

**UTILISATION OF DECANTER CAKE FROM PALM OIL MILLING PLANT
AS NEW SUBSTRATE FOR THE PRODUCTION OF BIO-OIL THROUGH
CATALYTIC VACUUM PYROLYSIS**

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ABSTRACT

The present study was carried out to investigate the potential of palm oil decanter cake (PDC) as the new substrate for bio-oil production. Conversion of PDC into bio-oil was conducted through vacuum pyrolysis. Maximum bio-oil yield was 22.12% obtained at pyrolysis temperature of 500 °C. The chemical characterisation of bio-oil was studied using ¹H-NMR, FTIR, CHNS analyzer and GC-MS. The other properties like pH, calorific value and thermal volatilization were also determined. For comparison purpose, pyrolysis of palm kernel shell (PKS) was also conducted using the same method in PDC pyrolysis. The results indicate PDC bio-oil characteristic is better than that of PKS bio-oil in terms of lower oxygen content, higher pH and heating value. The pH value of PDC recorded to be 6.38, which is found to be higher as compared to that of other bio-oils. The calorific value of PDC bio-oil was found to be 36.79 MJ/kg, which is slightly lower than that of conventional liquid fuel such as gasoline and diesel fuel and much higher than that of bio-oils derived from lignocellulosic biomass. Fatty acid derived from decomposition of triglycerides dominated the composition of PDC bio-oils, while phenolic compounds were prominently found in PKS bio-oil. Effect of catalyst addition was studied by using single and dual stages of pyrolysis reactor. Single stage catalytic pyrolysis was conducted by mixing the catalyst with the biomass in a certain ratio prior to the experiment and was placed into the vacuum pyrolysis reactor. Catalytic reaction reduced the yield of PDC bio-oils, from 22.12 wt% to 15.22 – 17.09 wt%. Catalytic activity of CaO and MgO enhanced the formation of methyl ester through the transesterification reaction of fatty acid, which was produced from decomposition of PDC. Generally, the oxygen content was decreased in presence of catalysts. H-ZSM5 provides better oxygen content reduction than that of other catalysts, both for PDC and PKS. The presence of catalysts slightly affected the pH value and HHV of bio-oils. Dual stage catalytic pyrolysis was conducted by placing the catalysts separately into a catalyst reactor bed to catalyse the upgrading of pyrolytic vapor occurred. Less bio-oil were produced by dual stages catalytic pyrolysis. However, the ratio of O/C decreased while the calorific value slightly increased in dual stage pyrolysis. Bio-oils produced from PDC catalytic pyrolysis has relatively high calorific value than that of other bio-oils, and comparable to the HHV of petroleum fuels. Therefore, PDC bio-oil can be considered as potential alternative fuel. Kinetic studies of PDC pyrolysis were conducted by using thermogravimetry data. Coats-Redfern approach was employed to describe the kinetic model of the PDC thermal decomposition. It was found that the major decomposition of PDC occurred at 220 – 530 °C, represent for decomposition of hemicellulose, cellulose, lignin and triglycerides contained in PDC. Two stages of reaction were identified, first stage at 220 – 300 °C obeyed first order kinetic model, while second stage at 300 – 530 °C was best fit for second order kinetic model. Triglyceride decomposition dominated the whole pyrolysis reaction. As conclusion, decanter cake from palm oil milling plant has potential to be utilised as new substrate for the production of bio-oil through catalytic vacuum pyrolysis.

