composition products with hundreds of individual compounds which shows a remarkable degree of order with regard to the class and size of the molecules. The concept of FTS as an ideal polymerization reaction is realized that the main primary products, olefins, can undergo secondary reactions and thereby modify the product distribution. This leads to chain length dependencies of certain olefin reaction possibilities, which are again suited to serve as a characteristic feature for the kind of olefin conversion (Demirbas, 2007a).

1.6 Problem Statement

During the past two decades the world's fossil fuels energy demand had rapidly increased. Approximately 80% of the world primary energy consumption is still dependent on fossil fuel. Far too long dependency on fossil fuels has caused worldwide energy crisis and rising environmental complications such as air pollution and greenhouse gas emission, making it even more necessary to find the new best alternative option.

The tendency to renewable bio-energy is increased gradually in the course of the 21st century because of the declining fossil fuel resources. Furthermore, due to the increasing concerns over greenhouse gas emissions and energy security, there is a rebirth of interest in renewable bio-energy. Bio-energy is referred to all forms of renewable energy that are derived from biomass feedstock. Biomass feedstock such as forestry residues, agricultural and wood wastes like harvest residues, slash, sawdust, bark, etc. can be the main sources for energy, fuels, and chemicals.

Malaysia is one of the countries in the world that produces palm oil, leaving behind a huge amount of oil palm biomass (oil palm waste). Therefore there is a potential of biomass feedstock as energy resources in Malaysia. The amount of oil palm biomass (FPF 12%, EFB 22%, and OPS 6%) produced annually in Malaysia is estimated to be about 37 million tonnes in 2008 (MPOC, 2004; MPOB, 2009).

Currently, one of the main technologies available for the conversion of biomass into biofuel is through chemical reaction such as pyrolysis, gasification and liquefaction. However, since a large portion of biomass is wet, technology using pyrolysis and gasification would require the biomass to go through drying process first. Since most biomass usually has high moisture content, a drying process requires more heating energy due to the large latent heat of water vaporization. Thus, additional drying process makes the overall biomass conversion to biofuel expensive and uneconomical. In addition, water is a cheap and readily available "green" solvent. Nevertheless, subcritical and supercritical water treatment method has received considerable attention lately; it has the advantage of using wet biomass without the requirement of prior drying process. Further, the water content in biomass can actually be utilized during the reaction. Therefore, the main aim of this

work is to study the conversion of oil palm biomass into biofuel (bio-crude) using sub to supercritical water liquefaction technology with or without catalyst addition.

1.7 Research Objective

The overall goal of this research will be to assess the potential of a subcritical and supercritical solvent liquefaction using oil palm biomass feedstock such as fruit press fiber, oil palm shell, and empty fruit bench available in Malaysia. In this study, the results are aimed at the maximization of 2 responses which are selectivity of liquid product yield and biomass conversion. This goal will be accomplished by meeting the following objectives:

1-To characterize oil palm biomass Oil Palm Fruit Press Fiber (FPF), Oil Palm Shell (OPS) and Empty Fruit Bunch (EFB) based on their composition and structural properties.

2-To determine the effect of solvent (water, methanol, ethanol acetone and 1-4 dioxane) on oil palm biomass conversion and liquid products using subcritical liquefaction at different temperatures.

3-To determine the effect of catalysts (K_2CO_3, Na_2CO_3, NaOH, $ZnCl_2$) on the conversion and liquid products of oil palm biomass using subcritical liquefaction in different temperatures.

4-To optimize the various process parameters such as temperature, residence time, weight of catalyst, weight of biomass and particle size on conversion of FPF and liquid products yield using sub to supercritical liquefaction treatments.

5-To analyze model functional relationships between the operating variables on the desired responses based on the reliability of response surface methodology (RSM) in conjunction with central composite rotatable design (CCRD).

1.8 Scope of Study

The aim of this study was to use oil palm biomass such as oil palm Fruit Press Fiber (FPF), Oil Palm Shell (OPS) and Empty Fruit Bunch (EFB) to produce liquid products fuel (bio-fuel) and chemicals by using some protic and aprotic solvents such as water, methanol, ethanol , acetone and 1-4 dioxane by means of subcritical to supercritical treatment (SCW). The reactions were carried out in the absence of catalyst and in the presence of metal salt and alkali catalyst such as $ZnCl_2$, Na_2CO_3, K_2CO_3, and NaOH at the different temperatures.

