STUDY ON PYROLYSIS OF OIL PALM SOLID WASTES AND CO-PYROLYSIS OF PALM SHELL WITH PLASTIC AND TYRE WASTE

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ABSTRACT

Biomass is a renewable resource that can potentially be used to produce biofuels via the pyrolysis process. Oil palm solid wastes are a rich biomass resource in Malaysia, and it is therefore very important that they be utilized for more beneficial purposes, particularly in the context of the development of biofuels. In this study, the oil palm solid wastes from the plantation and mill activities were characterized and then pyrolyzed to produce oil and byproducts (char and gas). The effects of lignocellulosic as well as the contents from the proximate and ultimate analyses in producing the oil and byproducts during the pyrolysis process were studied. The palm shell was then selected as a model of lignocellulosic biomass for further use as feedstock in the co-pyrolysis process. In co-pyrolysis, there have been several investigations performed such as the study of synergistic effects of the use of palm shell with plastic and palm shell with scrap tyre, the optimization study on the co-pyrolysis parameters via response surface methodology, and the study on the effect of stepwise co-pyrolysis temperature in optimizing the recovery of fuels. The results showed that the use of co-pyrolysis technique can improve the characteristics of pyrolysis oil, e.g., increase the oil yield, reduce the oxygen content, reduce the water content, and increase the calorific value of oil. Moreover, this technique also benefits to the increase in the quality of byproducts. However, similar with the pyrolysis of palm shell alone, the oil yield from co-pyrolysis also contains the aqueous phase. The result of this study showed that the recovery of liquid fuel from the aqueous phase was successfully performed using a catalytic conversion.

ABSTRAK

Biojisim adalah sumber yang boleh diperbaharui yang berpotensi untuk digunakan dalam penghasilan bahan api bio melalui proses pirolisis. Sisa pepejal kelapa sawit adalah sumber biojisim yang kaya di Malaysia, dan ianya penting digunakan bagi tujuan yang lebih berfaedah, terutama dalam konteks pengembangan bahan api bio. Dalam kajian ini, sisa pepejal kelapa sawit daripada aktiviti perladangan dan kilang dikaji dan kemudian dipirolisis untuk menghasilkan minyak dan hasil sampingan (arang dan gas). Kesan lignoselulosik serta kandungan dari analisis proksimat dan ultimat terhadap hasil minyak dan produk sampingan semasa proses pirolisis juga dikaji. Tempurung kelapa sawit kemudian dipilih sebagai model biojisim lignoselulosik untuk digunakan sebagai bahan mentah dalam proses co-pirolisis. Dalam co-pirolisis, terdapat beberapa kajian yang dilakukan seperti kajian tentang sinergi keberkesanan penggunaan tempurung kelapa sawit dengan plastik dan tempurung kelapa sawit dengan sisa tayar, kajian pengoptimuman pada parameter co-pirolisis dengan kaedah response surface methodology, *dan kajian tentang keberkesanan peningkatan suhu bertahap co-pirolisis dalam mengoptimumkan penghasilan semula bahan api. Hasil kajian menunjukkan bahawa penggunaan teknik co-pirolisis dapat meningkatkan hasil minyak, mengurangkan kandungan oksigen, mengurangkan kandungan air, dan meningkatkan nilai kalori minyak. Selain itu, teknik ini juga memberi manfaat kepada peningkatan kualiti hasil sampingan. Walau bagaimanapun, sama dengan pirolisis tempurung kelapa sawit sahaja, hasil minyak dari co-pirolisis juga mengandungi fasa akueus. Hasil kajian menunjukkan bahawa penghasilan semula bahan api cecair dari fasa akueus telah berjaya dilakukan dengan menggunakan proses penukaran melalui pemangkinan.*

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This thesis is dedicated to my lovely mom and dad “Cut Nurmiati & Iskandar T.A”.

Faisal Abnisa

TABLE OF CONTENTS

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER IX

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Background

Fossil fuels such as petroleum and natural gas are predicted be phased out after 2042, and only the coal reserves that will be available until at least 2112 (Shafiee & Topal, 2009). This condition has made researchers try to put more attention to find solutions by utilizing alternative energy. One of the interesting options is the use of biomass as energy. Biomass is very abundant worldwide and can be easily found in diverse forms such as agricultural residues, wood residues, dedicated energy crops, and municipal solid waste (Easterly & Burnham, 1996). The use of biomass as an energy source also benefits the environment because it has been recognized as a carbon neutral energy source.

The conversion of biomass into energy can be achieved in several ways, such as thermal, biological, and physical methods. In thermal conversion, pyrolysis is one of the most promising processes that can be used to convert biomass to various types of products such as liquid, char, and gas. This technique has been recognized as an environmentally friendly method because no wastes are produced during the process. The process has also received more attention because it can produce liquid yield of up to 75 wt% with conditions of moderate temperature (~500 °C) and short hot vapor residence time (Bridgwater, 2006). The liquid from the pyrolysis process has the potential to be applied as fuels or feedstock for many commodity chemicals. Moreover, the byproduct from this process also has other values in other industry sectors. The obtained char can be used in different industries, such as for the production of briquettes, adsorbents, carbon black pigment, and chemicals. The gas produced from the pyrolysis of biomass has a significant calorific value; thus, it can be potentially used as gaseous fuels or to offset the total energy requirements of the pyrolysis plant.

The research to produce liquid fuel via the pyrolysis of biomass has been performed since the last four decades. In 1972, the energy crisis has pushed researchers to put more attention to maximize the production of pyrolysis oil by minimizing the byproducts of char and gases (Antal and Grønli, 2003). One of the best use of pyrolysis was achieved in the 1980s (Vamvuka, 2011). This technique has successfully led to several improvements, such as the high yield of oil production. The technique has later been called fast pyrolysis. Although the issue of oil quantity has been addressed, the improvement in oil quality still requires further research.

Currently, several research efforts are focused in finding the suitable technique to produce high-grade pyrolysis oil and to explore more new variations of biomass that can be used as feedstock in the pyrolysis process. The oil produced from the pyrolysis of biomass has a high level of oxygen content and can cause many problems, such as low calorific value, corrosion problems, and instability. The current research finding showed that the technologies to eliminate the oxygen content are still expensive and can cost more than the oil itself. Therefore, the sustainability of this research seems necessary to overcome this cost and to improve the quality of pyrolysis oil that is expected to compete with fossil-based liquid fuel.

1.2 Problem statement

As mentioned earlier, aside from finding the proper technique to produce high-grade pyrolysis oil, one of the important studies in this area is also to find new biomass for feedstock in the pyrolysis process. The investigation on this issue is necessary because each country in the world has different sources of biomass that can be utilized for alternative energy. Malaysia is well known as the top largest producer of palm oil in the world and as consequence, the waste from this industry is also abundant. The residues from the oil palm industry are the main contributors to biomass waste in Malaysia, and these wastes require extra attention with respect to handling. A survey of the literature indicates that most of them are handled with unsatisfactory practices that negatively impact the environment. Therefore, it is very important that they be utilized for more beneficial purposes, particularly in the context of the development of biofuels via pyrolysis technology.

Furthermore, as the main product, liquid from the pyrolysis of lignocellulosic biomass generally contains a high level of oxygen, which causes low energy content, instability, and corrosiveness. Many researchers have tried to eliminate the oxygen content in the oil via techniques such as catalytic cracking and hydrodeoxygenation. However, the improvement through those technologies can potentially increase the production cost because of the complicated equipment and need for additional catalysts, solvents, and hydrogen-donors. Thus, a new approach is necessary to overcome this cost.

There is one technique that seems to be promising to produce high-grade pyrolysis oil from biomass and offers simplicity in design and operation. Moreover, it can be run without the presence of any catalysts or solvents and free of hydrogen pressure. This technique is called co-pyrolysis. Co-pyrolysis is a process that involves two or more different materials as a feedstock. The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. The initial research found in the literature has shown that the quality and quantity of oil are improved when the co-pyrolysis technique is used.

Therefore, this technique needs to be studied in detail to obtain a clear framework of the process mechanism.

In addition, phenomena on the presence of aqueous phase in the pyrolysis oil are also given attention in this research study. Oil from the pyrolysis of biomass typically consists of two different layers, which are in aqueous phase and organic phase. Many studies have been performed to upgrade the process to obtain liquid fuel from the organic phase of pyrolysis oil, but no literature was found on the direct utilization of the aqueous phase for liquid fuel production. The high water content might be the reason why this phase has not been investigated for further studies on liquid fuel production. However, several aromatic compounds still exist in the aqueous phase; therefore, it is important to perform research on this area to obtain an estimate of how much liquid fuel can be recovered from the aqueous phase.

1.3 Objectives of the research

This research attempted to obtain several scientific overviews from the use of oil palm solid wastes to produce pyrolysis oil, the use of co-pyrolysis technique with regard to improving the pyrolysis oil, and the production of liquid fuel from the aqueous phase. The specific objectives and approaches are as follows:

1) *To study the potential of oil palm solid wastes as feedstock for pyrolysis oil.*

   All of the wastes that came from the oil palm industry were investigated to get an overview of their characteristic in producing the pyrolysis oil. The focus of this study is to understand the phenomenon that occurs during the pyrolysis process, which is specifically caused by the effects of lignocellulose in the oil palm solid wastes as well as the contents from the proximate and ultimate analyses.

2) *To observe whether a beneficial interaction from the co-pyrolysis of biomass and plastic in terms of oil quality and quantity.*

   This research attempted to demonstrate a simple method to produce a high-grade pyrolysis oil by maximizing the use of biomass wastes. In this study, the results of the pyrolysis of biomass alone are compared with those of the pyrolysis of biomass/plastic mixtures (1:1 weight ratios). Palm shell was selected as the representative of biomass and polystyrene was selected as the representative of plastic waste. The collected results were compared to determine whether there was improvement in the quantity and quality of the oil product.

3) *To optimize the operating conditions for liquid production from the co-pyrolysis of biomass and plastic via response surface methodology (RSM).*

   This study focused to identify the parameter that has the largest influence on the liquid yield production. Three effective parameters were chosen: temperature, feed ratio, and reaction time.

4) *To optimize the fuel recovery from the stepwise co-pyrolysis of biomass and scrap tyre.*

   Similar with plastic, scrap tyre also has important properties as fuel; therefore, the presence of scrap tyre in the pyrolysis of biomass is expected to contribute to the improvement in the quality and quantity of pyrolysis oil. The effect of stepwise co-pyrolysis temperature and the different ratio between palm shell and scrap tyre in feed were studied. Several new findings were reported especially with regard to the production of organic and aqueous phases during co-pyrolysis, the energy density of the obtained chars, and the production of hydrogen and methane gases.

5) *To investigate how much liquid fuel can be recovered from the aqueous phase of pyrolysis oil.*

This study was performed using catalytic conversion. The process was supported by two different HZSM-5 catalysts with temperatures set at 405 °C, 455 °C, 505 °C, and 555 °C.

1.4 Workflow of the thesis

Figure 1.1 shows the steps in performing the research that were described in this thesis. The first investigation of this research is to study the potential of oil palm solid wastes as feedstock for pyrolysis oil. The main aim is to propose the use of oil palm solid wastes to generate second-generation biofuels. In Malaysia, the volume and type of oil palm solid residues are expected to rapidly increase and will become a serious problem in the future. Therefore, the use of these wastes for fuels is expected to benefit the increase in the energy security in Malaysia, solve several environmental problems, and solve particular issues on waste management. In this study, the waste from the oil palm industry is divided into two groups, namely, from plantation activities and from mill activities. All of the residues were then pyrolyzed to produce liquid, char, and gas. The interest of this study was focused on the exploration of the lignocellulosic effect in producing biofuels during pyrolysis. After pyrolysis, the products, with an emphasis on the pyrolysis oil, were characterized using various approaches.

The second work was aimed to investigate the improvement on the quality and quantity of pyrolysis oil obtained during co-pyrolysis. In this study, palm shell was selected as a model from lignocellulosic biomass, and polystyrene was selected as the representative of plastic waste. After several scientific results were obtained, the study then continued to determine the best parameter that can influence liquid production (objective 3). In this regard, RSM was used to determine the optimum and experimental design matrix according to the central composite design (CCD) method. The feedstock used in this experiment is also the same with that used in the second objective.

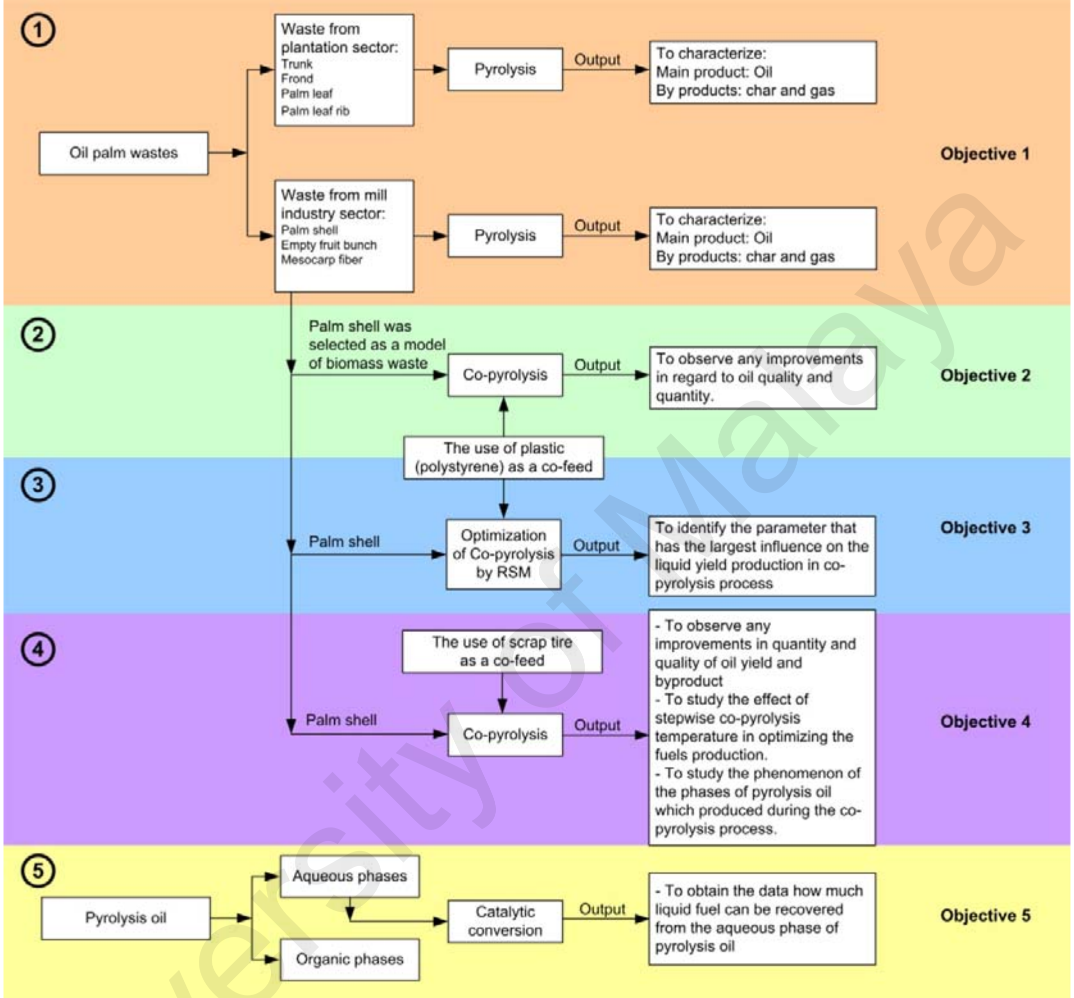


Figure 1.1: Detailed workflow of the thesis

Furthermore, the next study examines another material that has a similar characteristic to plastic, which can be used in co-pyrolysis. The result from our study indicated that the waste of scrap tyre meets the criteria. In this study, the co-pyrolysis of palm shell and scrap tyre was performed. The result from objective 3 indicates that the parameter with the most significant effect on pyrolytic liquid yield is the ratio; thus, this parameter was applied again in objective 4 to obtain more detailed information about the co-pyrolysis products, including the presence of organic and aqueous phases of liquid product, the characteristic of oil product, and the characteristic of byproducts.