ABSTRAK

Kajian ini telah dijalankan untuk menyelidik potensi kek penyiring minyak sawit (PDC) sebagai substrat baru untuk pengeluaran minyak-bio. Penukaran PDC kepada minyak-bio dijalankan melalui pirolisis vakum. Hasil minyak-bio maksima 22.12% diperolehi pada suhu pirolisis 500 °C. Pencirian kimia minyak-bio dikaji menggunakan ¹H-NMR, FTIR, penganalisis CHNS dan GC-MS. Sifat-sifat lain seperti pH, nilai kalori dan pemeruapan terma juga telah ditentukan. Bagi tujuan perbandingan, pirolisis tempurung isirong sawit (PKS) juga telah dijalankan dengan menggunakan kaedah yang sama dalam PDC pirolisis. Keputusan menunjukkan ciri minyak-bio PDC adalah lebih baik daripada minyak-bio PKS dari segi kandungan oksigen rendah, pH dan nilai pemanasan yang lebih tinggi. Nilai pH PDC direkodkan 6.38 didapati lebih tinggi berbanding dengan minyak-bio yang lain. Nilai kalori PDC minyak-bio didapati 36,79 MJ/kg, rendah sedikit daripada bahan api cecair konvensional seperti petrol dan minyak diesel. dan jauh lebih tinggi daripada minyak-bio yang dihasilkan daripada biojisim lignoselulosa. Asid lemak yang diperolehi daripada penguraian trigliserida menguasai komposisi PDC minyak-bio, manakala sebatian fenolik adalah jelas dominan dalam PKS minyak-bio. Kesan pemangkin telah dikaji dengan menggunakan reaktor pirolisis peringkat tunggal dan dwiperingkat. Pada pirolisis peringkat tunggal, pracampuran pemangkin dengan biojisim dalam nisbah tertentu diletakkan ke dalam reaktor pirolisis vakum. Tindak balas bermangkin mengurangkan hasil PDC bio-minyak, daripada 22.12% berat untuk 15,22-17,09% berat. Aktiviti mangkin CaO dan MgO mempertingkatkan pembentukan metil ester melalui reaksi transesterifikasi asid lemak, yang dihasilkan daripada penguraian PDC. Secara umumnya, kandungan oksigen menurun dalam penggunaan pemangkin. H-ZSM5 menyediakan pengurangan kandungan oksigen yang lebih baik daripada itu pemangkin lain, kedua-dua untuk PDC dan PKS. Kehadiran pemangkin sedikit memberi kesan kepada nilai pH dan HHV minyak-bio. Pada pirolisis dwiperingkat, pemangkin diletakkan secara berasingan ke dalam reaktor lapisan tetap. Minyak-bio dihasilkan oleh pirolisis pemangkin dwiperingkat lebih sedikit berbanding dengan pirolisis pemangkin peringkat tunggal. Walau bagaimanapun, nisbah O/C menurun manakala nilai kalori menaik dalam pirolisis pemangkin dwiperingkat. Bio-minyak yang dihasilkan dari pirolisis pemangkin PDC mempunyai nilai kalori yang tinggi daripada minyak-bio yang lain, dan setanding dengan HHV bahan api petroleum. Oleh itu, PDC bio-minyak boleh dianggap memiliki potensi sebagai bahan api alternatif. Kajian kinetik PDC pirolisis telah dijalankan dengan menggunakan data termogravimetri. Pendekatan Coats-Redfern telah digunakan untuk menggambarkan model kinetik penguraian terma PDC. Ia telah mendapati bahawa penguraian utama PDC berlaku pada 220 – 530 °C, untuk mewakili penguraian hemiselulosa, selulosa, lignin dan trigliserida yang terkandung dalam PDC. Dua peringkat tindak balas telah dikenal pasti, peringkat pertama pada 220 – 300 °C mengikuti model kinetik tertib pertama, manakala peringkat kedua pada 300 – 530 °C adalah paling sesuai untuk model kinetik tertib kedua. Penguraian trigliserida mendominasi reaksi pirolisis keseluruhan. Kesimpulannya, kek penyiring minyak sawit mempunyai potensi untuk digunakan sebagai substrat baru untuk pengeluaran minyak-bio melalui pirolisis pemangkin vakum.

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LIST OF SYMBOLS

α	the change in extent of reaction
m	mass at
t	time
k	kinetic constant
A	pre-exponential factor of Arrhenius equation
E_a	Activation energy
R	Gas constant
T	Temperature
β	heating rate

LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller
CHNS	Carbon Hydrogen Nitrogen Sulphur
CPKO	Crude palm kernel oil
CPO	Crude palm oil
DTG	Derivative thermogravimetry
EFB	Empty fruit bunch
FAME	Fatty acid methyl ester
FCC	Fluid catalytic cracking
FFB	Fresh fruit bunch
FTIR	Fourier Transform Infra Red
FWO	Flynn-Wall-Ozawa
GC-MS	Gas Chromatography – Mass Spectrometry
GP	Glucopyranose
HA	Hydroxyacetone
HAA	Hydroxyacetaldehyde
HDO	Hydrodeoxygenation
HHV	Higher heating value
HMF	Hydroxymethyl-furfural
HPLC	High-performance liquid chromatography
H-USY	H-Ultra stable Y zeolite
H-ZSM	H-Zeolite socony mobile
IEA	International Energy Agency

KAS	Kissinger-Akahira-Sunose
LG	Levoglucosan
MPOC	Malaysian Palm Oil Council
NMR	Nuclear Magnetic Resonance
PDC	Palm oil decanter cake
PKS	Palm kernel shell
TG	Thermogravimetry
TGA	Thermogravimetry analysis

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the last three decades, world's energy consumption has been rapidly increasing due to the population growth and economic activities. Modern lifestyle which is required better health and environmental provision, accessibility and mobility, also contribute to energy consumption rising worldwide. The world primary energy demand increases by one-third from 2011 to 2035 as projected by International Energy Agency (IEA, 2013a). Oil demand (excluding biofuels) continues to grow steadily, reaching about 99 million barrels per day (mb/d) by 2035 — 15 mb/d higher than in 2009, while global oil production reaches 96 mb/d by 2035 (IEA, 2013a). It is clearly stated that the unbalance between oil demand and production, also oil price uncertainty, encourage people to find the new energy source. In Malaysia case, energy demand rapidly increases from 143 mboe (million barrels of oil equivalent) in 1990 to 503 mboe in 2011, and will reach almost 870 mboe in 2035 with the annual growth rate of 2.3% (IEA, 2013b).

World primary energy source, until 2035, is still dominated by fossil fuels – oil, coal, and natural gas. However, the share of fossil fuels in the world's energy mix will falls from 82% to 76%, while low-carbon energy sources (renewables and nuclear) meet around 40% of the growth in primary energy demand in 2035. Demand for the renewables raise the share of renewables from 13% in 2011 to 18% in 2035 (IEA, 2013b). As shown in Figure 1.1, share of renewables to total energy demand is dominated by electricity generation followed by heat production and transportation fuel. Compared to the fossil fuels, renewable energy provides advantages on the more secure,

reliable and sustainable energy path. Moreover, utilisations of renewable energy in long term offers benefit in reducing CO₂ emission and dependence on imported oil.