The best oil palm biomass, catalyst and solvent were chosen by comparing the results for statistical analysis. Then, the processes of biomass fragmentation by sub/supercritical solvent treatments were analyzed by constructing a response surface model (RSM). These methods were used to maximize the fragmentation extend, by comparing the amount of solid materials remaining after processes with the original amount introduced in each experimental run.

The chemical characterization of the liquid product generated after treatment allows for the determination of the types of compounds produced, their origin based on oil palm biomass structure and the extent of fragmentation laying the foundation for future work dealing with separation, collection and commercialization of products derived from this types of lignocelluloses biomass stream.

1.9 Thesis Organization

This study has been organized into the following sections:

Chapter 1: Introduction

This chapter provides an insight into world energy and energy resources, as well as renewable and green energy in Malaysia. In addition, there was also a background study on biomass, utilization, and thermal decomposition of biomass included in this chapter. The problem statement, objectives, and the outline of the report were also given in this chapter.

Chapter 2: Literature Review

This chapter supplies a thorough analysis and background study on the chemistry of lignocelluloses constituent. Then, a brief view on subcritical to supercritical treatment and its properties were also given. Furthermore, this chapter highlights the previous work done in the field of biomass decomposition using subcritical and supercritical liquefaction treatment. The reviews also gave attention on the effect of process parameters and addition of catalyst towards the liquefaction. Finally, the review touches on the process optimization studies as employed in this experimental work.

Chapter 3: Materials and Method

The lists of all materials and detailed description of the experimental procedures used in this study were provided in this chapter. The first section touches on the list of materials and chemicals used in addition to the experimental flowchart diagram. The next section describes on the preparation of the oil palm biomass (FPF,

OPS and EFB) for the experimental work followed by its characterization studies. Experimental setup and its procedure were explained subsequently in addition to the analytical method utilized in the study.

Chapter 4: Results and Discussion

In this chapter, some conclusions were presented along with a discussion of the results concerning the consecutive of the work. The results and discussions chapter were divided into three main parts based on the used solvents, catalysts, and design of experiments (DOE) method. In the first section, the effect of solvents such as water, methanol, ethanol, acetone and 1-4 dioxane on FPF, OPS, and EFB were investigated. While in second part, the effect of some various alkali catalysts such as K_2CO_3, Na_2CO_3, $ZnCl_2$ and NaOH were evaluated. In the next section, optimizations were studied on subcritical water liquefaction in order to establish the functional relationships between the operating variables on the desired responses using Design of Experiments (DOE) method and subsequently its optimization to obtain the optimum conditions based on Response Surface Methodology (RSM) of FPF in a batch system were studied. Lastly, optimizations studies on subcritical water liquefaction of FPF were conducted in order to establish the functional relationships between the operating variables on the desired responses using Design of Experiments (DOE) methodology in a batch system.

Chapter 5 – Conclusion and Recommendations

This chapter concludes on the finding of these studies and the recommendations for the improvements, which can be done for future research.

CHAPTER TWO - LITERATURE REVIEW

The literature review section provides a thorough analysis and background study on the research project with the aim of better understanding of the various terms and aspects used in this thesis. The chronological progress and achievements in this particular field of study based on established research and results obtained from legitimate resources are presented here. The review is divided into several sections, which touched on the aspects deemed vital to the research with the aim to provide an ideal flow of information and subsequently an easier understanding to the background study of the research. The sections mentioned earlier are as follow:

1- Preliminary discussions is on the lignocelluloses material chemistry which focuses on the three main constituents i.e. lignin, cellulose and hemicelluloses.

2- The definition of the subcritical and supercritical fluid as well as physicochemical properties of water in the subcritical and supercritical condition and vital properties (such as density, dielectric constant, ionic product, and hydrogen bonds) are discussed to provide a better understanding on their role in the liquefaction treatment.

3- The review on the comprehensive study which has been done on solvents and their classifications.

4-This section touches on the Design of Experiments (DOE) and the process optimization studies by focusing on Response Surface Metrology (RSM) and subsequent explanations of the related terms.