# PREPARATION AND OPTIMIZATION OF LIQUEFIED OIL PALM TRUNK BASED ADHESIVE FOR PARTICLEBOARD APPLICATION

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**UNIVERSITI SAINS MALAYSIA**

**2016**

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**by**

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**Thesis submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy**

**September 2016**

## ACKNOWLEDGMENT

First and foremost, all praises and thanks to Almighty Allah S.W.T, the most Gracious and the most Merciful, who has granted innumerable blessing, health and perseverance for me to finish my PhD journey. Peace be upon Prophet Muhammad S.A.W, his family and his companions.

I would like to convey the most profound appreciation to my supervisor Prof. Dr. Othman Sulaiman and my co-supervisor Dr. Mohd Firdaus Yhaya for their patience, inspiration and constant provision of my PhD study and related research. Their immense knowledge and guidance helped me a lot during lab works and writing of this thesis. I could not have imagined finishing my PhD study without their assistance.

Besides, I would like to express my sincere gratitude to Prof. Dr. Rokiah Hashim for her significant contribution, which inspired me to broaden my research from various perspectives. Her motivation and encouragement throughout this bittersweet PhD journey are greatly appreciated. Without her unconditional support, I would have despaired.

My warmest thank also goes to all my fellow friends, labmates, lecturers, administration and laboratory staffs in the School of Industrial Technology, Universiti Sains Malaysia for their precious assistance. My appreciation is extended to Universiti Sains Malaysia for providing me with modern facilities, research equipment and the opportunity to conduct this study.

In conclusion, I recognize that this research would not have been possible without the financial assistance of MyPhD Scholarship, MyBrain15, under the incentive of Ministry of Higher Education, Malaysia.

Finally yet importantly, I would like to thank my family, my parents Mr Awalludin Hasan and Mrs Jaliah Hj Shawal for raising me and giving the freedom for me to chase my dreams. To all my brothers Khairul Aizat Awalludin, Mohd Amri Awalludin and Mohammad Adli Awalludin also my sisters Nor Syahida Awalludin, Siti Zulaikha Awalludin and Siti Aishah Awalludin, thank you so much for supporting me spiritually throughout my entire PhD study and my life in general.

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## LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| Å | Angstrom |
| df | Degree of freedom |
| $Fv_{3d}$ | Flask value for 3 days formaldehyde release |
| $Fv_{3h}$ | Flask value for 3 hours formaldehyde release |
| $GtCO_2eq$ | $n\times10^{12}$ metric tons of $CO_2$ |
| $R^2_{Adj.}$ | Adjusted R-Squared |
| $R^2_{Pred.}$ | Predicted R-Squared |
| ANOVA | Analysis of variance |
| ASTM | American Society for Testing and Materials |
| BS EN | British Standard European Norm |
| C.V. | Coefficient of variation |
| CCD | Central composite design |
| CCRD | Central composite rotatable design |
| CI | Confidence interval |
| DoE | Design of experiment |
| EFB | Empty fruit bunches |
| EPP | Entry point projects |
| ETP | Economic Transformation Program |
| FAOSTAT | Food and Agriculture Organization of the United Nations, Statistics Division |
| FESEM | Field-emission scanning electron microscope |
| FPF | Fruit press fibre |
| FT-IR | Fourier Transform-InfraRed |

| | |
|---|---|
| GC-MS | Gas Chromatograph-Mass Spectrometer |
| GDP | Gross domestic product |
| GNI | Gross national income |
| JIS | Japanese Industrial Standards |
| MF | Mesocarp fibre |
| MPOB | Malaysian Palm Oil Board |
| M.W | Molecular weight |
| OPF | Oil palm frond |
| OPT | Oil palm trunk |
| PA | Polyamides |
| PKS | Palm kernel shells |
| PLA | Polylactide |
| PRESS | Predicted residual error sum of squares |
| RSM | Response surface methodology |
| R.T | Retention time |
| S.I | Similarity index |
| TGA | Thermogravimetric analysis |
| UF | Urea-formaldehyde |
| VIF | Variance inflation factor |
| WD | Working distance |

**PENYEDIAAN DAN PENGOPTIMUMAN PEREKAT BERASASKAN BATANG KELAPA SAWIT TERCAIR UNTUK APLIKASI PAPAN PARTIKAL**

## ABSTRAK

Pemanfaatan sisa batang kelapa sawit (OPT) melalui kaedah pencecairan merupakan subjek yang diberikan perhatian. Ujikaji pencecairan OPT dalam etilena glikol dan gliserol, dengan pemangkin $H_2SO_4$, pada suhu 150 °C telah dijalankan berdasarkan rekabentuk eksperimen (DoE) dengan bantuan perisian Stat-Ease Inc., Design-Expert® Versi 7. Rekabentuk $2^{4-1}$ pecahan faktoran telah digunakan di peringkat saringan di mana faktor-faktor seperti jenis pelarut, peratusan pemangkin asid sulfurik ($H_2SO_4$) dan masa pencecairan adalah penting kepada hasil pencecairan. Walaubagaimanapun, faktor stok suapan OPT dilihat kurang memberikan kesan. Faktor-faktor yang penting tadi beserta kesan percampuran pelarut pencecairan dikaji lebih lanjut dengan bantuan rekabentuk gabungan D-optimal. Proses pencecairan OPT dalam gliserol memberikan lebih banyak hasil berbanding dalam etilena glikol. Model yang telah dipilih ialah Linear (L) untuk campuran manakala 2–Faktor Interaksi (2FI) untuk proses. Ketika proses pengoptimuman dan pengesahan, keadaan eksperimen yang dicadangkan untuk hasil yang optimum ialah campuran 34% etilena glikol terhadap 66% gliserol, 4% $H_2SO_4$, dan masa pencecairan selama 116 minit. Berdasarkan tetapan ini, ujikaji berasingan yang juga bertujuan sebagai pengesahan terhadap kebolehupayaan model telah dijalankan. Keputusan menunjukkan hasil optimum pencecairan yang diperolehi daripada ujikaji ialah 81.53%, hampir menyamai nilai yang dianggarkan oleh model empirik iaitu 79.92%. Dengan itu, model L × 2FI yang telah dipilih diakui sah dan memuaskan. Ujian Tranformasi

Fourier-Inframerah (FTIR) dan Mikroskop Imbasan Elektron-Medan Pancaran (FESEM) yang dijalankan terhadap baki pencecairan menunjukkan partikel OPT telah mengalami degradasi lampau ketika dalam proses pencecairan. Hasil optimum pencecairan OPT yang diperolehi telah diaplikasi ke dalam papan partikal OPT. Campuran antara OPT tercair dan urea-formaldehid (UF) dijadikan sebagai perekat. Pelepasan formaldehid berkurangan apabila OPT tercair ditambah ke dalam papan partikal. Batang kelapa sawit tercair dilihat mempunyai sifat pemerangkap formaldehid. Walaubagaimanapun, penambahan OPT tercair menyebabkan kekuatan mekanik papan partikal berkurang. Ini kerana OPT tercair tidak mempunyai keupayaan perekatan setanding dengan UF. Walaupun begitu, beberapa papan partikal terikat oleh campuran OPT tercair/UF dilihat menepati Jenis 8 dan Jenis 13 berdasarkan piawaian Jepun, JIS A 3908: 2003. Ujian berasingan untuk pengoptimuman dan pengesahan telah dilakukan di mana matlamat ditetapkan berdasarkan piawai JIS A 3908: 2003 tersebut. Keputusan menunjukkan pelepasan formaldehid dan kekuatan mekanik berada di dalam julat seperti yang diramalkan oleh model empirik. Analisa termogravimetri (TGA) menunjukkan terdapat sedikit peningkatan kestabilan termal papan partikal dengan penambahan OPT tercair.