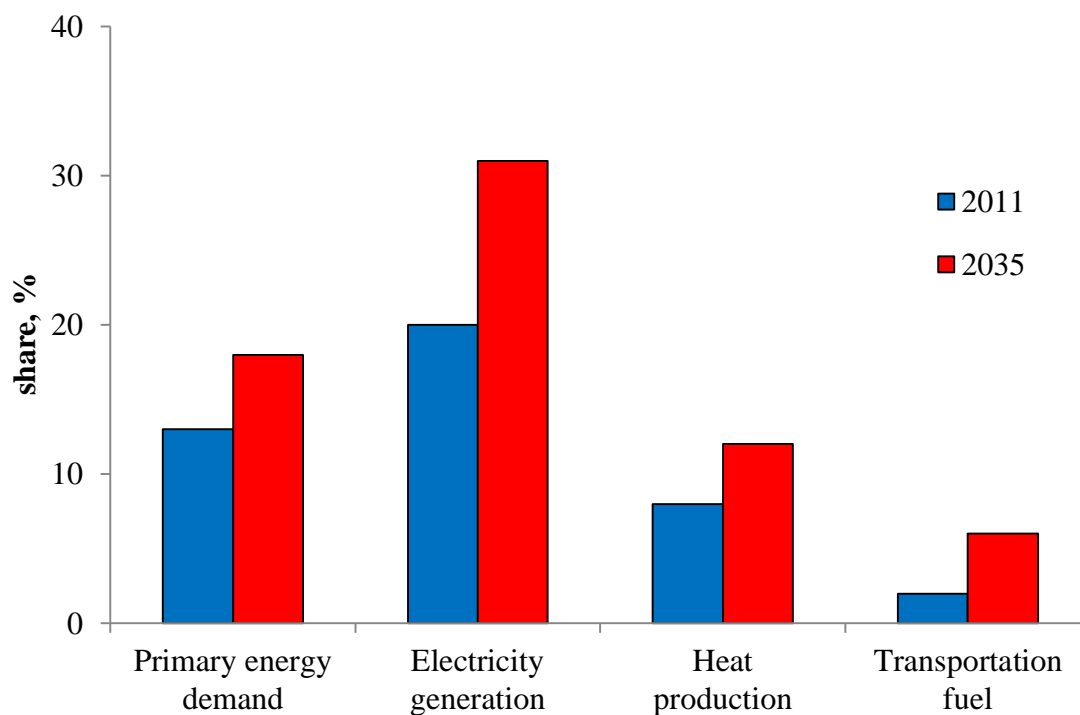


Figure 1.1: Renewable energy share in total primary energy demand by category in 2011 (actual) and 2035 (forecast)

Adapted from: International Energy Agency (2013)

Among the other renewable energy, such as hydro, wind, and solar photovoltaic, biomass is widely utilised due to its local availability at relatively low price. Biomass is the third largest primary energy source in the world, after coal and oil. It remains the primary source of energy for more than half of the world's population, and provides about 1250 million tons oil equivalent (Mtoe) of primary energy, which is about 14% of the world's annual energy consumption (Chen et al., 2009).

Even though the technology of conversion of biomass into alternative fuels is becoming mature, but the production cost of bio-fuel is still higher than that of conventional fossil fuels. Therefore, strong government incentives are usually needed to

make them competitive with fossil fuels. Government support is essential in application of bio-fuel. Globally, in 2012, an amount of US\$ 101 billion was spent by worldwide government to support renewable-energy development, includes US\$ 82 billion to those for electricity generation and US\$ 19 billion to biofuels for transport. European Union recorded almost 60% of total global subsidies or equivalent to US\$ 57 billion; followed by United States (US\$ 21 billion) and China (US\$ 7 billion) as illustrated in Figure 1.2. (IEA, 2013a). With abundant sources of biomass, particularly from palm oil industries and other agricultural based industry, Malaysia has supported the renewable developments through the 5th fuel policy. New source of renewable energy, particularly biomass such as palm oil waste, wood waste and rice husk are recommended to be utilised as energy sources to supplement the conventional energy supply (Shuit et al., 2009). This policy has been implemented in Small Renewable Energy Power Program since 2004 (Sulaiman et al., 2011).

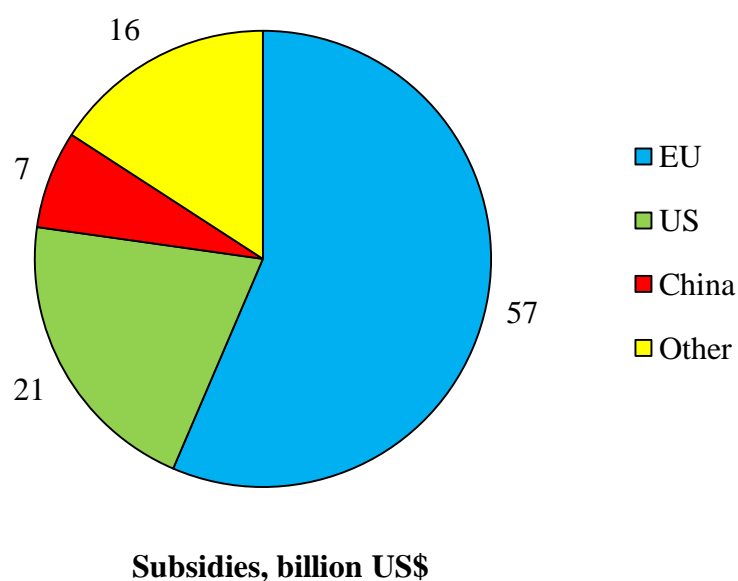


Figure 1.2: Subsidies for renewables development in 2012 by country.