In addition, the result from the pyrolysis of biomass alone and the co-pyrolysis experiment confirmed that the oil obviously consists of organic and aqueous phases. The organic phase from the co-pyrolysis process has the potential to be used as a fuel because it has a high heating value, whereas the use of the aqueous phase for fuel is not possible because it contains a lot of water. However, the result of the analysis showed that some of hydrocarbon sources still exist in the aqueous phase. This issue brings the following question: how much liquid fuel can be recovered from the aqueous phase? Therefore, in this study, we performed recovery of liquid fuel from the aqueous phase via the catalytic conversion technique.

1.5 Scope of the study

This study focused on the utilization of biomass waste to fuels via pyrolysis technology. Therefore, all of the materials used in this study were collected from waste collection point. The waste used from oil palm industry included palm shell, empty fruit bunch, mesocarp fiber, trunk, frond, palm leaf, and palm leaf rib. Polystyrene and scrap tyre were chosen as co-feed for the co-pyrolysis studies. The liquid was considered as the main product, whereas char and gas were referred as byproducts. Most of analyses were focused on the liquid product. The use of coals, catalysts, solvents, and any additional pressure in the co-pyrolysis process was beyond the scope of this study.

For the first objective, all of the parameters such as temperature, particle size, reaction time, and nitrogen (N_2) flow rate were set constant. The discussion in this study was concentrated on the lignocellulosic effect as well as the contents from the proximate and ultimate analyses of the sample in producing the oil, char, and gas. The same condition of the parameters was also applied in the second objective study. Subsequently, the optimization was performed using RSM with three effective parameters being studied: temperature, feed ratio, and reaction time. The oil at the optimum conditions was then used for further characterization. Furthermore, the recovery of the liquid fuel from the aqueous phase of the pyrolysis oil was carried out using HZSM-5/50 and HZSM-5/70 catalysts. The effect of temperature on the liquid yield is also described in this study. All of experiments were performed using a fixed-bed reactor made of stainless steel.

1.6 Importance of the proposed research

a. The use of oil palm solid wastes for biofuels production in Malaysia via pyrolysis technology.
b. To find a simple and effective technique to produce high-grade pyrolysis oil that can be potentially used for fuel.
c. The use of this technique can significantly contribute to reduce the waste volume because more waste matter can be consumed as raw material for pyrolysis oil production.
d. This research will contribute to the finding of an alternative energy to substitute the depleting fossil fuel and is greener and renewable.

1.7 Outline of the thesis

The format of this thesis follows the article style format as mentioned in the University of Malaya guidelines. All of the works that were described in this thesis have been published in several ISI journals. The overall outlines as well as the organizational pattern of this thesis are discussed in this section. The thesis comprises nine chapters, and each chapter is introduced as follows.

Chapter 1: This chapter explores the research background, problem statement, objective of the research, workflow of thesis, scope of the study, the importance of research proposed, and outline of the thesis.

Chapter 2: This chapter presents a comprehensive literature review and the relevant discussions regarding the co-pyrolysis process from several points of view, including the process mechanism, feedstock, the exploration on co-pyrolysis studies, co-pyrolysis phenomena, characteristics of byproducts, and economic assessment. Additionally, several outlooks based on studies in the literature are also presented in this paper. The content of this chapter has been published in the Journal of Energy Conversion and Management (Abnisa, F; Wan Daud, W.M.A. Energy Conversion and Management, 2014, 87: 71-85).

Chapter 3: Characterization of bio-oil and bio-char from pyrolysis of palm oil wastes. This chapter describes the work for objective 1. The scope of this chapter is limited only to residues from oil palm mill activities. This work has been published in the Journal of Bioenergy Research (Abnisa, F; Arami-Niya, A. Wan Daud, W.M.A; Sahu, J.N. Bioenergy Research, 2013, 6: 830-840).

Chapter 4: Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis. This chapter is addresses objective 1, where the described work refers to the pyrolysis of biomass waste from oil palm plantation activities. The publication of this work can be found in the Journal of Energy Conversion and Management (Abnisa, F; Arami-Niya, A; Wan Daud, W.M.A; Sahu, J.N; Noor, I.M. Energy Conversion and Management, 2013, 76: 1073-1082).

Chapter 5: Pyrolysis of mixtures of palm shell and polystyrene: an optional method to produce a high-grade of pyrolysis oil. This chapter addresses objective 2. The work that is described in this chapter has been published in the Journal of Environmental Progress & Sustainable Energy (Abnisa, F; Arami-Niya, A; Wan Daud, W.M.A; Sahu, J.N. Environmental Progress & Sustainable Energy, 2014, 33: 1026-1033).

Chapter 6: Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesize liquid fuel: an optimization study. This chapter contains the optimization study that is mentioned in objective 3. This study has been published in the Journal of Fuel (Abnisa, F; Wan Daud, W.M.A; A. Ramalingam, S; Azemi, M.N.M; Sahu, J.N. Fuel, 2013, 108:311-318).

Chapter 7: Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tyre. This chapter covered the research for objective 4. The work has been published in the Journal of Energy Conversion and Management (Abnisa, F; Wan Daud, W.M.A. Energy Conversion and Management, 2015, 99:334-345).

Chapter 8: Recovery of liquid fuel from the aqueous phase of pyrolysis oil using catalytic conversion. The work described in this chapter is related to objective 5. This work has also been published in the Journal of Energy & Fuels (Abnisa, F; Wan Daud, W.M.A; Arami-Niya, A; Ali, B.S; Sahu, J.N. Energy & Fuels, 2014, 28:3074-3085).

Chapter 9: This chapter summarizes important results and main conclusions associated with the research objectives. In addition, several recommendations are also provided in this chapter.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

The decrease of fossil fuel resources such as coal, petroleum, and natural gas has encouraged research to develop new approaches to find or invent renewable fuel. One article has predicted that the coal reserves will be available until at least 2112, and it will be the sole fossil fuel in the world after 2042 (Shafiee & Topal, 2009). Several efforts are currently underway to find alternative energy sources and develop technologies which have high efficiency and are environmentally-friendly. In this regard, most of the effort has been contributed by research into biomass energy. During the last three decades, more than half of the global research has been focused on biomass as renewable energy (56%), followed by solar energy (26%), wind power (11%), geothermal energy (5%), and hydropower (2%) (Manzano-Agugliaro et al., 2013). The high percentage of research into biomass energy can be supported by the availability of biomass resources which are the world's largest sustainable energy source and represent approximately 220 billion dry tons of annual primary production (Moreira, 2006).

Beside the effect of decreasing of fossil fuels, environmental concerns also play an important role in the development of renewable energy. The risk and reality of environmental concerns have drastically increased globally and become more apparent during the past decade, particularly after Earth Summit '92 (Agarwal, 2007). Acid rain, ozone layer depletion, and global climate change are negative effects that have resulted from the increase in environmental problems which are due to the emissions of primary pollutants (sulfur dioxide, oxides of nitrogen, hydrocarbons, and carbon monoxide), and are mainly produced by fossil fuel combustion (Kalogirou, 2004; Krupa et al., 2007). To minimize environmental concerns, it is necessary to consider controlling the pollutant emissions. The optimal use of renewable energy resources can be an optional solution since it significantly contributes to decreasing the negative environmental impacts, reducing the dependence on the use of fossil fuels, and is followed by an increase of net employment and the creation of export markets (Manzano-Agugliaro et al., 2013).

There are numerous alternative energy sources available worldwide which can be used to substitute fossil fuels. It is particularly important to consider selection of the proper alternative energy through several factors such as the availability of the source, economic benefit, and environmental benefit. In this respect, biomass is one of the potential sources that can respond to all of the challenges of factors. Biomass is very abundant and can be easily found in diverse forms such as agriculture residues, wood residues, dedicated energy crops and municipal solid waste (Easterly & Burnham, 1996). Bildirici (2013) studied economic growth and biomass energy in the 10 selected developing and emerging countries. The author concluded that biomass energy is a stimulus for economic growth and contributes to poverty reduction in developing countries because it meets the energy needs at all times and for all countries, without any expensive conversion devices. Furthermore, the use of biomass as an energy source has been proven to have environmental benefits since it has been determined as a carbon-neutral energy source (Ahtikoski et al., 2008).

Biomass is widely accepted as a potential source of energy and is the only renewable energy source that can be converted into several types of fuels, including liquid, char, and gas, which also promise flexibility in production and marketing. Pyrolysis is generally chosen as a recommended process to achieve this goal. This process has received more attention recently because it can produce the highest liquid yield of up to 75 wt.% with conditions of moderate temperature (~500°C) and short hot vapor residence time (~1 s) (Bridgwater, 2006; Guillain et al., 2009). Nevertheless, the yield of other products also can be optimized by adjusting the parameters of operating conditions. The liquid from the pyrolysis process is known as pyrolysis oil or bio-oil, and has potential as use for fuels or feedstock for many commodity chemicals. In terms of fuels, Bridgwater et al. (1999) noted that without an upgrading process, the oil can be directly used in many applications including boilers, furnaces, diesel engines, and turbines for the generation of electricity. In addition, the greatest advantage of pyrolysis oil compared with fossil fuel is that the use of this oil has received positive comments as a more environmentally-friendly fuel because it contributes minimally to the emission of greenhouse gases (Vitolo et al., 1999).

Despite the oil from pyrolysis being environmentally-friendly, the fuel characteristic of it remains lower than fossil fuel, especially with regard to combustion efficiency. In this case, the high composition of oxygenated compounds in pyrolysis oil is responsible for this problem. Several researchers have reported that oil from the pyrolysis of biomass generally contains an oxygen content of around 35-60 wt.% (Bridgwater et al., 1999; Guillain et al., 2009; Oasmaa & Czernik, 1999; Parihar et al., 2007). It can be identified in the form of more than 200 different compounds in the oils, and is mostly found as water (Oasmaa & Czernik, 1999). However, the high level of oxygen in pyrolysis oil creates a low caloric value, corrosion problems and instability (Lu et al., 2009).

Improvement in the quality of pyrolysis oil is important to assist and provide a solution for several challenges in its applications; therefore, efforts to eliminate the oxygen content are becoming a priority. Many studies have been undertaken to achieve this goal through upgrading techniques. Among them, catalytic cracking and hydrodeoxygenation (HDO) are the most commonly used techniques. Catalytic cracking is a method that involves the addition of a catalyst to the pyrolysis process. This method can be divided into two options: off-line catalytic cracking (using bio-oil as raw material) and on-line catalytic cracking (using pyrolysis vapors as raw material) (Hew et al., 2010). Zhang et al. (2007) have determined that catalytic cracking is a cheaper method than HDO, but the results do not seem promising because of high coke production during the process (8–25 wt%) and the poor quality of the fuels obtained. Moreover, according to Scheirs (2006), there are also some problems associated with the use of a catalyst in the pyrolysis process:

- The catalyst is a consumable and therefore adds to the running cost;
- The catalyst can have a short life-cycle due to poisoning/deactivation;
- The catalyst leads to increased levels of solid residue, which require disposal.

Furthermore, HDO is an upgrading method that is suitable for converting low-grade pyrolysis oil into hydrocarbons (Toba et al., 2011). This process has received a lot of attention because of the significant increase in hydrocarbon fuel obtained (Joshi & Lawal, 2012). However, the method is complex and costly because of the complicated equipment, the need to add catalysts, and the high-pressure requirements for the reaction. Thus, a new approach is necessary to overcome this cost.

2.2 Importance of the co-pyrolysis process

Simplicity and effectiveness are especially important in developing a technique to produce the ideal synthetic liquid fuel. In this regard, the idea of co-pyrolysis of biomass can be an optional technique that shows promise by meeting these two criteria. Co-pyrolysis is a process which involves two or more different materials as a feedstock.

Many studies have shown that the co-pyrolysis of biomass has successfully improved the oil quantity and quality without any improvement in the system process. In contrast to catalytic cracking and HDO, co-pyrolysis has shown promise for future application in industry because of its attractive performance/cost ratios.

The successful key of this technique mainly lies with the synergistic effect which comes from the reaction of different materials during the process. A previous study has shown that the yield of oil obtained from incorporating plastic was higher than that obtained with woody biomass alone and also had a higher caloric value, which comes from hydrocarbon polymers consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable gas with a high calorie value (Panda et al., 2010).

The idea of blending oil from biomass with oil from plastic (or waste tyre) seems impossible, and may increase operation costs. Oil from biomass cannot be completely mixed with oil from plastic or waste tyre because of the polar nature of pyrolysis oil of biomass. If these oils are mixed together, an unstable mixture forms, which breaks (phase separation) after a short period of time. If pyrolysis of biomass and plastic (or waste tyre) occurs independently or separately, more energy is required and the cost for oil production will significantly increase. The co-pyrolysis technique is found to be more reliable to produce homogenous pyrolysis oil than the blending oil method. The interaction of radicals during the co-pyrolysis reaction can promote the formation of a stable pyrolysis oil that avoids phase separation (Martínez et al., 2014). Önal et al. mentioned that several reaction radicals during co-pyrolysis can be formed as follows: initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), isomerization via vinyl groups], and termination by disproportionation or recombination of radicals (Önal et al., 2014).