**PREPARATION AND OPTIMIZATION OF LIQUEFIED OIL PALM TRUNK BASED ADHESIVE FOR PARTICLEBOARD APPLICATION**

## ABSTRACT

Utilization of waste oil palm trunk (OPT) through liquefaction is the subject of interest. Liquefaction of OPT in ethylene glycol and glycerol, with $H_2SO_4$ as a catalyst, at a temperature of 150 °C was carried out based on experimental design (DoE) aided by software Stat-Ease Inc., Design-Expert® Version 7. A $2^{4-1}$ fractional factorial design used in screening phase showed that factors such as types of solvents, percentage of sulphuric acid ($H_2SO_4$) catalyst and liquefaction time found to be important. However, factor of OPT loading was found to be less important. Those important factors and different solvent mixtures were studied further by implementing combined D-optimal design. Liquefaction of OPT in glycerol found to give more yield than in ethylene glycol. The selected empirical model was Linear (L) for mixture, while 2–Factor Interactions (2FI) for process. For optimization and model verification, the proposed solution for an optimal result was a mixture between 34% ethylene glycol to 66% glycerol, 4% $H_2SO_4$, and 116 minutes liquefaction time. Under this condition, a separated experiment was conducted for verification purposes. The optimum result showed that the actual liquefaction yield obtained was 81.53%, closed to the predicted value by the empirical model that was 79.92%. Thus, selected model L × 2FI was considered as valid and adequate. The Fourier Transform-Infrared (FTIR) and Field Emission-Scanning Electron Microscope (FESEM) analyses were conducted on the remaining liquefaction residues. Results showed that OPT particles have suffered extreme degradation process during liquefaction process. The optimal liquefied OPT was then applied in the OPT particleboards. Mixtures of liquefied OPT/urea-formaldehyde (UF) were used as binder. Formaldehyde release test conducted showed a reduction in formaldehyde when liquefied OPT was added into the particleboard. Liquefied OPT seems to behave like formaldehyde catcher. However, with the addition of liquefied OPT, mechanical strength of OPT particleboards was reduced. The reason is because liquefied OPT did not have comparable adhesive properties like UF. Even so, some of the manufactured particleboards bonded with mixtures of liquid OPT/UF meet Type 8 and Type 13 as referred to Japanese Standards, JIS A 3908: 2003. A separated set for optimization and validation purposes was carried out in which the goals set to meet the JIS A 3908: 2003 standards. The results for formaldehyde release and mechanical strength obtained were within the range predicted by the empirical model. Thermogravimetric analysis (TGA) showed a minor increase in thermal stability properties of the particleboards with the addition of liquefied OPT.

# CHAPTER 1 – INTRODUCTION

The introductory chapter is intended to present the research background and the idea of the study (Section 1.1). The idea later has been directed to the problem statement that explained the research gap of the study (Section 1.2). After the problem statement identified, we came out with the specific objectives and the possible hypotheses (Section 1.3 and Section 1.4 respectively).

## 1.1 Research Background

The total number of the world's population now exceeds 7.2 billion people. The population is expected to grow between 9.6 and 12.3 billion people by 2100 (Gerland *et al.*, 2014). Certainly, the demand for food, fossil fuels, biofuels and other necessities such as construction materials, furniture and vehicles will also increase. In order to cater the food, biofuel and raw material demands, more farms and plantations are expected to be opened and improved in the coming years. Simultaneously, this agricultural extensification[1] and intensification[2] lead to the increasing of agricultural wastes worldwide. This current situation is expected to cause more agricultural pollution and vast emission of greenhouse gases such as carbon dioxide and methane (Burney *et al.*, 2010). In a dataset issued by FAOSTAT Emissions database, between 1997–2011, the global greenhouse gas emissions from biomass burning were estimated ranging from 6 to 8 $GtCO_2eq$[3] annually (Rossi *et al.*, 2016). Pollution caused by agriculture and industry, together with the greenhouse

[1] Expanding the area of cultivated land.
[2] Improving crop yield and quality from the land that already under cultivation.
[3] $GtCO_2eq = n \times 10^{12}$ metric tons of $CO_2$ equivalent (UN climate change panel IPCC).

effect has led to global warming problem that trigger the climate change. It has been a serious global concern for environmentalists. The awareness to address this issue has amplified the interest in the more eco-friendly technology and research development (Hirose *et al.*, 2002).

As the world's largest crude palm oil exporter, Malaysia is moving forward with the increasing demand of palm oil for foods and biofuels (AIM, 2013; Wicke *et al.*, 2011). The world's palm oil consumption in 2009–2010 was recorded at 45.1 million tons compared to the consumption in 2000–2001, that was only 21.9 million tons (Khin *et al.*, 2013). In a projection made by Corley (2009), the demand will surge between 93 and 256 million tons by 2050 annually. This is one of the reasons for the blooming palm oil industry in Malaysia in recent decades. Dramatically, the oil palm agricultural wastes have also increased (Hashim *et al.*, 2010). Efforts to utilize such wastes need to be upgraded.

The regular utilization practices are through simple mechanical processes like shredding, chipping and palletizing. Approximately 75% of the wastes in the form of oil palm trunks (OPT) and oil palm fronds (OPF) are left rotten in the plantation as mulch and nutrient recycling. The remaining 25% solid wastes like empty fruit bunches (EFB), palm kernel shells (PKS) and mesocarp fibre (MF) have been used in direct combustion as boiler fuel and to generate electricity in palm oil mills and refineries (Awalludin *et al.*, 2015). The continuous combustion of biomass material can worsen the greenhouse effect.

Other than combustion, methods like gasification, pyrolysis and liquefaction are suitable for converting the oil palm wastes into value-added products. Due to the increasing awareness about the harmful effect of combustion, utilization method through liquefaction is gaining more attention from researchers. Liquefied biomass substances are suitable for plastic, composite and resin industries (Briones *et al.*, 2015; Doh *et al.*, 2005b; Kishi *et al.*, 2006; Xie *et al.*, 2015). According to Pan (2011), liquefied biomass by means of solvolysis contains a combination of functional groups from the organic solvents and the biomass feedstock that are useful in variety of applications.