Source: International Energy Agency (2012)

World production of oils and fats stood at 179 million tonnes in 2011. As shown in Figure 1.3, Palm oil and palm kernel oil jointly accounted for 55.76 million tonnes (31%) of that to dominate the oil production; followed by soybean oil and rapeseed oil, contributed 41.75 million tonnes (23%) and 23.46 million tonnes (13%), respectively. Malaysia currently is the world's second largest producer and exporter of palm oil with the production of 18.911 million tonnes of crude palm oil (CPO) in 2011 from 5.0 million ha of plantation area. From this industry, Malaysia received total revenue of 80.4 billion RM in 2011, increased of about 34.60% from previous year revenue according to Malaysian Palm Oil Council. (MPOC, 2011)

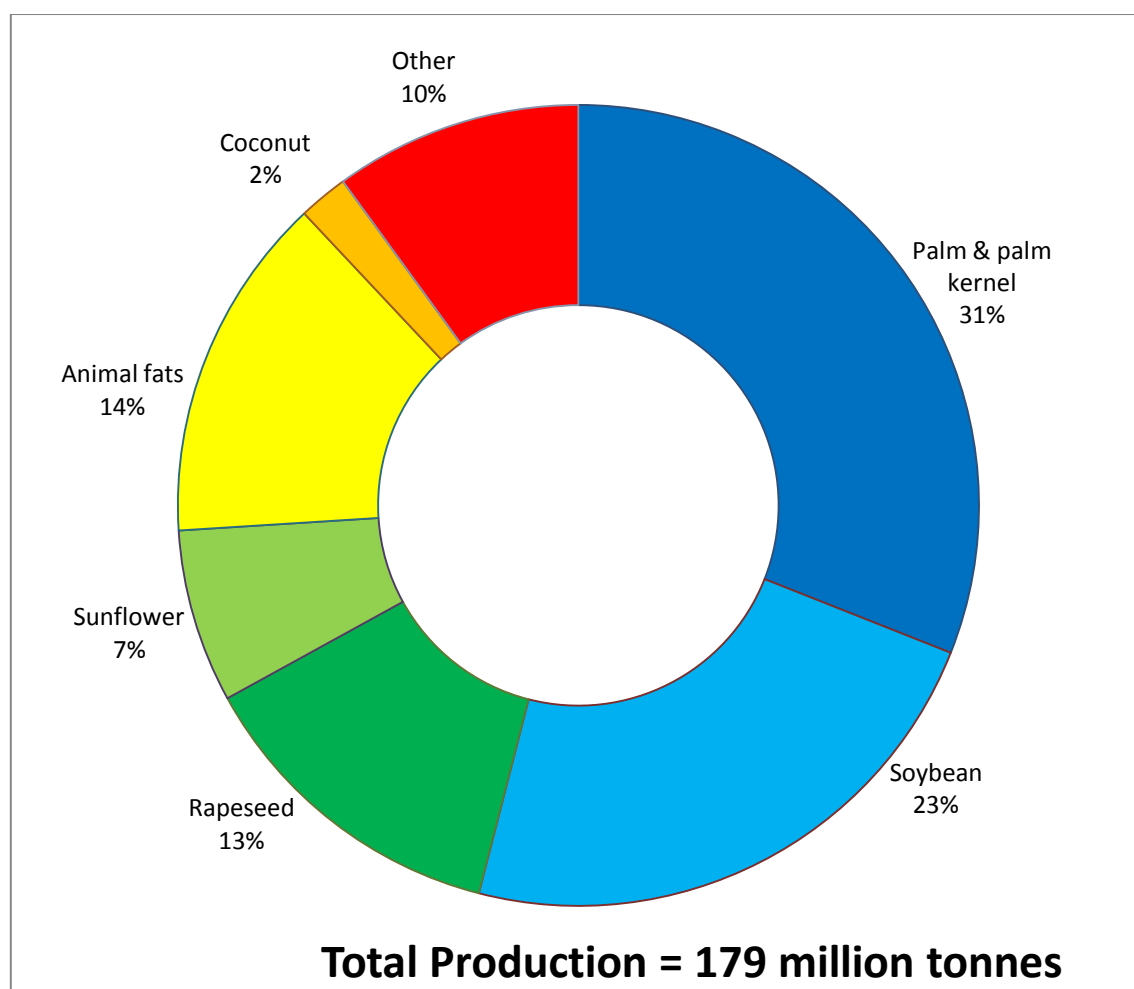


Figure 1.3: World's oils and fats production in 2011

Source: MPOC (2011)

From the processing of fresh fruit bunch (FFB), palm oil milling plant produces 22.8 wt% as crude palm oil (CPO) and crude palm kernel oil (CPKO) while the rest is released into the environment and considered as by-product and waste (Chavalparit et al., 2006). The major solid phases generated from the milling operations are empty fruit bunches, palm fibre, and palm kernel shell. The other biomasses are generated from palm oil plantation in form of trunk, leaves and stalks. In average, one hectare of palm oil plantation produces about 50 – 70 tonnes biomass residue (Shuit et al., 2009), thus approximately 300 million tonne of biomass was generated from palm oil industry in 2011.