Furthermore, the main benefit of using co-pyrolysis method is the fact that the volume of waste can be reduced significantly as more waste is consumed as feedstock. It also has the added benefits of reducing the landfill needed, saving costs for waste treatment, and solving a number of environmental problems. Since the disposal of waste in landfills is undesirable (Garforth et al., 2004), this method could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and may enhance energy security. In addition, from an economic point of view, co-pyrolysis has been found to be a promising option for a biomass conversion technique to produce pyrolysis oil. Kuppens et al. (2010) investigated the economic consequences of the synergetic effects of flash co-pyrolysis. They concluded that the use of co-pyrolysis techniques is more profitable than pyrolysis of biomass alone and that it also has potential for commercial development.

2.3 Mechanism of the co-pyrolysis process

The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. Basically, the process is performed in a closed reactor system with moderate operating temperatures and in the absence of oxygen. For the purposes of oil production, there are three basic steps required for the co-pyrolysis process: preparation of samples, co-pyrolysis, and condensation. Figure 2.1 illustrates the steps used in co-pyrolysis to produce oil. Prior to co-pyrolysis, the samples should be dried and ground. The drying process can be performed using the oven method (temperature at 105°C for 24 h). For industrial application, the heat demand for feedstock drying can be covered by internal heat sources through process integration. Researchers suggested that the byproducts char or gas can be combusted to provide the necessary heat for endothermic pyrolysis and other intermediate processes, such as biomass drying (Venderbosch & Prins, 2010a; Veses et al., 2014). The main aim of the drying process is removing the moisture content of sample. High moisture content in feed results in the oil product having a high water content; therefore, Bridgwater (2012) suggested that the maximum moisture content in the dried feed material should be 10%. The dried samples also benefit from the grinding process, and small biomass particles with a size of less than 2-3 mm are needed to achieve high biomass heating rates (Bridgwater, 2012).

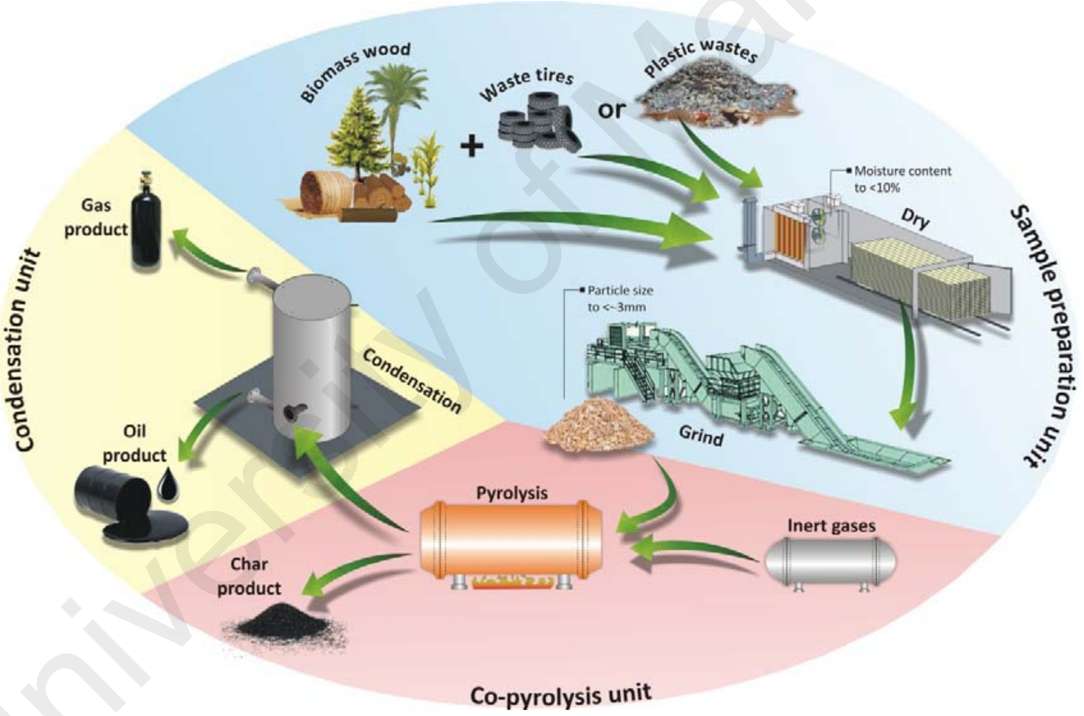


Figure 2.1: Co-pyrolysis of biomass

As can be seen from Figure 2.1, there is an optional feature in the co-pyrolysis process: inert gas. Inert gas is used to accelerate sweeping vapors from the hot zone (pyrolysis zone) to the cool zone (condenser). Short hot vapor residence times of less than 2 s are needed to minimize secondary reactions and maximize oil yield (Bridgwater, 2012). In application, nitrogen (N_2) is an inert gas that is commonly used since it is found to be cheap compared to others. Many studies have proven that the use of inert gases in the pyrolysis process has an effect on liquid yield (Abnisa et al., 2011; Acıkgoz et al., 2004; Demiral & Şensöz, 2006; Pütün et al., 2004). The proper setting of the inert gas flow rate is needed to attain maximum oil yield, while very high flow rates of inert gas actually decrease the total oil yield. However, the use of inert gas is dependent on the type of reactor used. The fluid bed reactor, circulating fluid bed reactor, and entrained flow reactor are the types which need a high flow rate of inert gas (Vamvuka, 2011). For vacuum and ablative reactors, the use of inert gas is not compulsory. For ablative reactors, according to Bridgwater & Peacocke (2000), nitrogen purging and the use of any inert gases is not required, but is included in the laboratory tests for control purposes, to ensure safety in the feeder and residence time control in the reactor.

Furthermore, the pyrolysis process is also influenced by many parameters, including the type of biomass, temperature, heating rate, reaction time, and particle size of feed. Detailed discussions of the effect of parameters on optimum oil yield in the pyrolysis of biomass have been thoroughly reviewed by Akhtar and Amin (2012). For co-pyrolysis, as a general rule, temperature can be adjusted within the range of 400-600°C to maximize the production of oil. In this temperature range, more than 45 wt% oil can be produced. However, the optimum temperature required to produce the maximum oil yield is dependent on the characteristics of feedstock. Therefore, characterization with regard to thermogravimetric analysis should be performed to obtain an overview of the thermal behavior of material (Velghe et al., 2011).

Condensation is an important step in the production of pyrolysis oil. Without this step, only the char and gas products can be obtained from the process. The vapors generated during the process pass through the condensation unit to change the physical state of matter from the gas phase into the liquid phase. Vapor product residence time in the reactor can be controlled by the addition of inert gas. Bridgwater (1999) noted that pyrolysis vapors can be characterized as a combination of true vapors, micron-sized droplets and polar molecules bonded with water. Rapid cooling of the pyrolysis vapors is required to produce a high liquid yield. The lower vapor temperature (< 400°C) leads to secondary condensation reactions and the average molecular weight of the liquid product decreases. Thus, the temperature in pipelines from the pyrolysis unit to the condensation unit should be maintained at > 400°C to minimize liquid deposition; also, blockage of the equipment and piping system should be avoided (Bridgwater et al., 1999).

In contrast to normal pyrolysis, co-pyrolysis has a special parameter which is called the ratio of feedstock. According to researchers, this parameter is very important since it has a significant effect, leading to the production of extra oil. Sharypov et al. (2002) conducted a study into co-pyrolysis of wood biomass and a synthetic polymer mixture. Their study concluded that the most important parameter for liquid production is the biomass/plastic ratio in the feedstock. The same tendency was also found by Abnisa et al. (2013), who performed a study into co-pyrolysis of palm shell and polystyrene waste mixtures for the synthesis of liquid fuel. Their study included screening three effective parameters (temperature, feed ratio, and reaction time) and an optimization study using response surface methodology. Their results showed that the ratio of feed was the most significant variable affecting liquid yield production.

The type of reactor used also has a large function in the co-pyrolysis process. Bridgwater et al. (1999) highlighted the critical features of successful pyrolysis reactors, which have been defined as very high heating rates, moderate temperatures, and short vapor product residence times for liquids. Several comprehensive reviews have been published to explore the type of pyrolysis reactor for liquid production (Bridgwater, 2012; Isahak et al., 2012; Vamvuka, 2011; Venderbosch & Prins, 2010a, 2010b). Each reactor has known advantages and disadvantages in operation and scaling. For fast pyrolysis, the fluidized bed reactor is recommended because of its relative ease of scalability and simple operation compared with other reactor types. Most studies on co-pyrolysis were performed using a fixed-bed reactor (Abnisa et al., 2014; Cao et al., 2009; Jeon et al., 2011; Liu et al., 2013; Önal et al., 2012, 2014). Fei et al. (2012) noted that the extent of contact between the used feedstock is an important factor to achieve the synergistic effect; therefore, the synergistic effect is more likely to occur when pyrolysis is carried out on a fixed-bed reactor than on a fluidized-bed reactor. However, a new research finding in 2014 stated that the auger reactor is more effective for co-pyrolysis. Martinez et al. (2014) performed the co-pyrolysis of biomass and waste tyres using two different reactors, namely, the fixed-bed reactor and auger reactor. The results of their comparison study showed that the auger reactor produces more liquid yield than the fixed-bed reactor for the 90/10 of biomass/waste tyre blend. The experimental results from the auger reactor also revealed a remarkable upgrade for some liquid properties, such as lower total acid number, lower density, higher pH, higher calorific value, and lower oxygen content.

2.4 Feedstock for the co-pyrolysis process

A diversity of renewable energy resources can be found around the world, including biomass energy, wind energy, solar energy and geothermal energy. Among these, biomass is the only source of renewable energy that can produce fuels in the form of solid, liquid and gas, through assistance of the pyrolysis process. Although fuels from biomass, especially wood-based biomass, typically have a lower energy content than fossil fuels, the use of co-pyrolysis technology is improving this condition. In this section, the discussion only focused on the selection and availability of feedstock which can potentially be used in the co-pyrolysis process.

2.4.1 Selection of feedstock

Some types of biomass have the potential for use in the co-pyrolysis process to improve the quality and quantity of pyrolysis oil. In this regard, the selection of biomass wastes is becoming an important issue requiring study. Currently, many kinds of biomass have been successfully used as feedstock in the co-pyrolysis process in research, which can be categorized into four groups: agricultural residues, wood residues, municipal solid wastes (MSW) and dedicated energy crops. The list of feedstock types is shown in Table 2.1. From the list it can be seen that most feedstocks are dominated by MSW. Therefore, it can be noted that co-pyrolysis plays an important role in MSW treatment management. Zaman (2010) studied the comparison of MSW treatment technologies using the life cycle assessment method. The author reported that although the sanitary landfill has a good impact on the environment, there are some major problems, such as photochemical oxidation, global warming and acidification, which are still not solved. However, pyrolysis is comparatively more favorable to the environment since it can address the global warming, acidification, eutrophication and eco-toxicity categories. Also, it has higher energy recovery efficiency compared to other thermal technologies.

As can be seen from Table 2.1, the use of biomass as a material in co-pyrolysis studies varies widely. Among of the various sources, plastic is one of the biomass types that is commonly used in co-pyrolysis to produce pyrolysis oil. Plastics are largely synthetic materials, made from an extremely inexpensive, but nonrenewable resource, crude oil (see Figure 2.2) (Buekens & Schoeters, 1998). Because of its origin, plastic contains hydrogen and carbon; thus, it can be pyrolyzed into hydrocarbon fuels. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes into monomeric units. Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, and the presence of catalysts and other conditions (Panda et al., 2010). The liquid product from pyrolysis of plastic has a competitive calorific value compared to conventional fuels, which were around 40 MJ/kg. Therefore, the presence of plastic in the pyrolysis of other biomass types can make a positive contribution to the heating value through synergy.

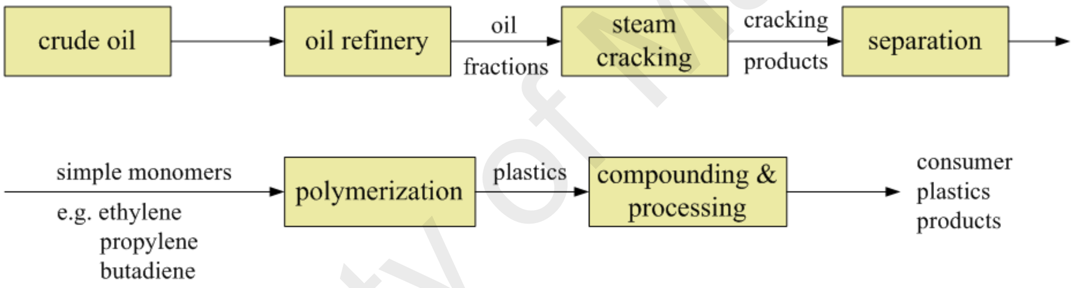


Figure 2.2: Actual production flow-chart of plastics (Buekens & Schoeters, 1998)

Another material with similar characteristics to plastics is tyres. Tyres are primarily made from rubber (60-65 wt%) and carbon black (25-35 wt%), with the rest consisting of accelerators and fillers, which are added during the manufacturing process. Many different synthetic and natural rubbers are used, e.g. styrene–butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber. Generally, synthetic rubber is made by the polymerization of a variety of petroleum-based precursors called monomers, while natural rubber comes from the *Hevea* tree (Martínez et al., 2013). Pyrolysis of tyres can produce the oil, char and gas yields of 25-75 wt%, 26-49 wt%, and 5-57 wt%, respectively, depend on parameter settings. According to Martínez et al. (2013), oil produced from the pyrolysis of tyres can reach an energy content of up to 44 MJ/kg. Oil containing a very low level of oxygen has a high H/C atomic ratio (around 1.5), and consists of aliphatic and aromatic compounds.