In addition, oil palm wastes also have the potential to be used as an alternative raw material for many applications. For example, the composite board industry uses many raw materials derived from forest resources. Like wood, oil palm wastes contain plant fibres, which can replace the plant fibre obtained from forest trees. This replacement can save more forests from deforestation and simultaneously reduce the dumping problem of oil palm wastes. As a response, research on new eco-friendly materials gains attention from researchers around the world. Using material that exhibits positive environmental qualities has become main priority (Hashim *et al.*, 2016).

## 1.2 Problem statement

Researchers around the world have studied liquefaction of biomass from forest and agricultural wastes and other lignocellulose products. Among the tree species involved were Japanese beech (*Fagus crenata Blume*) (Yamazaki *et al.*, 2006), poplar (*Populus ssp.*), alder (*Alnus ssp.*), linden (*Tilia ssp.*) and chestnut wood (*Castanea sativa Mill.*) (Kržan *et al.*, 2005) and Chinese tallow (*Triadica sebifera* syn. *Sapium sebiferum*) (Pan *et al.*, 2007). In terms of agricultural crops, among the wastes studied were corn stover (Xiao *et al.*, 2011), corn bran (Lee *et al.*, 2000b), bagasse and cotton stalks (Hassan *et al.*, 2008), moso bamboo (*Phyllostachys angusta*) (Yip *et al.*, 2009), grapevine cane (*Vitis vinisera* L.) (Alma *et al.*, 2006) and oil palm (*Elaeis guineensis*) EFB (Ahmadzadeh *et al.*, 2009). Other study involving lignocellulose products were cotton wool and filter paper (Kržan *et al.*, 2009) and waste paper (Lee *et al.*, 2002a).

For years, Malaysia has been strengthening its palm oil industry as a vital source of national income. Malaysian palm oil industry provides a continuous supply of biomass waiting to be explored. Therefore, we take this opportunity to assess the suitability of converting waste OPT by means of liquefaction, specifically through solvolysis process. Among the question that arises is what will happen to the OPT particles when undergo solvolysis process? Before that, solvolysis can be defined as a process of breaking down one or more bonds in a substance/solute by solvent. It may involves fragmentation, substitution and elimination reactions where the solvent acts as the nucleophile (Jensen, 1981). Hence, we conducted a study of OPT liquefaction through solvolysis by ethylene glycol and glycerol.

There are various uses of liquefied biomass. Among the applications that have been tried and evaluated such as resol-type phenolic resin used in phenolic foam (Lee *et al.*, 2002c), novolak phenol formaldehyde resin (Li *et al.*, 2012), liquefied wood/polyurethane films (Kurimoto *et al.*, 2001), resin applications in moulding (Zhang *et al.*, 2007), wood ceramics (Hirose *et al.*, 2002), carbon fibres (Ma *et al.*, 2010; Ma *et al.*, 2011), liquefied wood/epoxy resin (Kobayashi *et al.*, 2001), polymer composites (Doh *et al.*, 2005a), mesoporous activated carbon fibre (Ma *et al.*, 2014) and fuel for gas turbines (Seljak *et al.*, 2012). To our knowledge, no liquefaction of waste OPT and its possible application ever attempted by any researcher. However, there have been a few studies about liquefaction of other oil palm wastes such as EFB fibres used in phenolated EFB resin (Fan *et al.*, 2011), MF and PKS used for producing bio oil (Chan *et al.*, 2014).

In a study done by Kunaver *et al.* (2010b), they added different types of liquefied Southern European hardwoods and softwoods into melamine–formaldehyde and melamine–urea–formaldehyde based particleboards. Results obtained showed that the formaldehyde release from those particleboards was reduced significantly. Therefore, we conducted an experiment regarding this finding using liquefied OPT as adhesive mixture in urea-formaldehyde-based OPT particleboards. Besides formaldehyde release test, we also conducted the mechanical strength tests, thermal properties and microscopic observation of the OPT particleboards.

Most research on liquefaction of biomass, including oil palm wastes were conducted through several methods and experimental designs. Consequently, we performed the study on OPT liquefaction in solvents and its application as adhesive mixture in OPT particleboard with the help of Response Surface Methodology (RSM) software. This is necessary, so that the findings can be explained statistically. Our biggest hope is to provide a reliable model of the biomass liquefaction process that generates desired product, together with its potential application, in a more selective and controllable manner.

## 1.3 Objectives

The work designated in this PhD study was aimed to prepare and characterize the liquefied oil palm trunk (OPT) for adhesive mixture in OPT particleboard. Oil palm trunk was selected as the liquefaction feedstock due to its availability in the form of oil palm plantation waste in Malaysia. In OPT liquefaction process, glycerol was used as one of the liquefaction solvents because glycerol could be obtained as palm oil biodiesel by-product (Kunaver *et al.*, 2010b). In general, this study harnesses the oil palm industrial wastes potential for conversion into more value-added product. The study adopted response surface methodology (RSM) that statistically analysed the significance of variables and their interactions during liquefaction process. The specific objectives are as follows:

1. To determine how factors such as liquefaction time, amount of catalyst, feedstock loading and types of solvents affect the liquefaction yield of OPT.
2. To evaluate the optimum conditions for the liquefaction of OPT through the application of response surface methodology (RSM).
3. To investigate the effect of adding the mixture between liquefied OPT with urea formaldehyde in OPT particleboards to the particleboard mechanical strengths, physical properties and formaldehyde release.

## 1.4 Hypotheses

Based on previous studies regarding the biomass liquefaction, factors such as liquefaction time, the amount of catalyst, feedstock loading and types of solvents have been greatly influencing the final yield of biomass liquefaction. Our assumptions were:

1. The longer the liquefaction time, the higher the liquefied OPT yield.
2. The higher the amount of catalyst, the quicker the liquefaction reaction occurs.
3. The lesser the amount of OPT feedstock loading, relative to the amount of liquefaction solvent, the higher the yield.
4. Liquefaction of OPT in ethylene glycol will gives higher yield due to its low viscosity that permits more solvent attack on OPT, if compare to glycerol that has a higher viscosity.

By adding the mixture between liquid OPT and urea formaldehyde in OPT particleboards, it manipulates the mechanical strengths and formaldehyde release properties of the OPT particleboards. Our expectations were:

1. Higher content of liquefied OPT in OPT particleboards strengthens the particleboards mechanical strength.

2. Liquefied OPT/urea formaldehyde mixture reduces the formaldehyde emission from the OPT particleboards.

## 1.5 Research benefits

### 1.5.1 Benefit to the country

This PhD study was conducted as a response to the government's vision to become a developed nation by 2020. This study is hopefully may help in boosting Malaysia gross domestic product (GDP) in the future. On October 2010, Malaysian government launched the Government's Economic Transformation Program (ETP) to bring Malaysia into high-income nation by the year 2020. Empowering the oil palm industry is being emphasized to achieve the goal. Besides harvesting oil palm for its vegetable oil, the utilization of oil palm biomass wastes in the form of OPT, EFB and OPF has been chosen as one of the entry point projects (EPP) to achieve the goal. This downstream industry is predicted to contribute a supplementary RM 3.3 billion in gross national income (GNI) and the creation of 1000 new employment. Therefore, by the completion of this research, it helps to enrich the variety in the field of oil palm biomass utilization (Umar *et al.*, 2014).