Nowadays, these solid wastes are currently considered as the by-product since they are used for economic purposes such as for solid fuels. The palm fibre and palm kernel shell are being used by nearly all palm oil milling plants as solid fuel to generate steam and electricity to be used by the mill. Traditionally, biomasses are being transformed into the fuel source by drying under the sun. However, direct combustion of palm oil biomasses potentially raises environmental issues related to the gas emission and particulate matters. Therefore, biomass is preferred to be transformed into other types of fuel, e.g. bio-ethanol, bio-oil, syn-gas, hydrocarbon or bio-char prior usage. Several reports on conversion of palm oil biomass into energy sources have been published in the two last decades. Conversion of the empty fruit bunch (EFB) into bio-oil through the thermochemical process was successfully conducted in the fixed bed reactor (Lim and Andrése, 2011; Misson et al., 2009) as well as fluidised bed reactor (Sulaiman and Abdullah, 2011; Abdullah and Gerhauser, 2008; Abdullah et al., 2010). Zin et al. (2012) reported the production of hydrogen from EFB bio-oil through steam reforming processes. Hydrogen-rich gas with a composition suitable for liquid fuel synthesis gas was successfully obtained by gasification of EFB (Ogi et al., 2010; Mohammed et al., 2011; Ismail et al., 2011; Inayat et al., 2012; Mohammed et al., 2012a). Recently, biological processes were applied to utilise EFB as substrate in production of bio-ethanol (Piarpuzán et al., 2011; Kim and Ho, 2012), butanol (Noomtim and Cheirsilp, 2011) and bio gas (O-thong et al., 2012).

Palm kernel shell (PKS) accounts for 6 – 7 wt% of the total fresh fruit bunch (FFB) processed. PKS can be transformed into carbonaceous material by the

thermochemical process such as carbonization or torrefaction. Densification of carbonaceous PKS provides briquetted char with high gross calorific value of approximately 30 MJ kg^{-1} (Jamaluddin et al., 2013). This value is comparable to that of coal ($31\text{-}34 \text{ MJ kg}^{-1}$) (Channiwala and Parikh, 2002). In addition, thermal degradation of PKS is also intended to produce bio-oil via pyrolysis (Asadullah et al., 2013; Kim et al., 2010) and hydrogen-rich gas through gasification (Khan et al., 2014a, 2014b; Yusup et al., 2014). Palm kernel shell was also utilised for non-energy purpose, including adsorbent (Jumasiah et al., 2005; Choong et al., 2006; Ismaiel et al., 2013) and building materials (Alengaram et al., 2013; Alengaram et al., 2011; Yew et al., 2014; Muntohar and Rahman, 2014).

Palm oil decanter cake (PDC) is a by-product from palm oil milling decantation process. In the last stage of the clarification process of crude palm oil, extracted palm oil is introduced into the decanter unit. Extracted palm oil is separated into three phases in the decanter; oil phase, aqueous phase, and solid phase. Oil phase in the top of decanter cake are collected as the product for further processing while the aqueous phase is discharged as palm oil milling effluent. The separated fine solid particles suspended in extracted palm oil are decanted after certain residence time. A screw conveyor in the bottom of the decanter discharges the decanter cake from the decanter unit. The production rate of the decanter cake amount to about 4 – 5 wt % of the fresh fruit bunch processed. The composition of decanter cake varies by plant site location. Its' major constituents are carbon, hydrogen, oxygen, and nitrogen. Decanter cake may also contain phosphorus and magnesium (Chavalparit et al., 2006). The oil content of PDC was reported to be about 11.5 wt% (Maniam et al., 2013).

In recent years, some researchers have been trying to create and develop value added by-products from PDC. At many palm oil mills, decanter cake is usually mixed with other biomass wastes together with some chemical base plant nutrient and sent back to the plantation as fertilizer. The advantage of PDC as fertilizer was studied in lady's finger plant (Embrandiri et al., 2013). Composting of PDC mixed with other biomass wastes was considered as good practice as it will be helpful in recycling useful plant nutrients (Singh et al., 2010; Nutongkaew et al., 2013; Yahya et al., 2010). Currently, palm oil decanter cake (PDC) has attracted researchers' attention to utilise it

as substrates for valuable by-products. Biological process of PDC has been conducted to produce cellulase and polyose (Zanirun et al., 2013; Nafis et al., 2012). PDC was also investigated as the substrate for bio-surfactant (Noparat et al., 2014), bio-butanol (Loyarkat et al., 2013), and bio-diesel production (Maniam et al., 2013). The capability of decanter cake as adsorbent for heavy metal and organic pollutant removal from aqueous solution have also been investigated (Dewayanto et al., 2009; Sahad et al., 2012).

Conversion of biomass into energy sources has been practiced from long time ago. Direct combustion of biomass, historically, has been the primary source of energy throughout the world, particularly for residential activity and small industry in the rural area. Unfortunately, direct burning of loose biomass in conventional grate is always associated with low energy efficiency and contributes adverse impact to the environment, particularly the air quality. Modern technology which offers clean and efficient energy conversion is required to improve the attractiveness of biomass utilisation as energy sources. Many techniques have been developed to transform biomass into energy. Hernandez (2011) classified the conversion process into two categories biochemical and thermochemical. Biochemical usually consists of two processes: gasification or hydrolysis followed by fermentation to form ethanol. Thermochemical processes required relatively high temperature and sometimes high pressure to decompose biomass into the smaller molecular weight compound that can be converted into hydrocarbons, alcohols or aromatics via the catalytic process.