Table 2.1: Type of biomass used in co-pyrolysis process research to obtain liquid products

Types of biomass	Biomass
Agricultural residues	Pine cone (Brebu et al., 2010), corn residues (cobs and stover) (Aboyade et al., 2013), sugarcane bagasse (Garcìa-Pèrez et al., 2002), cattle manure (Sánchez et al., 2007), rice husk (Ye et al., 2008), corn stalk (Cordella et al., 2013), wheat straw, oat straw (Ateş, 2011)
Wood residues	Beech wood (Sharypov et al., 2002), pine wood (Sharypov et al., 2002), fir sawdust (Liu et al., 2013)
Municipal solid wastes (include industrial wastes)	Palm shell (Abnisa et al., 2013), potato skin (Önal et al., 2012), waste electrical and electronic equipment (Liu et al., 2013), polystyrene waste (Abnisa et al., 2013), sewage sludge (Samanya et al., 2012), wheat straw (Samanya et al., 2012), legume straw (Wei et al., 2011), walnut shell (Kar, 2011), scrap tyres (Pinto et al., 2013), recycled plastic (Pinto et al., 2013), hazelnut shell (Haykiri-Acma & Yaman, 2010), LDPE waste (Sharma & Ghoshal, 2012), olive pomace (Kabakcı & Aydemir, 2013), polypropylene waste (Paradela et al., 2009), polyethylene waste (Miranda et al., 2013), PVC waste (Zevenhoven et al., 2002), carpet disposal, residues of paper, residues of plastic/metal/drinking cartons sorting installation (Velghe et al., 2011), HDPE waste (Williams & Williams, 1997), apricot (Ohmukai et al., 2008), jatropha cake (Rotliwala & Parikh, 2011).
Dedicated energy crops	Rapeseed (Samanya et al., 2012), switchgrass (Weiland et al., 2012), sorghum (Cordella et al., 2013), willow (Cornelissen et al., 2008a)

Table 2.2: Estimation of the global plastic production in 2009 and 2010 (PlasticsEurope, 2010: PlasticEurope 2011)

Countries	Yearly production (MT)	
	2009	2010
China	34.50	62.28
Europe	55.20	56.98
NAFTA	52.90	54.33
Rest of Asia	37.95	39.75
Middle East and Africa	18.40	17.23
Latin America	9.20	13.25
Japan	12.65	13.25
CIS	6.90	7.95

Table 2.3: Estimation of tyre production for several countries in 2006 and 2007 (Crain Communications Inc, 2013; Malaysian Rubber Board, 2012)

Countries	Yearly production (in thousands of units)	
	2006	2007
China	274,230	336,700
U.S	200,281	195,000
Japan	175,916	176,207
South Korea	81,508	85,853
Germany	75,342	75,218
France	59,000	61,300
Brazil	42,216	not available
Indonesia	41,300	44,300
Russia	40,417	42,330
India	32,880	33,695
Canada	30,216	33,303
Italy	32,017	31,140
Poland	28,931	30,747
Thailand	26,931	not available
Turkey	23,905	25,795
Romania	14,761	16,600
Malaysia	11,560	13,420

Petroleum is a valuable and finite natural resource. More than 70% of petroleum is used in the transportation sector (Ghosh & Prelas, 2009). When petroleum is used as a transport fuel, this means that petroleum is the end product; as consequence, the world may run out of petroleum. Nevertheless, some petroleum is still stored in other forms, such as plastics and tyres. Since plastics and tyres have the same important properties as fuel, these wastes require extra attention with respect to management. The wastes can be used further to produce second-generation biofuels through pyrolysis. However, not all wastes need to be converted into fuel, because a proportion of them can be sent for recycling into new products. In this regard, the efficiency of the consumption of plastic or tyre wastes for liquid fuel production should be considered. In terms of improvements in the efficiency of consumption, the co-pyrolysis process can be used as an option.

2.4.2 Availability of feedstock

An important criterion for selecting the proper materials as alternative energy sources is its availability. In this context, biomass has been found to be sufficient for meeting this criterion. Biomass can be obtained from forestry residues, agricultural residues, agro-industrial wastes, animal wastes, industrial wastes, sewage, municipal solid wastes, and food processing wastes; thus, as consequence, the total accumulation of biomass will always be high. Each country has different sources of biomass depending on a number of factors such as geographical conditions, population levels, economic development, agricultural development, forest development, industrial growth, food demand and lifestyle. This means that all of the countries in the world have the same opportunities with regard to the co-pyrolysis process for the production of liquid fuel from biomass.

Furthermore, the availability of plastics as a feedstock is confirmed as being sufficient for the future sustainability of pyrolysis oil production. Plastics are globally available in an abundance. A report released by PlasticsEurope (Association of Plastics Manufactures) mentioned that the global plastics production has increased every year since 1950 (PlasticsEurope, 2011). The total global plastics production has grown from around 1.7 million tons (MT) in 1950 to 265 MT in 2010. An estimation of the global plastic production in 2009 and 2010 is shown in Table 2.2. However, the high production of plastics has a linear relationship with increased end-of-life plastic. In 2009, around 43.6% of total plastic production was considered waste in Europe and the amount was increased by around 3% in the next year. Thus, there is room for further use of this material in order to minimize the disposal of valuable plastics in landfills.

Around 1.5 billion tyres are produced worldwide every year, which will eventually be categorized or interpreted as waste tyres (Williams, 2013). An overview of tyre production for several countries in 2006 and 2007 is shown in Table 2.3. Waste tyres are known to have a significant impact on increasing the urban waste stream and it will become a major threat to the environment. Approximately 64% of waste tyres are sent to landfill or illegally dumped or stockpiled, with only 13% of them being recycled (Quek & Balasubramanian, 2013). In landfills, waste tyres are not easily degraded, but tend to float to the top over time due to trapped gases, thus breaking landfill covers. The incineration of waste tyres requires the expensive control system of air emissions because this process produces toxic gases, which contain carcinogenic and mutagenic chemicals. Special treatment and attention are needed to tackle waste tyres, and pyrolysis has been found to be a technically feasible way to treat tyres and recover valuable products.

Wastes of plastics and tyres are considered to be potential sources to use as a co-feed in co-pyrolysis to produce liquid fuel. As well as those materials having high energy content, the sources are particularly easy to find and available in huge amounts in all countries around the world. Pyrolysis of the blends of those materials with other biomass wastes will encourage the creation of innovative new concepts in waste management, energy security enhancement, and environmental concerns. Therefore, it is important to note that development of the co-pyrolysis process to produce liquid fuel may be applicable in most countries.

2.5 Exploration of co-pyrolysis studies

The exploration of co-pyrolysis studies is necessary in order to generate ideas with regard to producing high-grade pyrolysis oil. For this reason, many efforts have been made by researchers to explore this technique, and have revealed many interesting findings. An overview of studies of the co-pyrolysis of biomass wastes with emphasis on pyrolysis oil production is described below.

2.5.1 Use of plastics in co-pyrolysis

Most co-pyrolysis studies have selected plastics as one of the co-feeds, with the aim of improving the oil yield in terms of quality and quantity. The summaries of studies on co-pyrolysis of biomass mixed with plastics to produce pyrolysis oil are shown in Table 2.4. All of the experiments listed in Table 2.4 were performed without any catalysts, solvents or additional pressure. Abnisa et al. (2014) investigated the co-pyrolysis of palm shell and polystyrene (PS) to obtain a high-grade pyrolysis oil. Palm shell is well known as a waste generated from the palm oil mill industry, and is available in huge amounts in Malaysia; around 5.2 MT were produced in 2009. Furthermore, over 280,000 Tons of waste PS is produced annually in Malaysia, most of which is contributed by food packagers. The experimental results showed that by adding the same weight ratio of PS in the pyrolysis of palm shell, the yield of oil increased to about 61.63 wt%, while the pyrolysis of palm shell alone only yielded oil at a level of about 46.13 wt%. The high yield of oil was obtained with a process temperature of 500°C, a heating rate of 10°C/min, a reaction time of 60 min, an N_2 flow rate of 2 L/min. Moreover, the quality of oil was improved when PS was involved in the pyrolysis of palm shell. For the pyrolysis of palm shell alone, a high heating value (HHV) of oil product was obtained, of about 11.94 MJ/kg. However, pyrolysis of palm shell mixed with PS raised the HHV of oil up to 38.01 MJ/kg. Lastly, the authors concluded that the use of palm shell and PS wastes for the recovery of liquid fuel by co-pyrolysis is the key to overcoming environmental problems stemming from the high volume of palm shell waste generated by the palm oil industry; also, it can be noted that this is an optional solution to increasing energy security in Malaysia.

Table 2.4: Summaries of studies on co-pyrolysis of biomass mixed with plastics

Ref.	Type of materials		T (°C)	Liquid yield (wt%)			Calorific Value (MJ/kg)	
	Biomass	**Type of plastics**		**Biomass alone**	**Mixture materials (1:1 weight ratio)**	**Extra yield**	**Biomass alone**	**Mixture materials (1:1 weight ratio)**
(Abnisa et al., 2014)	Palm shell	PS	500	46.13	61.63	15.5	HHV = 11.94	HHV = 38.01
(Brebu et al., 2010)	Pine cone	LDPE	500	47.5	63.9	16.4	GCV = n.d	GCV= 46.33
		PP	500		64.1	16.6		GCV = 45.58
		PS	500		69.7	22.2		GCV = 46.43
(Cornelissen et al., 2008a)	Willow	PHB	450	49.71	64.24	14.53	HHV = 16.10	HHV = 20.22
(Cornelissen et al., 2008b)	Willow	PLA	450	48.85	51.30	2.45	HHV = 16.13	HHV = 18.49
(Önal et al., 2012)	Potato skin	HDPE	500	23.00	39.00	16.00	HHV = 32.00	HHV = 45.61
(Liu et al., 2013)	Fir sawdust	Waste electrical and electronic equipment	500	46.30	62.30	16	Not reported	Not reported
(Paradela et al., 2009)	Pine residue	Plastic waste contained: 56% PE, 17% PS and 27% PP	400	32.00	53.00	21	HHV = 20	HHV = 45
(Rutkowski & Kubacki, 2006)	Cellulose	PS	500	45.50	58.80	13.3	Not reported	Not reported
(Rutkowski, 2009)	Pinewood sawdust	PS	450	46.00	67.00	21	Not reported	Not reported
(Cornelissen et al., 2009)	Willow	Biopearls	450	50.10	52.79	2.69	HHV = 16.10	HHV = 19.10
		Solanyl			59.24	9.14		HHV = 15.70
		Potato starch			51.52	1.42		HHV = 19.20

Brebu et al. (2010) explored the co-pyrolysis of pine cone with synthetic polymers. The polymers used included low density polyethylene (LDPE), polypropylene (PP), and PS. In their study, pine cones were obtained from a forest in Izmir (Turkey), while commercial polymers of LDPE, PP, and PS were selected which were free from any stabilizers, fillers and pigments. The pyrolysis temperature was 500°C with a heating rate of 10°C/min. Liquid was found to be the main product of the experiment and yields varied from 47.5 to 69.7 wt%. The lowest liquid yield was obtained from the pyrolysis of pine cone (47.5 wt%). However, by mixing the pine cone and polymers in the same weight ratio, the liquid yield obviously increased. Furthermore, Brebu et al. also reported that the energy contents of oils from the pyrolysis of mixed materials were higher than those produced by the pyrolysis of pine cone alone.

The utilization of biopolymers in co-pyrolysis has also attracted the attention of some researchers. Cornellissen et al. have performed several studies regarding the use of biopolymers in co-pyrolysis to produce liquid fuel. Several biopolymers that have been tested include polylactic acid (PLA), corn starch, polyhydroxybutyrate (PHB), biopearls, eastar, solanyl and potato starch (Cornelissen et al., 2008a; Cornelissen et al., 2008b; Cornelissen et al., 2009). Willow was selected as a representative biomass in their study. The process was performed in a semi-continuous home-built pyrolysis reactor, flushed with nitrogen gas, and the temperature was set around 450°C (723 K). They found that the flash co-pyrolysis of willow/biopolymers blends generally results in improved pyrolysis characteristics: a synergetic increase in pyrolysis yield, a synergetic reduction of the water content in oil yield, an increase in heating value, and the production of easily separable chemicals. Among them, PHB was found to be the biopolymer with the most potential for use in co-pyrolysis since it can produce the highest oil yield and has the highest heating value.

Some interesting observations can be made from the data obtained, which are presented in Table 2.4. The presence of plastics in the pyrolysis of biomass has clearly improved the liquid yield. The pyrolysis of mixtures of biomass and plastics is able to produce extra liquid, typically between 1.42 and 22.2 wt%. This finding was also supported by

Szuba and Michalik, who mentioned that the increase in the yield of liquid products through co-pyrolysis may vary in the range of 2-23 wt% (Szuba & Michalik, 1982). At the same time, the energy content of the liquid, represented by the calorific value, showed a significant increase. Based on the data in Table 2.4, all types of plastics are known to improve the calorific value of the liquid product. However, the concentration of energy produced from the co-pyrolysis of biopolymers was found to be lower compared to the oil produced from synthetic plastics.

2.5.2 Use of waste tyres in co-pyrolysis

There is growing interest among researchers in the use of waste tyres as a fuel source through the process of pyrolysis. As a research output, several comprehensive reviews on various aspects of waste tyres pyrolysis for liquid production have been published in 2013 (Martínez et al., 2013; Quek & Balasubramanian, 2013; Williams, 2013). In co-pyrolysis, many studies of pyrolysis of waste tyres mixed with other materials have been carried out. However, studies which focused on the pyrolysis of waste tyre/wood-based biomass blends are currently still limited. Therefore, some effort should be made to examine the existence of synergistic effects when employing various pyrolysis conditions for the pyrolysis of waste tyre/biomass. Several studies which involved waste tyres in the co-pyrolysis process are summarized in Table 2.5. All of the data summarized in Table 2.5 were collected from experiments without using catalysts and solvents or any additional pressure.

As can be seen from Table 2.5, the studies have been classified into two categories: co-pyrolysis of waste tyres with wood-based biomass and co-pyrolysis of waste tyres with waste oils. In studies of the co-pyrolysis of waste tyres with wood-based biomass, the addition of waste tyres was used with the aim of obtaining extra oil. From the studies performed by Alias et al. (2011) and Cao et al. (2009), it is indicated that the presence of waste tyres in the pyrolysis of biomass significantly contributes to the increased oil yield. Furthermore, as tyre mass is increased in the pyrolysis of biomass, the calorific value of the oil obviously increases. Therefore, co-pyrolysis overcomes a defect of the low calorific value of the oil derived from the pyrolysis of biomass alone.

The second classification in Table 2.5 is the co-pyrolysis of waste tyres with waste oils. For this classification, waste oils were used to improve the quantity and quality of pyrolysis oil from waste tyres. This approach is economical and has great potential as an eco-friendly option. Waste oils such as waste lubricant oil, bilge water oil and oily sludge can be categorized as hazardous waste, since these pose an environmental hazard due to both their metal content and the presence of other contaminants. Thus, a proper option to manage waste should be considered, and co-pyrolysis has been suggested as an alternative technology for conversion of these kinds of waste materials for energy recovery and environmental protection. Önenç et al. (2012) studied co-pyrolysis of scrap tyres with oily wastes and concluded that co-pyrolysis of scrap tyres with oily waste could be an environmentally friendly method for the transformation of hazardous waste into valuable products such as chemicals or fuels.

2.6 Synergistic effects on co-pyrolysis

A synergistic effect is the main factor responsible for all improvements in oil quality and quantity. This phenomenon has been considered an interesting area to be researched by a number of groups. Generally, the research is focused on the study of synergistic effects or the interactive effects between the feedstock used. Some common findings in co-pyrolysis studies are discussed in this section.