### 1.5.2 Benefit to the socioeconomic

In the coming years, we believed that the findings through this work would help to trigger more discoveries that are important. Biomass waste from oil palm industry, which once considered as a burden could be transformed into a valuable raw material. Oil palm planters especially who involved in small-scale plantation business will have an alternative option to generate side income and at the same time helps to reduce financial problems within their family.

### 1.5.3 Benefit to the environment

It is well known that biomass like oil palm trees are good $CO_2$ absorbent during its lifetime. Burning this kind of biomass will release the $CO_2$ back to the atmosphere and worsen the global warming problem. Previous studies proved that liquefied biomass is suitable to be used as adhesive or in polymer-plastic applications. Hence, oil palm biomass contains many carbon elements, conversion into products instead of burning will preventing carbon molecules from escaping into the environment.

## 1.6 Thesis structure

Overall, this PhD thesis contains five chapters. **Chapter 1** introduces the problem statement, study objectives, hypotheses and the benefit of this study. This chapter discussed about the background of the study and its direction. The justification of this study is discussed under problem statement. The objectives are mentioned about which aspect should be considered, while hypotheses declaring about expected outcome or findings.

**Chapter 2** concerns about the literature reviews regarding biomass utilization, the reason of using OPT and glycerol in liquefaction study. Some previous studies related to liquefaction were also presented. This part gives an overview on liquefaction method and variables involved. Liquefaction through solvolysis is a subject of interest.

**Chapter 3** covers the preliminary study phase of OPT liquefaction. The preliminary study aimed to gain fundamental insight into the catalytic solvolysis of

OPT in glycerol and ethylene glycol before conducting the main experiment. This phase acts as a screening stage to identify factors that may be important or *vice versa*, in influencing the results of OPT liquefaction. Simultaneously, it helps to finalize the experimental design by narrow down any unsupported assumptions.

**Chapter 4** is the optimizing study on OPT liquefaction after screening out the variables that were not important during the screening phase in Chapter 3. The liquefied OPT filtrates were visually inspected by stereomicroscope and FESEM, while its functional groups were examined by FT-IR analysis. The yields were analysed by GC-MS instrument.

**Chapter 5** is dealing about the effect of several liquefied OPT/urea formaldehyde mixtures to the mechanical strength and formaldehyde release of OPT particleboards. All experiments in Chapter 3, 4 and 5 were done statistically by means of response surface methodology (RSM) software Stat-Ease Design-Expert® Software Version 7. The significance of the produced model for OPT liquefaction and OPT particleboards manufacturing was examined through Analysis of variance (ANOVA).

**Chapter 6** highlighted the general conclusions from this study and suggesting the future works that could be done to sustain and improve the knowledge in biomass liquefaction. The entire course of the study can be summarized by the workflow in **Figure 1.1**.

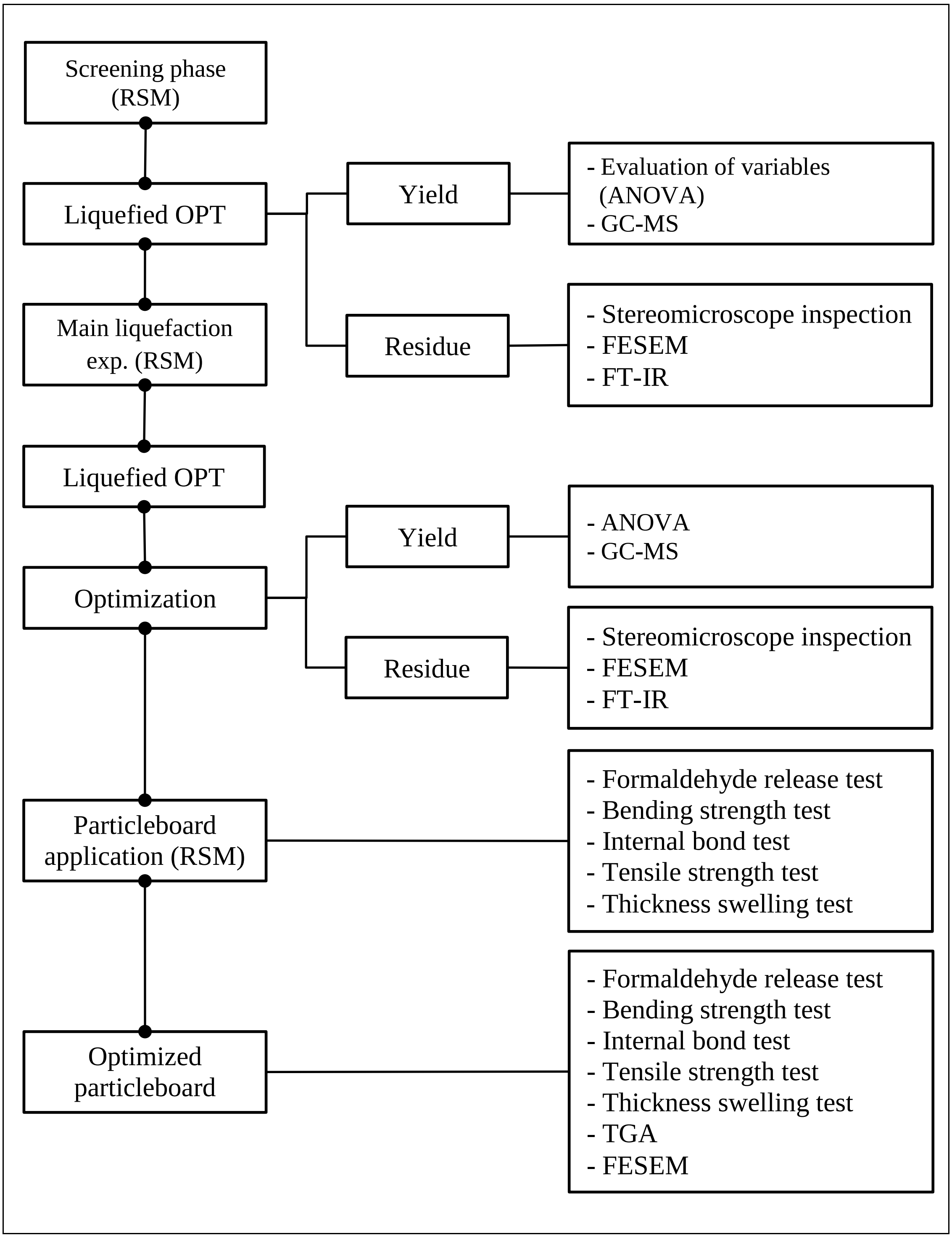



**Figure 1.1** Workflow of the research

# CHAPTER 2 – LITERATURE REVIEW

## 2.1 Biomass utilization

Biomass is a natural material derived from living or recently living organism, simply known as organic matter. Biomass may originates from forestry, marine products, crops, municipal solid waste and agricultural wastes (Demirbaş, 2000b; Demirbaş *et al.*, 2002; Wirsenius, 2000). Utilize in Oxford Dictionary means "Make practical and effective use of…" therefore, biomass utilization, in general, is an action of make practical and effective use of organic materials.