There are two main pathways in the thermochemical process of biomass conversion: pyrolysis and gasification. Pyrolysis is thermal decomposition of biomass in the absence of oxygen. Main products of pyrolysis are bio-oil or pyrolytic liquid, solid char and gas. Bio-oil produced from biomass contains high oxygenated compounds. This causes problem of the instability of the oil during storage, where viscosity, calorific value, and density all are affected. Therefore, utilisation of the oil requires a general decrease in the oxygen content in order to separate the organic product from the water, increase the heating value, and increase the stability (Mortensen et al., 2011). Hydrodeoxygenation, a catalytic reaction between bio-oil and hydrogen becomes the most common bio-oil upgrading process. In this process, oxygen is eliminated from bio-

oil as water. Otherwise, the bio-oil can be upgraded by hydrocracking, where the chemical compounds in the bio-oil were cracked into smaller molecules. Feasibility of co-processing of bio-oil upgrading in a Fluid Catalytic Cracking (FCC) facilities of crude oil refinery were also investigated (Mante et al. 2012; Fogassy et al. 2011; Stefanidis et al. 2011). Instead of catalytic upgrading of bio-oil, the addition of catalyst during the pyrolysis process was proposed as the alternative pathway to enhance the bio-oil properties. The direct use of catalysts could decrease the pyrolysis temperature, increase the conversion of biomass and the yield of bio-oil, and change the distribution of the pyrolytic liquid products then improve the quality of the bio-oil obtained (Aho et al., 2011; Stefanidis et al., 2011; Torri et al., 2010; Abu Bakar and Titiloye, 2013).

1.2 PROBLEM STATEMENT

Even though the palm oil industry contributes major income for Malaysia, it raises environmental concern due to the waste generated. From the processing of fresh fruit bunch (FFB), palm oil milling plant produces 22.8 wt% as crude palm oil (CPO) and crude palm kernel oil (CPKO) while the rest is released into the environment and considered as by-product and waste (Chavalparit et al., 2006). Recent study also reported that palm oil biomass residue has potential energy value of RM 6.379 billion annually (Sulaiman et al., 2011). One of the solid phases generated from the milling operations is palm oil decanter cake with the production rate about 4 – 5 wt % of the fresh fruit bunch processed. Currently, the decanter cake from palm oil milling plant is usually mixed with other biomass wastes together with some chemical base plant nutrient and sent back to the plantation as fertilizer. Therefore, PDC is still under-utilisation as an added value by product.

A thermochemical process by means pyrolysis seems to be promising option in converting biomass into biofuel. The pyrolysis process may convert almost of all biomass components such as cellulose, hemicellulose and lignin into biofuel. Bio-oil produced from pyrolysis becomes an attractive option due to its advantages. Bio-oil is considered as the lowest-cost liquid biofuel, and categorised as green energy since its combustion is having a net zero carbon footprint (Chiaramonti et al., 2007). Furthermore, bio-oil has high-energy density compared to fuel gases produced by

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the last three decades, world's energy consumption has been rapidly increasing due to the population growth and economic activities. Modern lifestyle which is required better health and environmental provision, accessibility and mobility, also contribute to energy consumption rising worldwide. The world primary energy demand increases by one-third from 2011 to 2035 as projected by International Energy Agency (IEA, 2013a). Oil demand (excluding biofuels) continues to grow steadily, reaching about 99 million barrels per day (mb/d) by 2035 — 15 mb/d higher than in 2009, while global oil production reaches 96 mb/d by 2035 (IEA, 2013a). It is clearly stated that the unbalance between oil demand and production, also oil price uncertainty, encourage people to find the new energy source. In Malaysia case, energy demand rapidly increases from 143 mboe (million barrels of oil equivalent) in 1990 to 503 mboe in 2011, and will reach almost 870 mboe in 2035 with the annual growth rate of 2.3% (IEA, 2013b).

World primary energy source, until 2035, is still dominated by fossil fuels – oil, coal, and natural gas. However, the share of fossil fuels in the world's energy mix will falls from 82% to 76%, while low-carbon energy sources (renewables and nuclear) meet around 40% of the growth in primary energy demand in 2035. Demand for the renewables raise the share of renewables from 13% in 2011 to 18% in 2035 (IEA, 2013b). As shown in Figure 1.1, share of renewables to total energy demand is dominated by electricity generation followed by heat production and transportation fuel. Compared to the fossil fuels, renewable energy provides advantages on the more secure,

reliable and sustainable energy path. Moreover, utilisations of renewable energy in long term offers benefit in reducing CO₂ emission and dependence on imported oil.