Table 2.5: Several studies of the use of waste tyres in co-pyrolysis

Classification	Ref.	Materials description	System configuration and operation conditions	Relevant results and observations
Co-pyrolysis of waste tyres with wood-based biomass	(Alias et al., 2011)	Waste tyres without wire steel were mixed with empty fruit bunches with a ratio of 1:1.	The experiment was performed using a fixed bed reactor. Co-pyrolysis was carried out under a nitrogen atmosphere at a temperature of 500°C. Pyrolysis oils were collected in an ice/water condenser.	The products of liquid, char, and gas were obtained at levels of 42.80 wt%, 33.20 wt%, and 24.00 wt%, respectively. The liquid product was significantly decreased when the empty fruit bunches were pyrolyzed alone without being mixed with waste tyres.
	(Cao et al., 2009)	Tyre powder with a particle size less than 165 µm mixed with sawdust powder (198-350 µm). The ratios of tyre to sawdust in the feed were varied at 0:100, 40:60, 60:40, and 100.	Feedstock of 100 g was put into the fixed-bed pyrolysis reactor. Before heating the reactors, they were first blown for 30 min with nitrogen. The reactor was heated to the designated temperature of 500°C at 20°C/min and held at that temperature for a minimum of 3.5 h.	The liquid yield reached 45.0 wt%, 46.2 wt%, 47.0 wt% and 47.2 wt% when tyres mass occupied 0%, 40%, 60% and 100% in the mixture, respectively. The liquid derived from pyrolysis of sawdust alone had a HHV of 28.51 MJ/kg, while the value was increased to 42.44 MJ/kg when tyre mass accounted for 60% of the mixture.
	(Martínez et al., 2014)	Pine woodchips (15 mm) containing bark and waste tyres (5 mm) were used for the experiments.	Two reactors with different scales were used in this study. The first part of the co-pyrolysis experiment was carried out in a fixed bed reactor (74 cm length and 1.6 cm internal diameter). The reactor was heated externally at temperature of 500ºC with a heating rate of 80ºC/min. The reaction time was set to 15 min. Different feedstock mixtures on mass basis were studied in the fixed bed reactor: 100% biomass (100/0); 90% biomass and 10% waste tyres (90/10); 80% biomass and 20% waste tyres (80/20) and 100% waste tyres (0/100). The auger reactor with a pilot plant scale was used for second part of the co-pyrolysis experiment. Experiments were set at 500ºC using nitrogen as a carrier gas at 5 l/min and a mass flow rate of 5 kg/h. The residence time of the feedstock inside the reactor was fixed at 5 min.	The results from the first part of the experiment showed that the pyrolysis of biomass alone yielded around 50.0 wt% oil, whereas the pyrolysis of tyre only resulted in about 47.6 wt% oil. Remarkably, no increase in liquid yield was observed in the pyrolysis of mixtures of pine woodchips and waste tyres. For the second experiment, the liquid yield was 52 wt% for the pyrolysis of pine woodchips. An increase in the liquid yield was found for the 90/10 blend (56.0 wt%), which was obviously higher than that for the liquid yield obtained from a fixed bed reactor (48.5 wt% for the 90/10 blend). The authors noted that the lowest calorific value was obtained for pyrolysis of the biomass, while the highest was obtained for the pyrolysis of tyres. In addition, all calorific oils increased with an increased waste tyre ratio in the blend.

Co-pyrolysis of waste tyres with waste oils	(Uçar et al., 2005)	Two different types of scrap tyres, passenger car tyre (PCT) and truck tyre (TT), were mixed with waste lubricant oil (WLO). Both tyres were ground to the desired particle size of 1.5–2.0 mm. The scrap tyres contained no steel thread or textile netting. Each tyre was mixed with an equal ratio of WLO.	Co-pyrolysis experiments were carried out in a fixed bed reactor and under nitrogen atmosphere at temperatures of 550, 650 and 800°C. The reactor was purged before experiments using a nitrogen gas flow of 25 ml/min for 10 min to remove any air inside. Liquid products were condensed in the first two traps by cooling with an ice bath.	The addition of WLO in the pyrolysis of scrap tyres is aimed at obtaining extra oil. The results showed that co-pyrolysis with WLO produced more oil than pyrolysis of tyres alone. Co-pyrolysis of PCT with WLO produced liquid about 67 wt%, while co-pyrolysis of TT with WLO produced a higher liquid yield of about 72 wt%. An increase in the co-pyrolysis temperature had no effect on the oil quantity. The calorific values for co-pyrolysis oils were slightly higher than those of pyrolysis oils and close to those obtained for commercial diesel.
	(Siva et al., 2013)	Scrap tyre (ST) with a particle size of less than 2 mm was mixed with oily wastes, including bilge water oil (BW) and oily sludge (OS). The ratios of ST:BW and ST:OS were fixed at 1:1.	The pyrolysis experiments were carried out in a fixed bed design and stainless steel reactor (L; 210 mm; Ø; 60 mm) under atmospheric pressure using a semi-batch operation. The co-pyrolysis experiment was performed at 500°C.	The pyrolysis of scrap tyres at a temperature of 500°C produced an oil yield of 44.1 wt%. The increase in oil yield from co-pyrolysis processes of ST:BW and ST:OS was found to be 64.8 and 62.4 wt%, respectively. The HHV of pyrolysis oils was obtained about 43.8, 44.8 and 44.9 MJ/kg for pyrolysis of ST, co-pyrolysis of ST:BW, and co-pyrolysis of ST:OS, respectively.
	(Önenç et al., 2012)	Scrap tyre (ST) samples were shredded, crumbed and sieved from the sidewall rubber of scrap tyres to produce a size of 1.5–2.0 mm. The scrap tyres contained no steel thread or textile netting. The average rubber composition of the scrap tyres was 35 wt% natural rubber and 65 wt% butadiene rubber. Bilge water oil (BW) and oily sludge (OS) were selected as the oily wastes.	A glass reactor with an internal diameter of 30 mm and a total length of 350 mm was used in semi-batch operation under self-generated pressure. Pyrolysis was performed at 400 and 500°C on individual BW, OS and ST and at 500°C on a ternary mixture with a BW:OS:ST weight ratio of 1:1:2.	All experiments from pyrolysis of the individual components showed that the maximum oil yields were achieved at 500°C. At 500°C, the oils were obtained at levels of about 77.5, 71.3 and 39 wt% for the pyrolysis of BW, OS and ST, respectively. The oil yield of co-pyrolysis (BW:OS:ST mixture of 1:1:2) was around 50.5 wt%.

2.6.1 Mechanism of synergistic effects

Synergistic effects can be achieved through radical interactions during the co-pyrolysis reaction. According to Johannes et al. (2013), data on the so-called positive or negative synergy depend on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors. Among these factors, the types of blending feedstock are a major factor that can significantly influence the synergistic effects; thus, synergistic effects on co-pyrolysis can be complicatedly varied (Fei et al., 2012).

Liu et al. (2013) (W.-J. Liu et al., 2013) performed a series of co-pyrolysis experiments at 773 K by varying the blending ratio of the biomass and waste electrical and electronic equipment (WEEE). Fir sawdust was selected as a representative biomass. The authors concluded that a significant increase in the pyrolysis oil yield can be indicated as the occurrence of synergistic effects during the co-pyrolysis process. Subsequently, the authors reported the existence of some mechanisms of synergistic effects, which were clearly observed in their study. One of the mechanisms explained was about hydrogen donors. The biomass has a higher H/C molar ratio than WEEE, and the relatively high hydrogen content in biomass can act as a hydrogen donor to WEEE during co-pyrolysis. A similar finding was also reported by Zhang et al. (2007). Water, one of the major components in biomass pyrolysis, is also expected to act as a reactive compound to promote further cracking of the WEEE tar to produce more volatile compounds, thereby increasing the pyrolysis oil yields.

Furthermore, some researchers contend that knowledge of the synergistic effects remains poor. Zhou et al. (2006) commented that the mechanism of the synergistic effect between biomass and plastic during co-pyrolysis is unclear. This opinion was also supported by Wang and Li (2008). Biomass and plastic have different decomposition mechanisms in the thermal pyrolysis process. The pyrolysis of biomass involves a series of exothermic and endothermic reactions (Demirbas, 2009), whereas the thermal pyrolysis of plastic occurs by a radical mechanism (initiation, propagation, and termination) (Önal et al., 2014). Jakab et al. (2000 and 2001) opined that biomass has lower thermal stability than plastics, which can affect their radical degradation mechanism by promoting the degradation of synthetic macromolecules. Sun et al. (2013) studied the co-pyrolysis of poplar wood and high density polyethylene (HDPE) in a micro-scale reactor using pyrolysis-gas chromatography/mass spectrometry. Their results explained that free radicals are formed from biomass pyrolysis and participate in reactions of plastic decomposition, yielding more light paraffins, because of the lower temperature of biomass component decomposition compared with that of polyolefins. Moreover, Önal et al. (2014) described that the synergistic effect in co-pyrolysis is complex because of various chemical species. According to the authors, several reaction radicals can be induced during co-pyrolysis of HDPE and biomass, including initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), and isomerization via vinyl groups], and termination by disproportionation or recombination of radicals.

Wang and Li (2008) investigated the synergistic interaction potential in the devolatilization characteristics of polylactic acid (PLA) and biomass mixtures during co-pyrolysis. The authors stated that some possible general reactions can be proposed, such as: (1) the decomposition of lignin and/or hemicellulose results in volatiles that react with PLA, which can then additionally react with cellulose; (2) the decomposition of biomass and PLA occurs simultaneously, resulting in interactions during the decomposition of biomass and PLA and/or interactions between volatiles after decomposition of biomass and PLA and/or interactions between condensables of biomass and PLA; (3) the formation of char as a decomposition product of the biomass may be the main cause for the changes in PLA degradation processes.

2.6.2 Increase in oil yield

As can be seen from Tables 2.4 and 2.5, the co-pyrolysis process has a tendency to increase the oil yield. Although there are many factors that might contribute to increase the oil yield, the nature of biomass is a fundamental factor that determines this. The amount of liquid can be easily predicted (low or high) when the composition of biomass has been measured. The composition of biomass is generally reported in terms of its proximate analysis. Proximate analysis is a method which measures the content of four separately identifiable constituents in a biomass: volatile matter, fixed carbon, moisture content, and ash content (Kreith, 1998). Initially, the analysis is addressed towards coals characterization, and then developed to characterize the biomass sample. In pyrolysis, volatile matter and ash content are the main factors that have an effect on liquid yield production. Numerous researchers have recognized that the presence of volatiles favors the production of a large amount of pyrolysis oil. Asadullah et al. (2008) noted that volatile matter is usually converted to bio-oil upon condensation. Omar et al. (2011) found that a high volatile content provides the advantages of high volatility and reactivity, which are favorable for liquid fuel production. Ash also plays an important role in determining the proportions of the liquid product of biomass pyrolysis. However, the high ash content (alkali metals) contributes to a decrease in the oil yield, and, as consequence, the char and non-condensable gases are produced in higher yields (Fahmi et al., 2008; Venderbosch & Prins, 2010b). Therefore, it can be highlighted that biomass with a low ash fraction favors high oil yields, and a high fraction of volatiles favors a higher oil yield.

For wood-based biomass, the result of proximate analysis is highly dependent on lignocellulosic contents. Lignocellulosic compounds include cellulose, hemicellulose, and lignin as primary components, and are generally contained in wood-based biomass. Different types of wood-based biomass have different percentages of lignocellulosic components. Among them, cellulose and hemicelluloses are components which play an important role in generating volatile matter. According to Qu et al. (2011), cellulose is more volatile than hemicellulose. Therefore, wood-based biomass with has a high amount of cellulose is potentially able to generate high volatile matter, which leads to an increase in oil yield. Lignin, which is composed of aromatic rings with various branches, decomposes over a wide range of low to very high temperatures with a very low mass loss rate. Therefore, wood-based biomass with a higher lignin content might have a relatively higher char yield. The effects of lignocellulose compounds on the production of volatile matter have been widely studied by many researchers (Kang et al., 2012; Qu et al., 2011; Wu et al., 2013; Yu et al., 2014), the results of which are depicted in Figure 2.3.

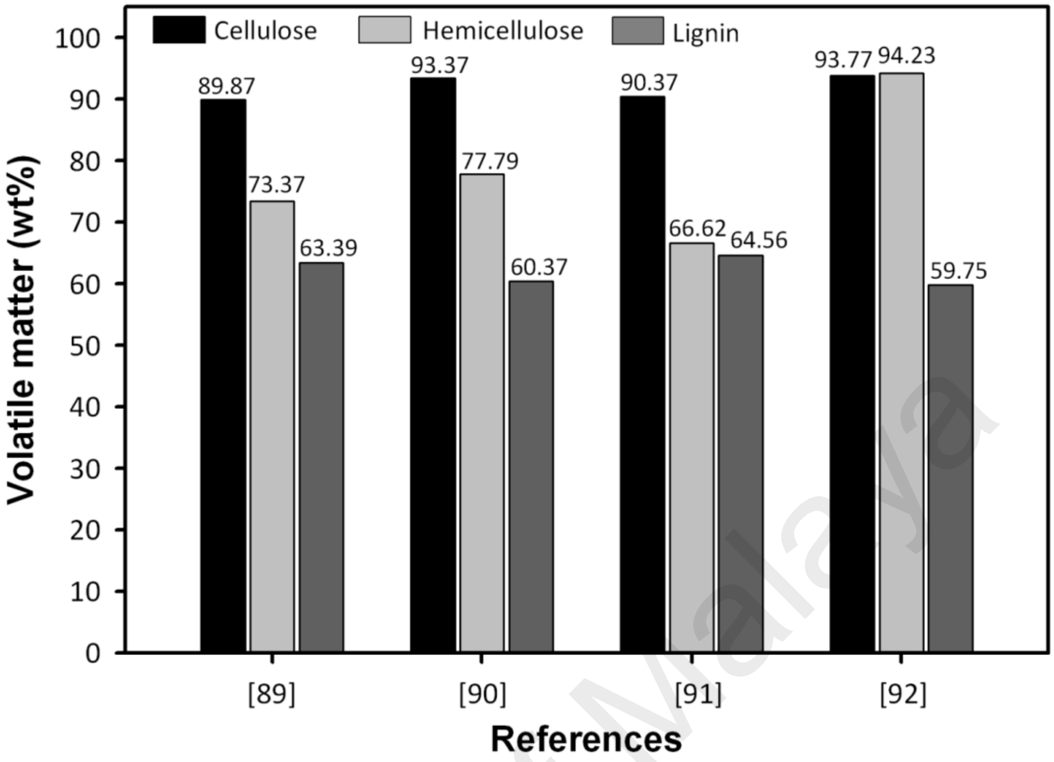


Figure 2.3: The definitive trend of biomass composition in producing oil via the pyrolysis process

The proximate analysis of plastics depends on their types. Table 2.6 shows the results of proximate analyses of plastics taken from the literature. From Table 2.6, it can be seen that all plastic types have high characteristics of volatile matter, which means that all types of plastic have the potential to produce a high liquid yield through the process of pyrolysis. Among the types of plastic, the value of volatile matter of more than 99.50 wt% was observed for high density polyethylene (HDPE), LDPE, PS, and polyamide. In the study performed by Demirbas in 2004, three types of plastic wastes (PS, PE, and PP) were pyrolyzed, and the results showed that PS yielded the higher liquid level (89.5 wt%) than PE and PP (Demirbas, 2004). The same tendency was also observed by Kiran et al., who studied the recycling of plastic wastes via pyrolysis (Kiran et al., 2000). The oil yield obtained was about 88.8 wt% at a temperature of 600°C and a heating rate of 5°C/min. Detailed products and components of the pyrolysis of several types of plastics have been reviewed by Kaminsky (1991).