In this study, we focused on the biomass derived from plant. The plant biomass is produced via photosynthesis, in which carbon dioxide and water are converted into organic matter by solar energy. Organic materials from plant consist of lignin, cellulose and hemicellulose or better known as lignocellulose. The world's most abundant renewable resources, in the form of lignocellulose that produced through photosynthesis are derived from agricultural wastes (Kundu *et al.*, 2015). Lignocellulosic biomass stored the sunlight energy in the form of chemical bonds. This kind of energy is released through the breaking down of bonds between carbon, oxygen or hydrogen molecules by means of combustion, digestion or decomposition (McKendry, 2002a). Energy derived from biomass is often called as bio-energy (Küçük *et al.*, 1997).

Combustion of biomass for energy was discovered even before pre-historic times, where wood fuel was used as heat source to warm up and illuminates the cave (Nogueira *et al.*, 2003). Even until now, this traditional practice is still being used at which the consumption exceeds 40% as energy supply, particularly in developing countries that still rely on inefficient method for cooking and heating (Demirbaş *et* *al.*, 2002; Hamelinck *et al.*, 2006). The reasons are that biomass is cheaper in price and it is easily available.

The current situation shows that the world fossil fuel prices are increasing decades by decades. This situation is driven by overwhelming demand on petroleum as fuel or petrochemical feedstock, which caused the dwindling of oil reserves. Therefore, studies on the use of biomass as an alternative option have blooming over the world (Pan *et al.*, 2009; Yang *et al.*, 2007). The advantages in biomass utilization as alternative resource include the fact that biomass is renewable and its readily available, give high energy security. Biomass is also environmental friendly because its utilization only releases carbon molecules that had been absorbed in their lifetime, as part of carbon cycle process. Unlike petroleum, this fossil fuel consumption causes the carbon reserved deep underneath the earth surface to escapes into the environment and simultaneously raises the carbon content in the earth atmosphere (Xu *et al.*, 2008). This current scenario is a major contributor to global warming that caused climate change.

However, there are some limitations in direct utilization of biomass, namely high moisture content and low calorific value that makes biomass utilization inefficient. Because of that, conversion is needed to resolve this problem (Zhong *et al.*, 2004). The effective use of biomass resources has been regarded as one of the greatest priorities for environmental protection (Doh *et al.*, 2005a). Biomass can be converted to produce several kinds of bio-fuels (Heinimö *et al.*, 2009; Naik *et al.*, 2010). Gaseous and liquid products obtain from biomass through conversion processes were found to be suitable as fuel for internal combustion engines (Rustamov *et al.*, 1998). For example, bio-ethanol and bio-diesel have been widely accepted as vehicle fuels in western countries (Hahn-Hägerdal *et al.*, 2006; Kumar *et* *al.*, 2009; Murugesan *et al.*, 2009). In addition, biomass is also used for electricity generation. It can be seen in country like United States that uses wood waste from forest by-products to reduce the consumption of coal, while animal husbandry waste in United Kingdom, agricultural residues such as waste sugar cane in Mauritius, rice husk in Thailand and oil palm wastes in Indonesia and Malaysia (Chungsangunsit *et al.*, 2005; Henkel, 2015; Mahlia *et al.*, 2001).

In some applications, biomass-derived chemicals are being used for petroleum-based product substitution (Chew *et al.*, 2008; Pan *et al.*, 2009). For example, bio-based plastic is currently replacing petroleum-based plastic. This includes polylactide (PLA), starch plastic, polyamides (PA) and cellulose polymers (Shen *et al.*, 2010). A study conducted by Yin *et al.* (2014), green plasticizers made from liquefied wood found to have excellent properties and also environmentally friendly. In the field of chemical industry, researches on finding substitution compound for petroleum such as acids, aldehydes, furans, catechols and phenol from biomass have also progressing well (Ahmed *et al.*, 2012).

Apart from that, the renewable properties of agricultural biomass make it as an excellent material replacement in wood-based industry. There are numerous studies proving that agricultural wastes are suitable for building material and other structural applications. For example, the study on rice hull–sawdust composite board by Kang *et al.* (2012) proved that the composite board has good sound-absorbing properties, which can be used as sound-barrier panels in building construction industry. Study on the utilization of date palm fronds by Hegazy *et al.* (2014) showed that this biomass is a promising raw material for oriented strand board manufacturing. In a study by Bajwa *et al.* (2011), they found great potential of cotton and guayule processing wastes to be used as fillers in thermoplastic composites. A research done by Rasat *et al.* (2013) on bio-composite board made from compressed OPF, their product possess good mechanical and physical properties. Besides, other oil palm wastes like OPT was successfully used in the manufacturing of self-bonding board (Saari *et al.*, 2014).

In Malaysia, studies on the utilization of biomass waste are thriving. Increasing awareness of the high potential biomass waste as a sustainable raw material at a competitive price has triggered more research on value-added products. Most studies have been focused on oil palm wastes utilization because these types of wastes are plentiful in Malaysia. As the world's second largest palm oil producer, the Malaysian palm oil industry generates massive amount of oil palm agricultural wastes in the forms of MF, EFB, OPF, PKS and OPT (Financie *et al.*, 2016; Kanadasan *et al.*, 2015). Failure to maximize these valuable biomass resources is a great loss for the country and its people.

## 2.2 The oil palm crop

There are two main species of oil palm tree, mainly *Elaeis guineensis* and *Elaeis oleifera* (Baudouin *et al.*, 1997). The most cultivated in Malaysian plantation is the monecious species of *Elaeis guineensis* belonging to the *Arecoideae* subfamily. This Tanera variety is a hybrid between the dura and pisifera variety (Keshvadi *et al.*, 2011; Zulkifli *et al.*, 2010). This crop is hermaphrodite, where both functionally male and female flowers are produced on the same tree in an alternating cycle (Adam *et al.*, 2011; Henderson *et al.*, 2015). Hot Malaysian climate, fair amount of sunshine and with high rainfall rate helps oil palm trees to grow well (Chuah *et al.*, 2006; Yusoff, 2006). Oil palm tree is a single-stemmed plant with height at maturity can reach up to 30 meters tall (Edem, 2002). The leaflets are “feather-like” shape or pinnate, can grow between 3–5 meters long (Sumathi *et al.*, 2008).