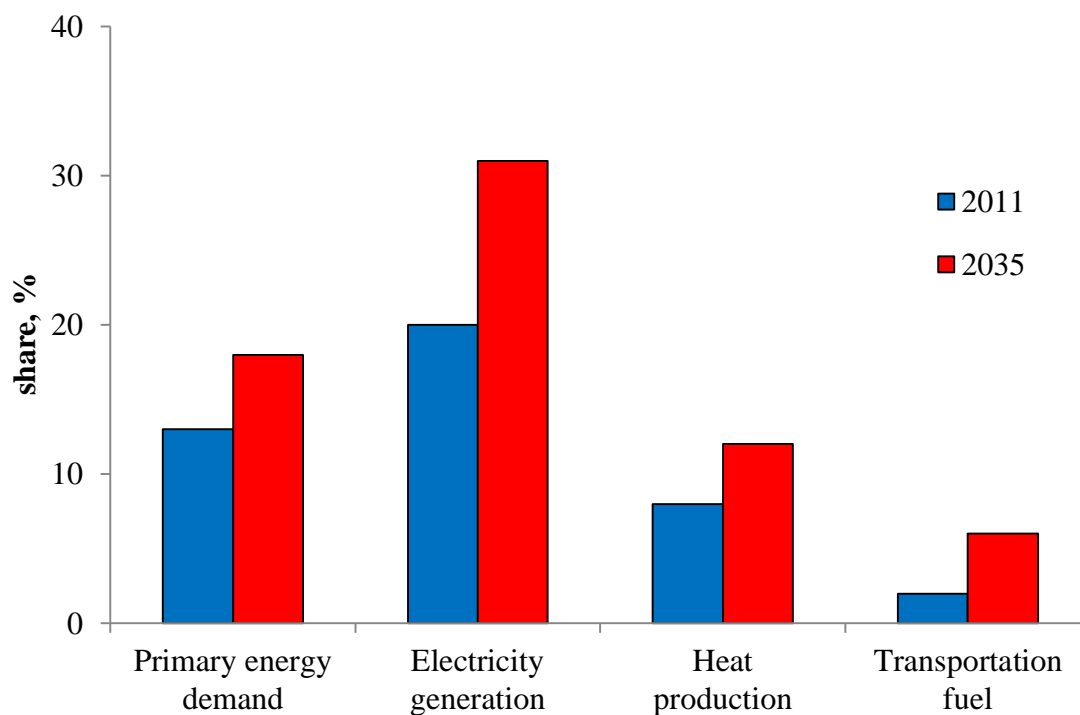


Figure 1.1: Renewable energy share in total primary energy demand by category in 2011 (actual) and 2035 (forecast)

Adapted from: International Energy Agency (2013)

Among the other renewable energy, such as hydro, wind, and solar photovoltaic, biomass is widely utilised due to its local availability at relatively low price. Biomass is the third largest primary energy source in the world, after coal and oil. It remains the primary source of energy for more than half of the world's population, and provides about 1250 million tons oil equivalent (Mtoe) of primary energy, which is about 14% of the world's annual energy consumption (Chen et al., 2009).

Even though the technology of conversion of biomass into alternative fuels is becoming mature, but the production cost of bio-fuel is still higher than that of conventional fossil fuels. Therefore, strong government incentives are usually needed to

make them competitive with fossil fuels. Government support is essential in application of bio-fuel. Globally, in 2012, an amount of US\$ 101 billion was spent by worldwide government to support renewable-energy development, includes US\$ 82 billion to those for electricity generation and US\$ 19 billion to biofuels for transport. European Union recorded almost 60% of total global subsidies or equivalent to US\$ 57 billion; followed by United States (US\$ 21 billion) and China (US\$ 7 billion) as illustrated in Figure 1.2. (IEA, 2013a). With abundant sources of biomass, particularly from palm oil industries and other agricultural based industry, Malaysia has supported the renewable developments through the 5th fuel policy. New source of renewable energy, particularly biomass such as palm oil waste, wood waste and rice husk are recommended to be utilised as energy sources to supplement the conventional energy supply (Shuit et al., 2009). This policy has been implemented in Small Renewable Energy Power Program since 2004 (Sulaiman et al., 2011).

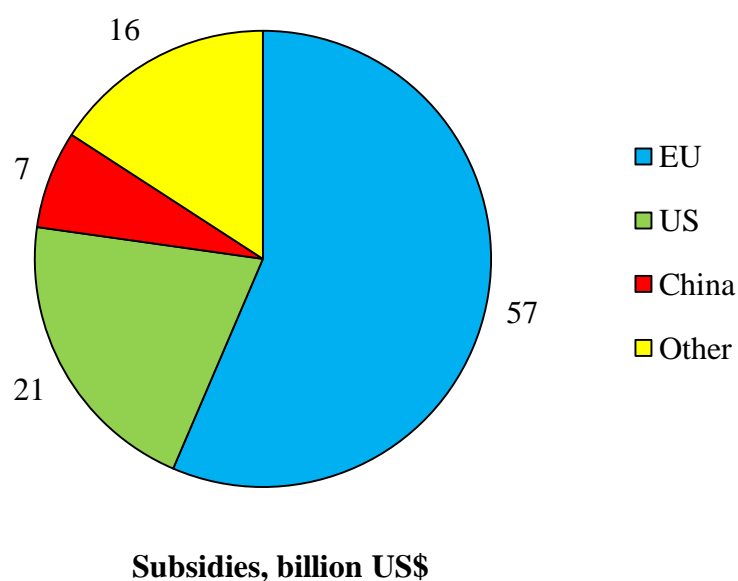


Figure 1.2: Subsidies for renewables development in 2012 by country.

Source: International Energy Agency (2012)

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Overall, material used in this research can be divided into three categories: biomass, catalyst and supported materials. This section provides useful information about the material's preparation and their pre-treatment prior to the experimental works. Origin of the materials and their technical specification is also described here if the information is available.

3.1.1 Decanter cake

Palm oil decanter cake (PDC) is semi-solid waste generated from the purification process of crude palm oil in milling plant. In this work, fresh PDC and palm kernel shell (PKS) were obtained from local palm oil milling plant LKPP Corporation, Sdn. Bhd. located in Kompleks Kilang LKPP Lepar, KM 43.5 Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang Darul Makmur, Malaysia. Preparation of raw materials prior to the experiments is summarised in Figure 3.1. In fresh condition, PDC contains more than 70 wt% of moisture, while moisture content of fresh PKS is around 14 – 20 wt%. Drying process was conducted in laboratory oven (Memmert) at 105 °C for 18 hours to obtain the final moisture content of 5 – 8 %. Prior to the experiments, dried PDC was ground and sieved to obtain the particle size of decanter cake within the range of 0.8 – 2.0 mm.