Table 2.6: Proximate analysis of plastics

Type of plastics	Plastics type marks	Moisture (wt%)	Fixed carbon (wt%)	Volatile (wt%)	Ash (wt%)	Ref.
Polyethylene terephthalate (PETE)	♳ PETE	0.46	7.77	91.75	0.02	(Zannikos et al., 2013)
		0.61	13.17	86.83	0.00	(Heikkinen et al., 2004)
High-density polyethylene	♴ HDPE	0.00	0.01	99.81	0.18	(Ahmad et al., 2013)
		0.00	0.03	98.57	1.40	(Heikkinen et al., 2004)
Polyvinyl chloride (PVC)	♵ V	0.80	6.30	93.70	0.00	(Hong et al., 1999)
		0.74	5.19	94.82	0.00	(Heikkinen et al., 2004)
Low-density polyethylene	♶ LDPE	0.30	0.00	99.70	0.00	(Park et al., 2012)
		-	-	99.60	0.40	(Aboulkas et al., 2010)
Polypropylene	♷ PP	0.15	1.22	95.08	3.55	(Jung et al., 2010)
		0.18	0.16	97.85	1.99	(Heikkinen et al., 2004)
Polystyrene	♸ PS	0.25	0.12	99.63	0.00	(Abnisa et al., 2014)
		0.30	0.20	99.50	0.00	(Park et al., 2012)
Polyethylene (PE)	♹ OTHER	0.10	0.04	98.87	0.99	(Jung et al., 2010)
Acrylonitrile butadiene styrene (ABS)		0.00	1.12	97.88	1.01	(Othman et al., 2008)
Polyamide (PA) or Nylons		0.00	0.69	99.78	0.00	(Othman et al., 2008)
Polybutylene terephthalate (PBT)		0.16	2.88	97.12	0.00	(Heikkinen et al., 2004)

According to observations made by Martínez et al. (2013), waste tyres have volatile matter and ash in the range of 57.50-73.74 wt% and 2.40-20.10 wt%, respectively. The volatile matter of the tyre consists mainly of polymeric compounds that come from natural rubber (NR) and synthetic rubber (SR), such as butyl rubber and styrene-butadiene rubber. The proportion of NR and SR are different between passenger car tyres (PCT) and truck tyres (TT). Generally, the composition of SR was found to be high in PCT, while TT was shown to have a high composition of NR. Ucar et al. (2005) performed a study to evaluate two different scrap tyres as hydrocarbon sources for pyrolysis. The results of the proximate analysis showed that TT had a higher volatile matter than PCT, while the ash content was found to be higher in PCT. They found that the product distributions from the pyrolysis of PCT and TT were quite different from each other. They also noted that the pyrolysis of TT yielded more liquid than that of PCT.

As described earlier, volatile matter is the key to producing pyrolysis oil. To maximize the generation of volatile matter, it is also important to adjust the parameters controlled in the pyrolysis process. According to Guldogan et al. (2000), temperature and heating rate are the pyrolysis parameters which most significantly affect the volatile matter yield. The study performed by Paethanom and Yoshikawa showed that moderate temperature conditions favor the generation of volatile matter (Paethanom & Yoshikawa, 2012). They analyzed the generation of volatile matter at three different temperatures (600, 800 and 1000°C), and the results showed that the highest volatile matter was obtained at 600°C, while higher pyrolysis temperatures resulted in higher fixed carbon contents. A similar trend was also found by Azeez et al. (2011) who studied the temperature dependence of fast pyrolysis volatile products from European and African biomasses. The experiment was carried out at temperatures between 300°C and 700°C with an interval of 50°C. The results revealed that most volatile products were obtained at 450°C and 500°C. Furthermore, Pan et al. (1996) explained that the faster the heating rate, the higher the volatile yield in pyrolysis.

2.6.3 Improvements in oil quality

Synergistic effects also significantly influence improvements in the quality of the oil obtained. These improvements can be clearly seen, especially with regard to fuel properties. Generally, the oil obtained from the pyrolysis of wood-based biomass alone has a lower calorific value, due to the high oxygen content. However, this can be solved by using the co-pyrolysis technique. From Tables 2.4 and 2.5, it can be seen that the oil obtained from co-pyrolysis showed an increased calorific value. This tendency can be explained by the increased hydrocarbon content of the oil. Therefore, observing the contents of C and H and the H/C ratio is important, since they can significantly control the calorific value. Önal et al. (2014) studied bio-oil production via the co-pyrolysis of almond shell and HDPE. The authors noted that liquid products obtained from the co-pyrolysis process had a higher energy content than those of pyrolysis of almond shell alone. This is due to the addition of HDPE to biomass, which increased the H/C ratio from 1.60 to 2.28. They also observed that elemental compositions of co-pyrolysis oils contain higher contents of C and H than pyrolysis oil of almond shell alone. In another study, Martínez et al. (2014) studied the co-pyrolysis of pine woodchips with waste tyres. The authors reported that the C and H contents in the liquid gradually increased with the proportion of waste tyres in the feedstock, whilst the O content decreased. They noted that a low heating value is the property with the greatest change since it increased from 14.9 to 19.0 and to 25.0 MJ/kg for biomass/waste tyre blends of 90/10 and 80/20, respectively. Thus, this showed an increase of up to 27% and 70%, respectively. Although a synergetic effect is observed for both blends, this effect is more significant for the 80/20 blend. From this finding, it can be concluded that the high proportion of waste tyre in biomass pyrolysis will contribute more to increasing the heating value.

The high water content of pyrolysis oil contributes to the low energy density; thus, for its utilization as a fuel, this content is undesirable. The water in pyrolysis oil mainly comes from moisture in the feedstock and from dehydration reactions occurring during pyrolysis. According to Wasterhof et al. (2007), drying the feedstock to obtain very low moisture levels (approaching zero) leads to a decrease in the water content. The authors also noted that from a practical point of view, such dry feedstock materials are, however, not realistic due to the high costs associated with the dryer. In this regard, the co-pyrolysis technique was found to be effective in controlling the water content of the oil. All wood-based biomass is hygroscopic, meaning that when exposed to air, it will release or pick up moisture until it is in equilibrium with the humidity and temperature of the air; because of this, wood tends to have a high moisture content. Unlike wood, plastics and tyres do not absorb much moisture and their water contents are far lower than the water content of wood. Therefore, the reduction of wood proportion and the addition of plastics or tyres as feedstock in pyrolysis will contribute to the reduction of water content. Cornellisen et al. (2008) performed research with the aim of reducing the amount of pyrolytic water by performing flash co-pyrolysis of willow and polylactic acid. The different blends of willow/polylactic acid with a w/w ratio of 10:1, 3:1, 1:1 and 1:2 were investigate and the authors concluded that the addition of polylactic acid clearly reduced the water content in the oil (up to 37%), which also increased HHV (up to 27%).

Viscosity is an important property in the chemical design process. Viscosity data are essential for various heat transfer considerations, calculating pressure drop, distillation calculations and mixing system considerations. For fuels, viscosity data are used to evaluate the effect on pumping and injecting. From some observations of co-pyrolysis studies, the condition of oil viscosity has not shown a definitive trend. Abnisa et al.

(2013) reported that liquid from the co-pyrolysis of palm shell and PS mixtures showed higher viscosity compared to the pyrolysis of palm shell alone. The decomposition of inorganic material in PS may have contributed to the higher viscosity. Cao et al. (2009) found a different trend with Abnisa et al. (2013), and reported that when tyre mass was increased in the mixture, the viscosity of the oil gradually decreased. The authors also reported that although the oil showed a decrease in viscosity, it was still higher than that of diesel oil 0#. There is a simple technique that can be used to reduce the viscosity of oil. According to Yu et al. (2007), adding methanol and/or ethanol to the pyrolysis oils reduced viscosity and slowed down the increase in viscosity and water content during storage. Blending of methanol or ethanol with pyrolysis oils may be a simple and cost-effective approach to converting pyrolysis oils into a stable gas turbine or home heating fuels.

Generally, the main compounds present in the oil produced by the pyrolysis of wood-based biomasses are alcohols, aldehydes, phenols, acids, esters, ketones, guaiacols, syringols and furans (Zhang et al., 2007). Among them, phenols have been found to be dominant in the oil (up to 55%) (Diebold, 2000). According to Samanya et al. (2012), the high level of phenols can contribute to increased acidity and instability of the oil. Martínez et al. (2014) stated that phenolic compounds originate from the decomposition of lignin contained within the biomass wood. The authors also mentioned that lignin-derived products are mainly responsible for the high molecular weight and viscosity of pyrolysis oils and thus, one of the aims of any upgrading process is to remove these compounds. In this regard, in a study of the co-pyrolysis of biomass with waste tyres, Martínez et al. proved that the percentage area of phenolic compounds was significantly decreased for biomass/waste tyre blends; this decrease was about 20% and 40% for the 90/10 and 80/20 blends, respectively. Thus, they concluded that a synergic effect towards phenolic compound removal was taking place. A similar tendency was also found by other researchers who studied the co-pyrolysis of palm shell and polystyrene (Abnisa et al., 2014). The authors noted that the quantity of phenol groups in the oil of mixed materials (50:50 ratio) was reduced (around 8.27%) compared to oil obtained from the pyrolysis of palm shell alone, while compounds consisting entyrely of hydrogen and carbon were identified as abundant in oil. However, it should be noted that there is a type of plastic which can give a positive contribution to increase the amount of phenols. A research study by Brebu and Spiridon (2012) identified abundant phenol compounds in polycarbonate, which has similar characteristics to lignin. The authors noted that the main pyrolysis products from polycarbonate are phenol, with its derivatives at carbon numbers C_{10}-C_{14}, and bisphenol, with its derivatives at C_{22}. In brief, the addition of polycarbonate in the pyrolysis of biomass to produce liquid fuel is not recommended since it can contribute to increase the phenol compounds in the oil.

The co-pyrolysis of biomass wastes has also been found to be effective in recovering hydrocarbon-based chemicals, which promote improvement in the fuel quality. The presence of hydrocarbon-based chemicals has been detected by many researchers through several types of analyses such as GCMS, FTIR, and ^{1}H NMR. Önal et al. (2014) reported that co-pyrolysis of HDPE and almond shell led to an increase in alkene fractions by 75% compared with the results obtained for individual biomass pyrolysis. In another study, Aboulkas et al. (2012) tried to co-pyrolize HDPE with oil shale. The authors noted that the oil obtained by co-pyrolysis had similar properties to commercial gasoline. In the oil obtained from co-pyrolysis, aliphatic components were dominant. This result was observed using two different analyses: FTIR and ^{1}H NMR. The research article released by Abnisa et al. (2014) showed that the hydrocarbon groups in oil from the co-pyrolysis of palm shell and PS were mostly found in the form of aromatics and benzene, with percentages of 39.59% and 32.99%. Cao et al. (2009) studied the behavior of co-pyrolysis feedstock between sawdust and tyre on the formation of polycyclic aromatic hydrocarbons. The authors reported that the percentage of tyre in the mixture had a great influence on the content of polycyclic aromatic hydrocarbons in the oil. The experiment showed that the total content of polycyclic aromatic hydrocarbons varied from 5.78×10^{-4}g g^{-1} to 2.2×10^{-3}g g^{-1} when tyre mass occupied 40% and 60% of the mixture, respectively.

The oil from pyrolysis of biomass generally has lower sulfur content at approximately 0.1 wt% (Abnisa et al., 2013a; Abnisa et al., 2013b). The addition of waste tyre in the pyrolysis of biomass can increase the sulfur content in the oil. This finding is clearly evident in the study performed by Martinez et al. (2014). The result from ultimate analysis showed an increment in sulfur content when tyre mass occupied 10% and 20%. The sulfur content increased by around 0.2 wt% and 0.4 wt% for the 90/10 and 80/20 blends, respectively, whereas no sulfur was detected for pyrolysis of biomass alone. Oil with high sulfur contents needs to be desulfurized before it can be used for combustion. One of the effective techniques that can be applied to remove the sulfur content is the oxidative desulphurization technique. This technique was found to be a very promising approach for the reduction of sulfur content of up to 92%, which only requires low temperature of 50 °C and atmospheric pressure for its process condition (M. F. Ali et al., 2006).

2.7 Byproducts of the co-pyrolysis process

Furthermore, the co-pyrolysis of biomass wastes also produces char and gas as byproducts. As reported by Bridgwater (2012), the byproduct of char from the pyrolysis of biomass is typically obtained in yields of up to 12 wt% on a dry-feed basis, together with gas with a proportion of around 13 wt%. Among the byproducts, gas from the pyrolysis of biomass has a lower calorific value than natural gas or pyrolysis tyre gas. However, co-pyrolysis may also increase the calorific value. Some information about the byproducts generated from the co-pyrolysis process is presented below.

2.7.1 Char

Bernardo et al. (2012) studied the physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. The char samples were obtained from the pyrolysis of three different waste mixtures: plastics, pine biomass, and tyre wastes. The authors noted that the addition of tyres to the waste mixture significantly increased the yield of char; otherwise, the addition of plastic in pyrolysis of pine biomass had no effect on the increase in char yield. The same tendency was also found by Lopez et al. (2011) in a study about the dechlorination of fuels in the pyrolysis of polyvinyl chloride (PVC)-containing plastic wastes. The authors stated that only a small quantity (0.6-1.3 wt%) of solid char was obtained from the pyrolysis of plastics or mixtures of plastics.