Oil palm began to bear fruits after 4–5 years of planting (Mahlia *et al.*, 2001; Rodríguez *et al.*, 2008). Oil palm fruits from mature oil palm trees took 5–6 months before it is ready to harvest. The fruitlets are in bunches, containing 45–55% edible oil (Edem, 2002; Sumathi *et al.*, 2008). The weight of the fruit bunches is normally around 15–30 kg but sometimes can reach up to 50 kg (Langeveld *et al.*, 2014). From fresh fruit bunches, products like palm oil, palm kernel oil and palm kernel cakes are obtained (Zwart, 2013). The productive lifespan of oil palm trees is approximately 25 years old (Salim *et al.*, 2012; Sulaiman *et al.*, 2012a). Oil palm is the world’s highest yielding oil crop (Shinoj *et al.*, 2011). Approximately around 4–5.5 $tons \cdot ha^{-1}$ of crude palm oil and palm kernel oil are produced in single harvesting cycle (Salim *et al.*, 2012; Zulkifli *et al.*, 2010). Malaysia is a small country with limited agricultural land. With high capability to produce edible oil in small-cultivated area, oil palm is favours by many local planters.

## 2.3 Availability of biomass in Malaysia in the form of oil palm wastes

The current world’s population is exceeding 7.2 billion people and expected to reach up to 12.3 billion by 2100 (Gerland *et al.*, 2014). This population growth causing the demand for food, including vegetable oils rose dramatically. Malaysia has strengthening its palm oil industry to cope with the demands. In early 1960s, there were only 54000 hectares of oil palm plantations in the country. By 2015, the rapid expansion of oil palm cultivated areas has achieved a staggering 5.64 million hectares, which covers 17% of the Malaysian soil. The expansion of oil palm cultivated area in Malaysia is depicted in **Figure 2.1** (Abdullah, 2003; Jalani *et al.*, 2002; MPOB, 2015; Shafie *et al.*, 2011; Sulaiman *et al.*, 2012b).

In a statistic data issued by MPOB (2016), as of April 2016, Malaysia has 452 productive fresh fruit bunch mills, 44 palm kernel crushers, 53 refineries and 19 oleo chemical facilities. Generally, one ton of palm oil is extracted from five tons of fresh fruit bunches (Stichnothe *et al.*, 2011). Once the oil extraction process completed, EFB, MF and PKS are remaining as wastes. One ton of fresh fruit bunches produces 23% EFB, 14% MF and 7% PKS. In 2008, 19.5 million tons of oil palm waste was contributed by EFB alone (Omar *et al.*, 2011). Most of these wastes are returned back to the plantation or being used as boiler fuels at extraction mills (Nordin *et al.*, 2013; Otti *et al.*, 2014).

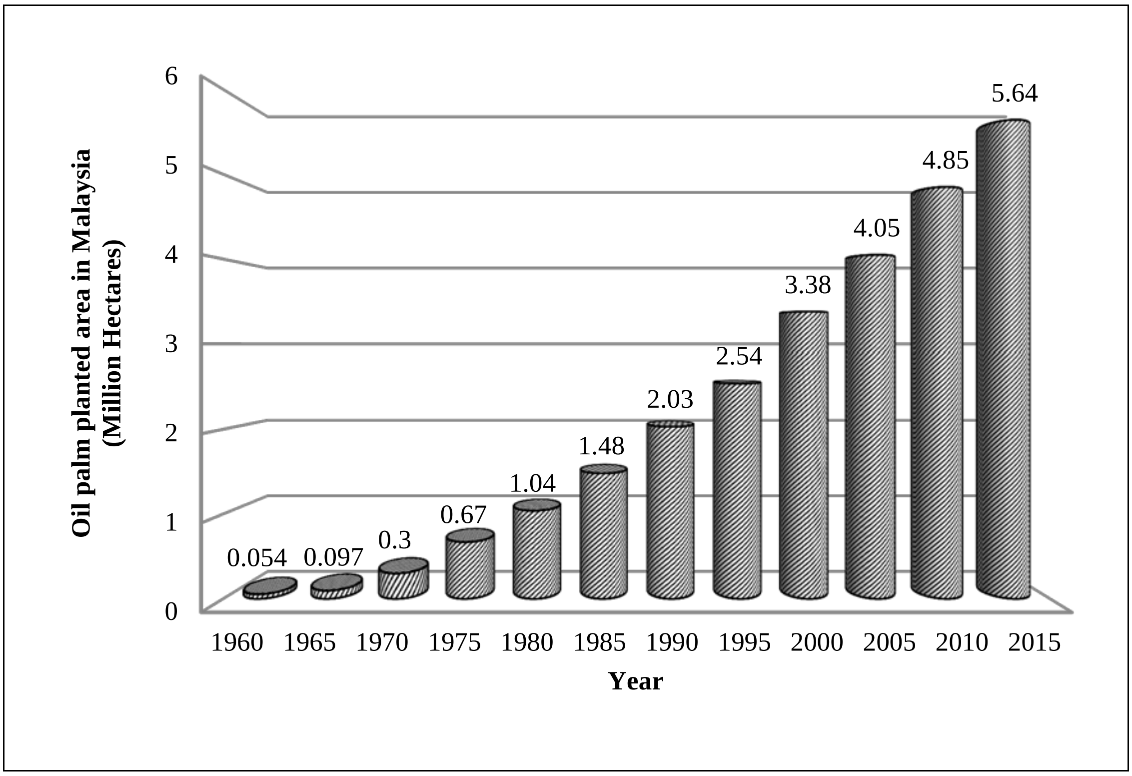



**Figure 2.1** The expansion of oil palm plantation area in Malaysia from 1960 - 2015

In 2009, Malaysian oil palm industry generated 77.3 million tons of biomass wastes as shown in **Figure 2.2**. The oil palm fronds and trunks were the major contributor, accumulated at 44.84 and 13.97 million tons respectively (Ng *et al.*, 2012). Most of the fronds are produced during fruit harvesting process. Meanwhile, it has been estimated that approximately 15 and 75 tons·ha$^{-1}$ of dried fronds and trunks respectively, were available during replanting season. Normal practice to dispose these wastes are through chipping and left rotten at the plantation for mulching purposes (Kong *et al.*, 2014). In 2012, the figure has increased with the estimation of 83 million tons (dry weight) of oil palm biomass wastes available in the country (AIM, 2013). The wastes are projected to reach 100 million tons dry weight by 2020 (Umar *et al.*, 2013).