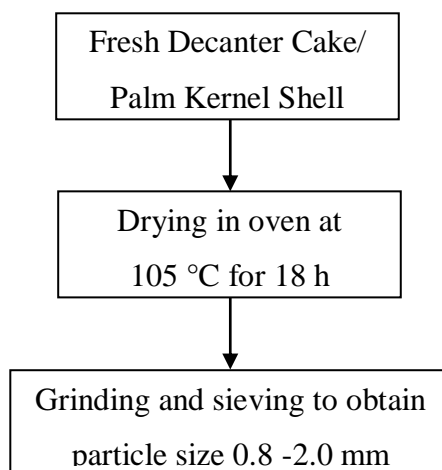


Figure 3.1: Schematic diagram of decanter cake preparation.

3.1.2 Catalyst

Four types of catalyst were employed in this study: calcium oxide (CaO), magnesium oxide (MgO), H-ZSM5 and gamma alumina (γ -Al₂O₃). CaO and MgO (reagent grade) were purchased from Sigma-Aldrich, while γ -Al₂O₃ (analytical grade) was purchased from Merck. H-ZSM5 (Si/Al = 30) was supplied by Zeolyst International. All of the catalysts were calcined at 550 °C for 3 h prior to the experiments, except CaO was at 900 °C. These calcination temperatures were chosen based on TGA plot of catalysts as shown in Figure 3.2. It clearly indicates that there was no weight loss at above calcination temperature. The catalyst was characterised by X-ray diffraction (Rigaku) with Cu K α as a source at a tube voltage of 30 kV and a current of 15 mA. The diffractogram patterns were collected in 2 θ range from 0° to 80° with step sizes of 0.02° and at a scanning speed of 1°/min. Thermal properties of catalysts were examined by using a Mettler Toledo TGA/DSC. Amount of 5 mg sample was placed into the thermogravimetry analyser and heating up from 25 °C to 1000 °C at heating rate of 10 °C/min in N₂ environment. The surface area of catalysts was determined from the adsorption isotherms of nitrogen at -196 °C onto the catalyst using Micromeritics ASAP 2000. All the samples were degassed at 105 °C prior to the

analysis and the adsorption of N_2 was measured at $-196\text{ }^\circ\text{C}$. Brunauer–Emmett–Teller (BET) equation was employed to calculate the specific surface area.

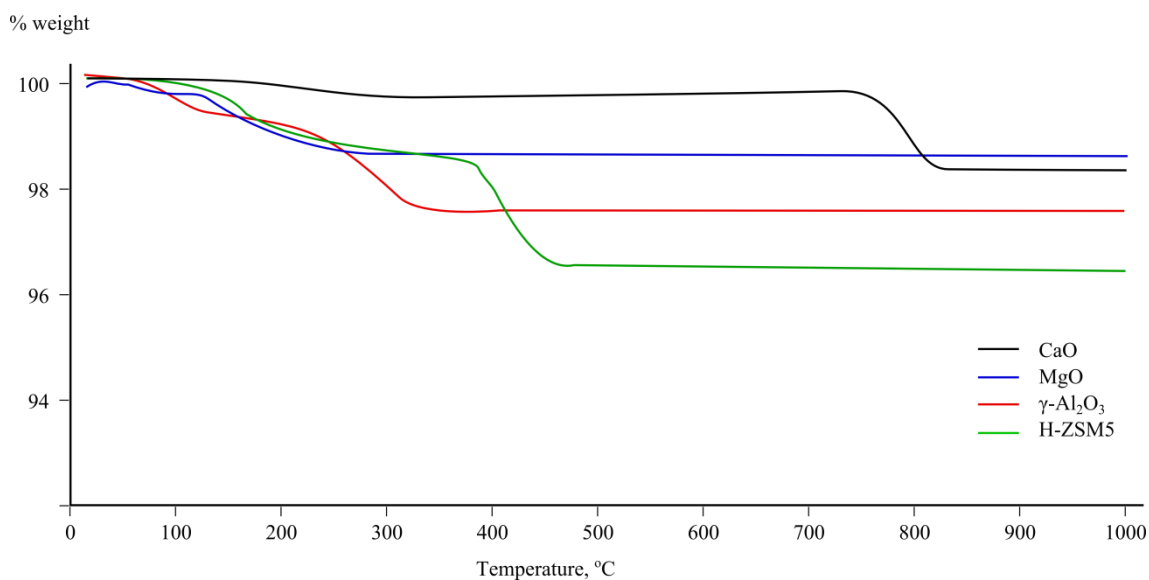


Figure 3.2: TGA plots of catalyst used to determine calcination temperature of catalysts.

3.1.3 Gases and chemicals

Some gases and chemicals were also utilised in the experiments, particularly for analysis purposes. High purity of oxygen (99.9 %) used in bomb calorimeter analysis was purchased from MOX-Linde. Helium, hydrogen and compressed air for GC-MS analysis were also supplied by MOX-Linde. Hexane (chromatography grade) and KBr (IR spectroscopy grade) were purchased from Merck Millipore.

3.2 EQUIPMENTS

In this work, pyrolysis of PDC was conducted in fixed bed under the vacuum pressure to produce bio-oils. This section describes the equipment used in the experiments; include the reactor design and apparatus arrangement for single and dual stage catalytic pyrolysis.