In addition, the quality of char from co-pyrolysis showed improvements in the calorific value. Paradela et al. (2009) noted that the solid products obtained from the co-pyrolysis of a mixture of materials (biomass and plastic wastes) had higher heating values than some coals. A similar observation was also found in a study of co-pyrolysis of biomass with waste tyres, which was performed by Martinez et al. (2014). Similarly, Brebu et al. (2010) reported that the char obtained from the pyrolysis of pine cone alone had a lower calorific value than the chars obtained from co-pyrolysis. This is due to the high oxygen content in the char derived from the pyrolysis of pine cone alone. The authors noted that the difference in the elemental composition of chars from synthetic polymers mixed with pine cone and with cellulose may be linked to the presence of lignin in pine cone. Furthermore, the authors also explained that the very low sulfur content was found in chars, making them attractive for use in incineration. This makes these products suitable for use as fuels, e.g. in co-combustion with coal or other wastes. Another application of char is its use as an adsorbent in water treatment to remove heavy metals. The chars formed from co-pyrolysis can also be potentially used as adsorbents through an upgrading treatment. Bernardo et al. (2012) performed a multistep upgrading of chars obtained from the co-pyrolysis of PE, PP and PS plastic wastes, pine biomass and used tyres. The textural and adsorption properties of the upgraded chars were evaluated and the results indicate that the chars are mainly mesoporous and macroporous materials, with adsorption capacities for methylene blue dye in the range of 3.59–22.2 mg/g. The authors noted that the upgrading treatments performed on the chars allowed carbonaceous materials with sufficient quality to be reused as precursors for adsorbents to be obtained.

2.7.2 Gas

According to Bridgwater (2006), high temperatures and longer residence times were found to be the best conditions to increase the conversion of biomass to gas. Since the process parameters required to maximize oil production are different for gas, in pyrolysis, gas is only obtained in low quantities. Generally, the gas produced by pyrolysis is in the range of 13–25 wt% of the used biomass. Specifically, Kim et al. (1997) tried to observe gas production from the pyrolysis of mixed plastics comprised of PE, PP, and PS. The results showed that under normal temperature and pressure conditions, liquid was the main product, with yields of around 75 wt%; gas yield was always lower than 10 wt%. Similar to plastic waste, the pyrolysis of tyre also tends to result in a low yield of gas. William (2013) tried to summarize the data from several studies related to the pyrolysis of waste tyres, and the author found that gas can be obtained in the range of 2.5 to 28.5 wt%. The author reported that a high yield of gas was usually generated under conditions including a high reaction temperature and a low heating rate. To understand the effect of waste mixture composition on gas production, a study performed by Paradela et al. (2009) can be a reference. The authors reported that the increase in biomass percentage led to an overall decrease in the effective liquid yield, while both the solid residue and gas fraction increased almost linearly with the biomass percentage.

The gas composition arising from the co-pyrolysis process is dependent on the composition of the feedstock used. Generally, the gas product released during wood pyrolysis contained CO, CO_2, H_2, CH_4, C_2H_4, C_3H_6, and minor amounts of other hydrocarbons (Mohan et al., 2006). For the pyrolysis of tyres, the main gas components were CO, CO_2, H_2S, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, and C_4H_{10} (Williams, 2013). Furthermore, the gas composition in plastics was found to be different depending on the type of plastics. Williams and Williams (1998) studied the pyrolysis of six main plastics in municipal solid waste, including HDPE, LDPE, PP, PS, PVC, and poly-(ethylene terephthalate) (PET). The authors reported that the main gases produced from the individual plastics were H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, and C_4H_8 and for the PET plastic CO and CO_2. The presence of hydrogen chloride was only observed and found to be high for the pyrolysis of PVC.

The gas produced from the pyrolysis process has a significant caloric value; therefore, it can be used to offset the total energy requirements of the pyrolysis process plant. Some of the factors that can increase the calorific value are high concentrations of hydrogen and other hydrocarbons. Hester and Harrison (2013) reported that at conditions of normal temperature (25°C) and atmospheric pressure, the calorific value of gas from wood biomass was about 16 MJ/Nm^3, while the gas produced from the conventional pyrolysis of municipal waste had a calorific value of the order of 18 MJ/Nm^3. The author also noted that the pyrolysis of tyre produced a gas with a much higher calorific value, of about 40 MJ/Nm^3, depending on the process conditions. In the study of the co-pyrolysis of biomass and plastic waste, Paradela et al. (2009) reported on three parameters (reaction time, temperature, and waste mixture composition) which affect the calorific value. Firstly, the authors noted that the increased reaction time increased the gas heating value, due to the increase in the number of alkanes released. Then, the authors noted that the elevated reaction temperature also increased the gas heating value, again due to the increased alkane release. Lastly, the author concluded that the increased biomass content in the waste mixture significantly decreased the gas heating value, mainly due to the decrease in hydrocarbons formation.

2.8 Economic feasibility assessment

Co-pyrolysis offers simplicity in design and operation, and in many cases has successfully produced oil with a high quantity and quality. Therefore, this technique can play a pivotal role in development of the biomass energy industry. There is an important note which showed that this technique is feasible from an economic point of view. Kuppens et al. (2010) used the net present value (NPV) to evaluate the economics of flash co-pyrolysis of 1:1 w/w ratio blends of biomass (willow) and biopolymers (PLA, corn starch, PHB, biopearls, eastar, solanyl, and potato starch). NPV is the best analysis method for selecting or rejecting an investment, either industrial or financial (Graham & Harvey, 2001; Pasqual et al., 2013; Vanreppelen et al., 2011). The rule in this analysis was that the project would be accepted if the NPV was greater than or equal to zero, and would be rejected when the NPV was less than zero (Aziz, 2013). In this regard, the study performed by Kuppens et al. showed that flash co-pyrolysis of willow with any biopolymer was economically more interesting than flash pyrolysis of pure willow, because the NPV of co-pyrolysis resulted in positive cash flows for all types of biopolymers used. This result is supported by some other estimations as well, including the initial investment expenditure, the production costs, and the possible revenues. The author also noted that the calculations in this research paper were from a case study in Belgium, but the economic model behind the case study can be adapted to other locations.

In addition, an economic evaluation of the co-pyrolysis process was also studied by Shelley and El-Halwagi (1999). A techno-economic feasibility study was performed to assess the viability of co-liquefying scrap tyres and plastic waste into liquid transportation fuels. The return on investment (ROI) approach was used to make investment decisions; if the ROI was positive then the investment was considered profitable. The authors noted that the co-liquefaction of waste plastic and scrap tyres as well as the liquefaction of scrap tyres alone was both technically and economically feasible. The results showed promising economics for the mixed materials case with an ROI of approximately 18%, as compared to only 12% for the plastics alone scenario. The author also reported that the tipping fees obtained for the raw materials used in the process were the key to overall profitability. Similarly, it is in agreement with another study performed in 1998 by Huffman and Shah (1998), who reported that the ROI depends on the tipping fees received for waste plastics and tyres. The high tipping fees received will be linearly contributed to the increase in ROI.

2.9 Discussion on co-pyrolysis scenarios

This review showed that many researchers have studied the potency of co-pyrolysis technique using various types of biomass wastes, and that the results are very encouraging. Different investigations were conducted to obtain oil with a high yield and high quality, which followed the various available standards. Several advantages can be obtained from using this technique such as reducing the consumption of fossil fuels, solving some environmental problems, increasing energy security, and improving waste management systems. Apart from these, this technique also offers simplicity in design and feasibility in regard to economic analysis.

There are some important factors which need to be highlighted in the feed system of the co-pyrolysis process. To obtain a high-grade liquid, adjustments of the types and ratios of feedstock are essential. The suitable combination of feedstock in co-pyrolysis can include wood-based biomass with waste plastic or wood-based biomass with waste tyre. Both options are acceptable, since many studies have proven that these combinations can provide improvements in the pyrolysis oil through synergistic effects. However, it should be noted that not all plastic types can be used in the process. PVC is not recommended as a feedstock material because it contains about 57% chlorine by weight, which will affect the diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid, which is very corrosive and toxic. The presence of 1–3% PVC in the feedstock stream results in the fuel oil product having a total chloride level of 5000–10000 ppm (Scheirs, 2006).

Furthermore, it is important to note that the main aim of the addition of plastic waste or tyre waste in the pyrolysis of wood-based biomass is to improve the quantity and quality of the oil produced. Hence, plastic or tyre waste can be called the additive material in the process. In this regard, the proportion of additive material was designed to be less than that of the main feedstock (wood-based biomass). Many studies have shown that a higher ratio of additive material in the pyrolysis of wood-based biomass can contribute to increase the oil quality. However, the minimum use of additive material in each process of co-pyrolysis is preferred; this is due to some considerations such as:

- The production of waste plastics or waste tyres in many countries is generally found to be lower than the generation of wood-based biomass. Thus, the limited source of additive material is expected to be used and should be sufficient for the amount of wood-based biomass available.
- Besides being used as the additive material in co-pyrolysis, some wastes are also needed for the recycling process. This strategy will provide a benefit of reducing the consumption of fresh raw materials for the production new plastic or tyre products, which leads to saving fossil fuel.

In addition, there are some studies which have used coal in the co-pyrolysis process to produce liquid fuel, and have also showed encouraging results. Zhang et al. (2007) co-pyrolyzed legume straw and Dayan lignite coal in a free fall reactor at temperatures from 500 to 700°C. The blending ratio of biomass in mixtures varied between 0 and 100 wt%. The authors noted that the higher blending ratio of biomass may decrease the char yield, and consequently the liquid yields obtained were higher. The same tendency was also found by Aboyade et al. (2013), who studied the co-pyrolysis of coal and agricultural wastes. Moreover, the rank of coal has an effect on the liquid yield. According to Wei et al. (2011), the use of high-rank coal in co-pyrolysis can produce a higher liquid yield than that of low-rank coal. However, no further explanations about oil quality were found in reports of the co-pyrolysis of biomass wood and coal. For the co-pyrolysis of coal with waste tyres, Kříž and Brožová (2007) reported that the increased proportion of waste tyres in the pyrolysis of coal contributed to increase the liquid yield, which had a relatively lower oxygen content. In addition, the type of reactor can significantly effect the oil yield quantity and quality. Acevedo et al. studied the pyrolysis of blends of coal and tyre wastes in a fixed bed reactor and a rotary oven. The authors found that the oil yield was always greater in the fixed bed oven than in the rotary oven. However, the oils obtained in the rotary oven were more aromatic and contained smaller amounts of oxygenated functional groups due to their higher residence time in the hot zone of the reactor.

As shown in the above paragraph, the use of coal in co-pyrolysis can be one option to produce liquid fuel. However, this option is not a benefit with regard to reducing the dependency on fossil fuel, since coal is a part of fossil fuel. Therefore, the use of coal in the co-pyrolysis process is not recommended.

Co-pyrolysis is a promising technique that can produce a high grade pyrolysis oil from biomass waste. This technique also offers several advantages on its application:

- Co-pyrolysis can be easily applied to existing plants of the pyrolysis of biomass.
- The low cost associated with upgrading processes from pyrolysis to co-pyrolysis: if a plant is run for the pyrolysis of wood-based biomass, there will be no need to invest money in a special plant for the use of waste plastics and tyres.
- No special equipment needs to be designed and constructed for co-pyrolysis. Some minor modifications maybe needed, but only for the feed preparation system.
- As a byproduct, solid fuel is sometimes poor in organic matter; the addition of waste plastics and tyres to wood-based biomass may improve its quality.
- The quantity and quality of desired products (oil, solid or gas) can be easily controlled by adjusting process parameters.

The primary disadvantage of co-pyrolysis lies in the biomass preparation unit. Given that this technique deals with many types of biomass, an additional pre-treatment system is required, which can substantially increase the cost for the installation and operation of such units.

CHAPTER III

CHARACTERIZATION OF BIO-OIL AND BIO-CHAR FROM PYROLYSIS OF PALM OIL WASTES

3.1 Introduction

Currently, the utilization of biomass for energy is expected to contribute substantially to the projected renewable energy supplies of the future. The availability of biomass is a basic parameter in the control of energy supplies. Theoretically, biomass resources are the world's largest sustainable energy source and represent approximately 220 billion oven dry tons of annual primary production (Moreira, 2006). As an alternative energy source, biomass can be used by direct combustion or be converted into other energy products, such as liquid bio-oil or bio-char. Over the past few years, the development of products from biomass through the pyrolysis technique has been intensively investigated.

Pyrolysis is one of the most promising processes to convert biomass to bio-oil, bio-char, and non-condensable gases. The process typically occurs at high operating temperatures and in the absence of oxygen. The pyrolysis involves a series of exothermic and endothermic reactions. The exothermic reaction that involves the cracking of organic matter into small fractions occurs at low temperatures during the initial stage of pyrolysis. As the process temperature is increased, some of the primary products are vaporized and cracked into secondary products. The conditions for the vaporization and secondary cracking are usually described as endothermic reactions (Cheung et al., 2011). Biomass such as wood, bagasse, rice hulls, rice straw, peanut hulls, oat hulls, wheat straw, rice hulls, and coconut fiber is commonly used in the process (Mohan et al., 2006; Zheng, 2007). Numerous studies have shown that as much as 70 wt% of biomass is converted to bio-oil via pyrolysis (Bridgwater & Peacocke, 2000). The bio-oil increases the added value of biomass because it is easy to store, pump and transport (Czernik & Bridgwater, 2004). However, the yield of bio-char as the other product of the pyrolysis process is approximately 15-25% (Mohan et al., 2006). The char may be used as solid fuels through its conversion into briquettes. It can also be mixed with biomass and be further used to satisfy the total energy requirements of the pyrolysis plant because it has a high calorific value (Ertaş & Hakkı Alma, 2010).

Bio-oil, as a renewable liquid, is the main product of the pyrolysis of biomass, which can potentially be used as a fuel or chemical feedstock. The physical form of the liquid is dark-brown in color and free-flowing and has a strong acrid smell. The chemical composition depends predominantly on the biomass used and the conditions used in the process. Bio-oil is derived from the depolymerization of cellulose, hemicellulose and lignin. In general, the major identified compounds of the bio-oil are water, acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds, and multifunctional compounds (Lu et al., 2009; Özbay et al., 2008). The oil has the disadvantages of corrosiveness, instability, a low heating value, and a high moisture content, which is the result of its high oxygen content (35-60 wt%) (Xiujuan Guo et al., 2011). As a consequence, the combustion properties of bio-oil need to be upgraded before it can be used as a substitute for conventional fuels.

Furthermore, the pyrolysis of biomass also produces gas and char as byproducts. The gas produced by using pyrolysis represents approximately 13 wt% of the used biomass. Because of its high calorific value, the gas product can be used to offset the total energy requirements of the pyrolysis plant (Horne & Williams, 1994). High temperatures and longer residence times are the best conditions for increasing the conversion of biomass to gas (Bridgwater, 2006). Additionally, the obtained char may be used in different industries, such as for the production of chemicals, activated carbon, carbon nanotubes, carbon fibers, etc. The produced bio-char is also a better fuel than the precursor biomass, which means that it can be used as a high-efficiency solid fuel (converted into briquettes alone or mixed with biomass) in boilers where bagasse or other biomass is burnt (Uzun et al., 2010). The production of hydrogen-rich gas by thermal cracking in the gasification process is another possible application of produced bio-char (Katyal et al., 2003). In addition, bio-char can be used in agriculture to reduce negative environmental and soil-quality repercussions of harvesting. Bio-char is highly absorbent and therefore increases the ability of soils to retain water, nutrients and agricultural chemicals and thereby prevents water contamination and soil erosion (Mullen et al., 2010).