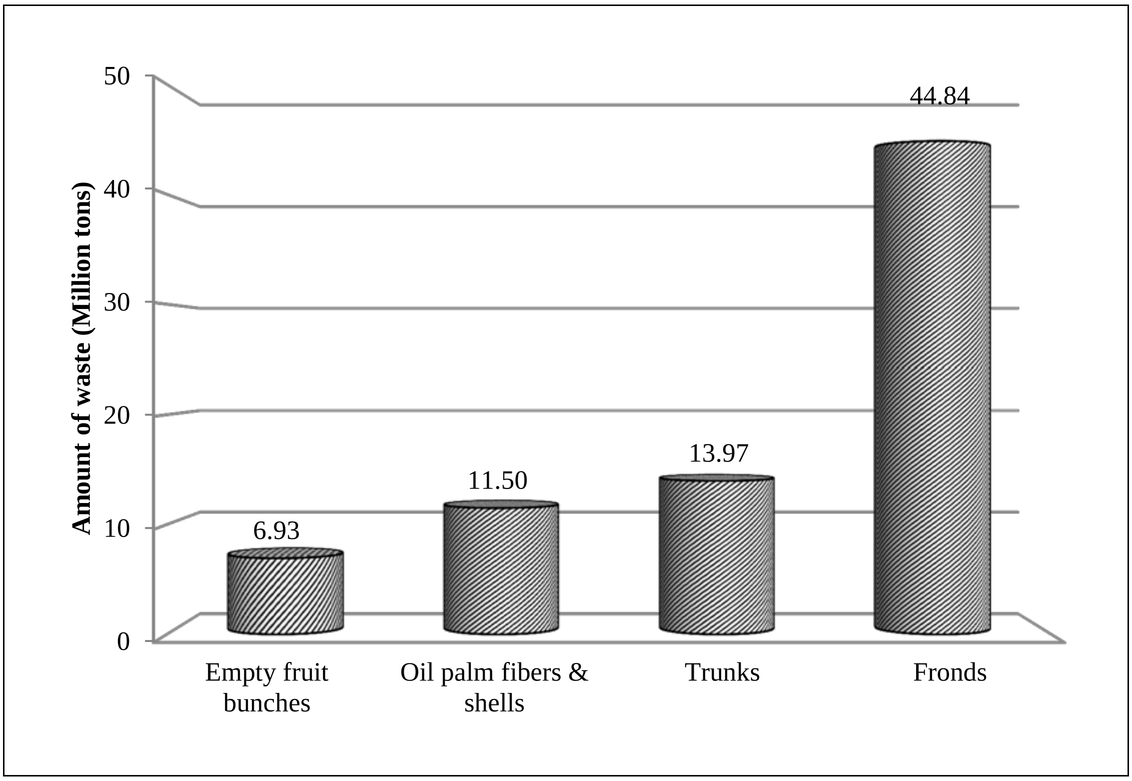
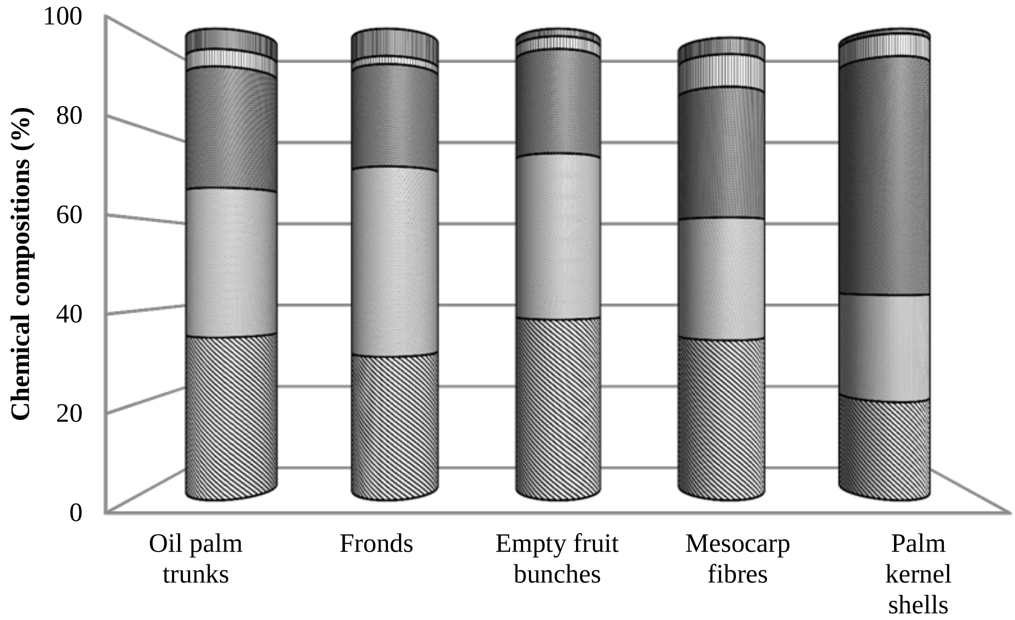



**Figure 2.2** Oil palm biomass waste in Malaysia (dry weight basis) in 2009 (Ng *et al.*, 2012)

## 2.4 Chemical composition of oil palm biomass

Oil palm wastes consist of lignin, cellulose, hemicelluloses and extractives. The chemical compositions of oil palm wastes like trunks, fronds, empty fruit bunches, mesocarp fibre and kernel shells are illustrated in **Figure 2.3**. Three major components namely cellulose, hemicelluloses and lignin build up the chemical compositions of oil palm wastes, which make this biomass also known as lignocellulose. Cellulose is a polysaccharide made up from D-glucopyranose units, linked together by β-(1-4)-glycosidic bonds (Han *et al.*, 1997). Cellulose is hydrophilic because it contains many hydroxyl groups (Alvarez *et al.*, 2003).




| | Oil palm trunks | Fronds | Empty fruit bunches | Mesocarp fibres | Palm kernel shells |
|---|---|---|---|---|---|
| Ash | 4.3 | 5.8 | 1.6 | 3.5 | 1 |
| Extractives | 3.7 | 1.7 | 2.7 | 6.9 | 4.8 |
| Lignin | 25.7 | 21.7 | 22.1 | 27.7 | 50.7 |
| Hemicellulose | 31.8 | 40.4 | 35.3 | 26.1 | 22.7 |
| Cellulose | 34.5 | 30.4 | 38.3 | 33.9 | 20.8 |

**Figure 2.3** Chemical compositions of oil palm biomass (Kelly-Yong *et al.*, 2007).

Hemicelluloses are complex branched structures of polysaccharide. The chemical formula for hemicellulose is generally $(C_5H_8O_4)_n$. However, it may vary considerably depend on the plant species (Yaman, 2004). Hemicelluloses and cellulose bonded together most probably by the hydrogen bonds. The molecular weight of hemicelluloses are lower compared to that of cellulose, pack with many acetyl and hydroxyl groups, thus makes hemicelluloses partially soluble in water (Frederick *et al.*, 2004). Hemicelluloses are comprise of xylan, arabinoxylan, glucuronoxylan, glucomannan, and xyloglucan (Kacurakova *et al.*, 2000). In a study by Shibata *et al.* (2008), hemicelluloses of oil palm biomass consist of simple sugars like arabinose, xylose, mannose, glucose and galactose and also some uronic acid. Xylose has been found to be the most dominant sugar oil palm biomass.

Acting as a binder, lignin supports the position of microfibrils and cell structures in oil palm biomass. Lignin is a complex chemical structure (Demirbaş, 2000a). A study conducted by Tomimura (1992) on nitrobenzene oxidation of milled oil palm trunk lignin, components of vanillin, syringaldehyde, *p*-hydroxybenzoic acid, vanilic acid and syringic acid have been found. There was no p-hydroxybenzaldehyde component observed. However, in a study by Sun *et al.* (1999b), they were able to identify small amount of *p*-hydroxybenzaldehyde due to *p*-coumaric acid degradation. The presence of syringyl, guaiacyl and *p*-hydroxyphenyl justified that oil palm trunk lignin has similar composition like those found in other straw or grass type lignin.

In this study, oil palm trunk (OPT) is a subject of interest since there is no any liquefaction of OPT ever attempted. Like other oil palm wastes, OPT is build up from more than 50% lignin and hemicelluloses, in combine. This is a great advantage since lignin and hemicelluloses are the most vulnerable components during solvent liquefaction process (Zhang *et al.*, 2012b).

## 2.5 Oil palm biomass conversion routes

There are few simple practices in utilizing the oil palm wastes such as mechanical shredding, peeling, densification and drying. Shredded EFB is a suitable medium for mushroom (*Vovariella volvacea*) cultivation and as raw material for medium density fibreboard processing (Prasertsan *et al.*, 1996). Besides that, dry EFB are being used as mulch in oil palm plantations to retain soil moisture, improve soil fertility and prevent the growth of weeds (Menon *et al.*, 2003; Shuit *et al.*, 2009). In palm oil mills, once the kernel oil extraction process completed, waste in the form of crushed PKS are often used as pavement in plantation or densified in briquette form and sold as combustion fuel (Chaiyaomporn *et al.*, 2010; Sulaiman *et al.*, 2011). This bio-briquette can be integrated with coal burning to generate electricity (Lu *et al.*, 1997; Shuit *et al.*, 2009). Another waste from palm kernel oil processing is palm kernel cakes, which directly used as ruminant feedstock (Abubakr *et al.*, 2013).

Moreover, maintenance pruning and fruit harvesting process generate large amount of OPF and leaves as wastes. Some of these wastes are chopped or pelleted for beef cattle food (Zahari *et al.*, 2003). The rest were left rotten as mulch in plantation (Yacob, 2007). During replanting, aged oil palm trees are cut down to make way for new oil palm progenies. Left behind OPT can be used in veneer board manufacturing through peeling processes. The veneers are then glued together as plywood (Hashim *et al.*, 2011b).

Other method used in oil palm waste utilization is through thermal conversion. Direct combustion in the other hand has been widely practiced. Palm oil mills in Malaysia are burning these wastes to cope up with their electricity demands and as boiler fuel. Approximately 0.075–0.1 kWh of electricity and about 2.5 kg of steam needed to produce 1 kg of palm oil.  Normally, PKS and oil palm fibres are used as fuel in the power plants due to their low moisture content properties (Aljuboori, 2013; Sulaiman *et al.*, 2010). Fuel from PKS also being used in cement industry. For example, a cement processing company namely Lafarge Malayan Cement Berhad adopted this bio-fuel as a partial substitute to coal in their cement kiln. This substitution trend can also be seen happening in other businesses such as in clay bricks manufacturing, rubber gloves, kernel crusher, activated carbon and power generation (Dit, 2007).

On October 2002, Malaysian government has made a joint venture with United Nations Development Program and the Global Environment Facility in implementing the Biomass Power Generation and Cogeneration (Biogen) project. This project aims to encourage on more grid-connected biomass-based power generation and cogeneration. The project hopes to reduce the combustion of fossil fuel and together helps the disposal of oil palm waste (Goh *et al.*, 2010). The palm oil fuel ash after the combustion process has potential to be used as pozzolan in cement processing (Tangchirapat *et al.*, 2007).

Besides direct combustion, there is also “indirect combustion” method or simply known as gasification that involve partial oxidation of biomass (Arena, 2012; Higman *et al.*, 2011). Gasification releases mixture of syngas like combustible $H_2$ and $CH_4$, and other gases such as CO, $CO_2$ and $N_2$. The combustible gaseous can be used for energy harnessing (Bulushev *et al.*, 2011; Demirbaş, 2004a). Research on gasification of waste oil palm have been conducted by many researchers and the findings are encouraging (Guangul *et al.*, 2014; Khan *et al.*, 2014; Sivasangar *et al.*, 2015). In comparison made with gasification of food waste, mangrove wood and waste paper, gasification of oil palm trunk yields more energy and $H_2$, under identical gasification conditions (Nipattummakul *et al.*, 2012).

The next conversion method is through pyrolysis. Pyrolysis is a thermal degradation process of biomass with the absence of oxygen and the products are in the form of fuel gases, bio-oil and charcoal. For example, slow pyrolysis is a method that has been widely used in charcoal processing (McKendry, 2002b). There are numerous studies on pyrolysis of oil palm wastes (Abnisa *et al.*, 2013b; Kim *et al.*, 2014; Salema *et al.*, 2012). Due to its promising potential, a commercial bio-oil plant has been set up and operated by Genting Bio-oil to produce bio-oil that suitable for chemical industry as well as fertilizers. The remaining char residue is structurally porous and can be used in activated carbon processing (Meier *et al.*, 1999; Sulaiman *et al.*, 2010).

## 2.6 Biomass conversion by means of liquefaction method

Liquefaction is a thermochemical conversion process of biomass to convert organic feedstock into liquid products. During liquefaction process, feedstock's components are broken down into light molecule fragments. These unstable and reactive fragments then repolymerize into various molecular weight compounds (Demirbaş *et al.*, 2000). Others have extensively studied the properties and the potential of liquefied biomass into various products (Chen *et al.*, 2009; Kobayashi *et al.*, 2005; Pan *et al.*, 2007). Liquefaction is a convenient and effective conversion process in which the resulting oily compounds has good flow properties that allowed it to be easily transported and applied in products (Zhang *et al.*, 2012a).

Liquefaction of biomass in a solvent or mixtures of solvents is also known as solvolysis (Pan *et al.*, 2009; Rezzoug *et al.*, 2002). Solvolysis causes the degradation of lignocellulose components into low molecular weight elements. It can be conducted under relatively mild temperature (120–180 °C) with or without catalyst, either in pressurize environment or at atmospheric pressure (Hassan *et al.*, 2008; Lin *et al.*, 2004). Solvolysis under mild temperature reduces the formation of tar compounds, which resulting from the crosslinking between aromatic and hydrocarbon components (Liu *et al.*, 2008). This helps to prevent tar from contaminating the processing equipment. Liquefied product contains numerous useful functional groups that applicable as resin precursor, bio-oil or chemical synthesis. Previous studies on the liquefaction of woody biomass is presented in **Table 2.1**.