Malaysia produces a high amount of agricultural waste each year (Goh et al., 2010), and most of it originates from the palm oil mill industry. Each ton of fresh fruit bunches will produce 0.91 tons of biomass waste during the process, which includes palm shell, empty fruit bunches (EFB), and mesocarp fiber (Sudirman et al., 2011). Figure 3.1 shows the wastes generated from oil palm trees. In 2007, researchers estimated that the amounts of waste were approximately 4.7, 15.8, and 9.6 million tons for palm shell, EFB, and mesocarp fiber, respectively (Mekhilef et al., 2011). In general, the wastes are not fully utilized and continue to be used to cover the road surface in plantation areas or burnt, which contributes to increasing CO_2 emissions (Abnisa et al., 2011). The conversion of palm oil waste to bio-oil and bio-char could solve the disposal problem, decrease the costs of waste treatment, increase the added value of the waste and solve some environmental problems.

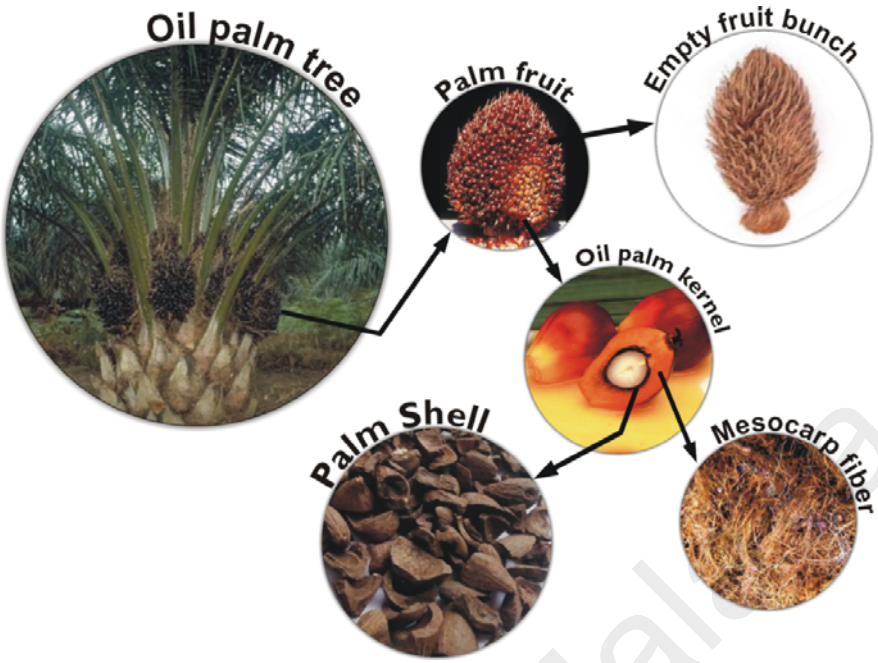


Figure 3.1: The wastes generated from oil palm trees

In this study, palm oil wastes, including palm shell, EFB, and mesocarp fiber, were characterized and then pyrolyzed in fixed-bed reactor. The same pyrolysis conditions of temperature, particle size, reaction time, and N_2 flow rate were used for all of the experiments to obtain the yields of bio-oil and bio-char. Furthermore, the products were characterized using several laboratory instruments to obtain an overview of their chemical and physical properties.

3.2 Materials and Methods

3.2.1 Raw materials

The palm oil wastes were obtained from Sime Darby Plantation in Selangor Darul Ehsan, Malaysia. The waste included palm shell, EFB, and mesocarp fiber. The samples were washed and subsequently dried under the sun for one day. The dried samples were ground and screened to give particle sizes that ranged from 1.0 to 2.0 mm, then dried again in an oven at 105 °C for 24 hours to remove moisture.

3.2.2 Pyrolysis procedure

The pyrolysis procedure was performed by charging 200 g of the sample into a 310 stainless steel reactor with a length of 127 cm, an internal diameter of 2.5 cm and outer diameter of 2.7 cm. The reactor was heated using an electric furnace, and the temperature was monitored using a K-type thermocouple placed inside the reactor. A detailed figure of the pyrolysis apparatus has been previously described by Abnisa et al. (Abnisa et al., 2011). Nitrogen gas (N_2) was used as an inert gas to purge air from inside the reactor; the purging was continued from the start of the process until its completion. The condensable products, as bio-oils, were collected in a series of condensers and stored at 0.5 °C; the products were subsequently weighed to obtain the weight of bio-oil. The bio-char was collected from the inside of the rector and weighed. The final yields of bio-oil and bio-char were calculated as follows:

$$Y_{OP} = \frac{X_1}{X_2} \times 100\% \qquad (3.1)$$

where Y_{OP} is the yield of product, X_1 is the mass of either bio-oil or bio-char, and X_2 is the initial weight of the raw material. The yield of gas was determined by difference.

Some literature studies (Bridgwater, 1999; Bridgwater & Peacocke, 2000; Mohan et al., 2006) and our previous study (Abnisa et al., 2011) have shown that the optimum yield of bio-oil is obtained under conditions of 500 °C, a particle size of 1 - 2 mm, a reaction time of 1 hour, and an N_2 flow rate of 2 L/min. Therefore, in this study, these same conditions were used for all of the experiments. The heating rate was 10 °C/min. To validate the data, each experiment was repeated in 3 - 5 replicates, and the average result was taken as the final yield. The reactor, condenser, and piping system were sterilized before being used for different samples to avoid contamination of the samples.

3.2.3 Characterizations

Before analysis, bio-oil was separated into two fractions by a centrifugation process based on a procedure developed by Bartero et al. (2011b). The process was performed by 8 min centrifugation at 3200 rpm and the fractions after centrifugation are referred to as upper and bottom layers. Afterwards, several laboratory tests were conducted to characterize the properties of the bio-oils. A Metrohm 827 pH meter was used to analyze the pH of the bio-oils, and the measurements were performed at room temperature. The water content was measured using a Karl-Fischer 737 KF Coulometer from Metrohm. Hydranal-coulomat AG (80 mL) and Hydranal-coulomat CG (5 mL) were used as anolyte and catholyte reagents, respectively. The densities of the bio-oils were measured using a pycnometer with volume of 25 mL. The analysis was performed at 24 °C.

To analyze the functional group compositions of the raw materials, bio-oils, and bio-chars, a Perkin Elmer FTIR spectrometer (Spectrum 400) was used to generate the infrared (IR) spectra of the samples. The samples were scanned in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Special preparation was performed for FTIR analysis of raw materials and bio-chars. The sample of 0.1 g was mixed with 1 g of spectroscopy grade KBr in mortar porcelain. The mixed sample was converted to a solid disc which was placed in an oven at 105 °C for 4 hours to avoid any interference with any existing water vapor of carbon dioxide molecules. A solid disc of pure KBr was used as a reference sample for background measurements.

The proximate analysis of both the precursors and the products was conducted according to ASTM D 7582-10 by using thermal gravimetric analysis (TGA), and the results were expressed in terms of moisture, volatile matter, fixed carbon and ash contents. The carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) contents of the samples were determined using a Perkin-Elmer model 2400, Series II CHNS/O analyzer. CHN combustion tube and reduction tube were used for this determination. As reported in literature (Abnisa et al., 2011; Luangkiattikhun et al., 2008; Sulaiman & Abdullah, 2011), palm oil wastes have very low sulfur content (around 0.1 wt%), thus, the value of it was not determined in this study. The results of the proximate and ultimate analyses of the palm oil wastes are listed in Table 3.1. The lignocellulosic contents of palm oil wastes were determined by using gravimetric method, and the results are presented in Table 3.2.

In this study, the high heating value (HHV) was calculated from the elemental compositions using the Dulong-type formula modified by Mott and Spooner (see Eq. 3.2) because the oxygen content in the products and raw materials were found to be greater than 15 wt% (Buckley, 1991; Mott & Spooner, 1940).

$$\mathrm{HHV\ (MJ/kg)} = 0.336\ \mathrm{C} + 1.418\ \mathrm{H} - \left(0.153 - 0.000720\ \mathrm{O}\right)\mathrm{O} + 0.0941\ \mathrm{S} \qquad (3.2)$$

Scanning electron microscopy (SEM) experiments were conducted to identify the physical morphology of the surfaces. A JSM-6390LV (JEOL, Japan) operated at a 3 kV accelerating voltage was used to characterize the morphology of the precursor and the bio-chars, which were dried overnight at approximately 105 °C under vacuum before SEM analysis. No conductive coating was applied to prepare the samples for SEM. In addition, to reduce the margin of error and to produce more reliable data, each analysis of products from all experimental works was repeated three times and the results were averaged.

3.3 Results and discussion

3.3.1 Raw materials

The lignocellulosic contents of palm shell, EFB, and mesocarp fiber are tabulated in Table 3.2. The observed cellulose content of EFB was greater than that of palm shell and mesocarp fiber, whereas a high hemicellulose content was found in the mesocarp fiber material. According to Mohan et al. (Mohan et al., 2006), during pyrolysis, the degradation of cellulose content began at 240 °C, and the reaction was complete when the temperature reached 360 °C. They also explained that lower temperatures of approximately 200-260 °C were needed to degrade hemicellulose. The organic acids, such as formic acid and acetic acid, are products formed from the degradation of the hemicellulose and cellulose, and the acid content is responsible for the low pH in bio-oil (Bridgwater & Peacocke, 2000). In addition, the degradation of hemicellulose resulted in more volatiles, less tars, and less chars than cellulose.

Table 3.1: Proximate and ultimate analyses of palm oil wastes

Type of palm oil wastes	Proximate analysis (wt%)				Ultimate analysis (wt%)			
	Moisture	Volatile	Fixed carbon	Ash	C	H	N	O[a]
Palm shell	4.7	73.5	13.2	8.6	52.05	5.37	0.49	42.10
EFB	6.9	79.4	10.8	2.9	43.06	5.98	0.55	50.42
Mesocarp fiber	8.6	78	7.6	5.8	45.03	6.15	0.94	47.89

[a] By difference

In this study, the highest lignin content was observed for the palm shell material. Lignin is known as the most thermally resistant component compare to cellulose and hemicellulose because it possesses a more complex chemical composition; therefore, high-temperature conditions from 280 to 500 °C are necessary to decompose the lignin. Approximately 25-30% of aqueous compounds gained from decomposition of the lignin was composed of methanol, acetic acid, acetone, and water. However, the presence of lignin in biomass favors the production of a high amount of char (Williams & Besler, 1993).

Results of the proximate and ultimate analysis of the untreated biomasses are given in Table 3.1. The proximate analysis gives the fixed carbon, volatile and ash content of the samples. As evident from the results in Table 3.1, all of the samples contained a high concentration of volatiles. This volatiles content was contributed by the degradation of hemicellulose at 200-260 °C contained in the samples (Mohan et al., 2006). The presence of volatiles favors the production of a large amount of bio-oil. Omar et al. have found that a high volatile content provides the advantages of high volatility and reactivity, which is favorable for liquid fuel production (Omar et al., 2011). A higher percentage of fixed carbon in palm shell compared to that in other raw materials is also notable because such a material would result in a product with a higher carbon content after pyrolysis.

Table 3.2: The lignocellulosic contents of palm oil wastes

Type of palm oil wastes	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Palm shell	27.7	21.6	44
EFB	51.2	22.5	21.3
Mesocarp fiber	23.7	30.5	27.3

The ultimate analysis showed that the raw materials of palm shell, EFB, and mesocarp fiber consisted of moderately high contents of carbon and oxygen. The hydrogen content in all the palm oil wastes was low. However, the nitrogen content was found to be the lowest in the palm oil wastes among the analyzed elements.

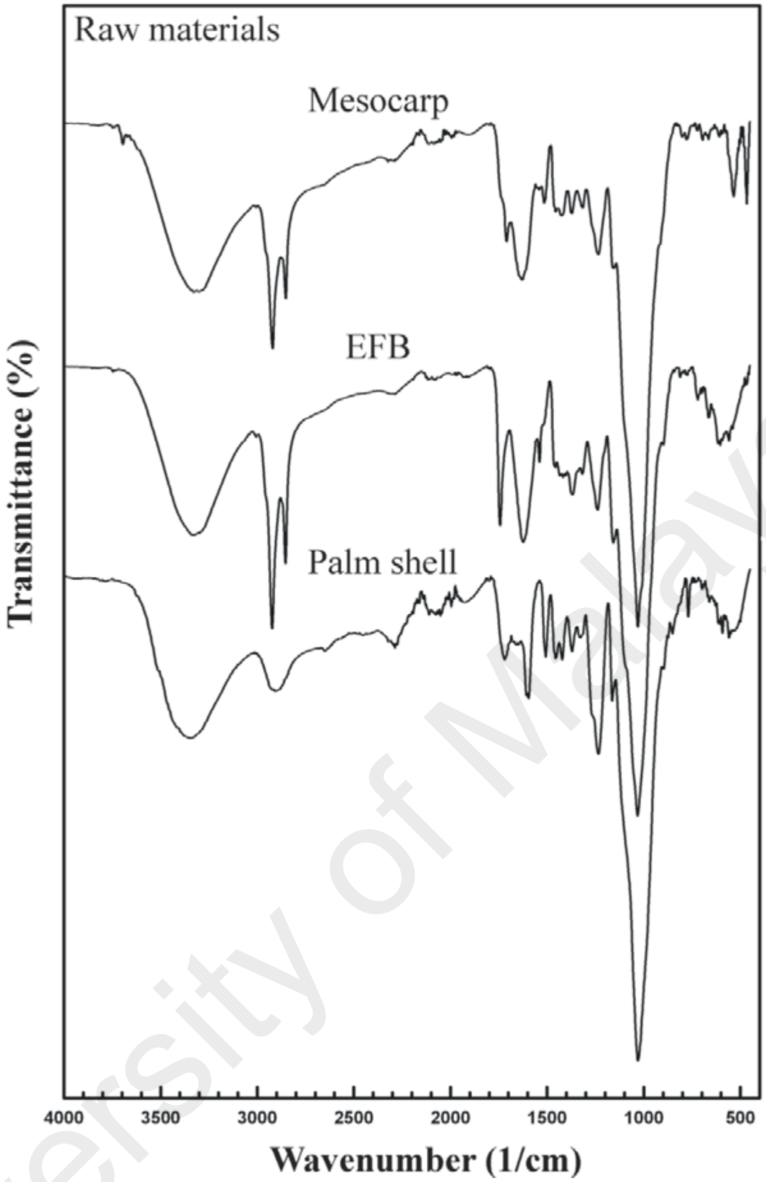


Figure 3.2: FTIR spectra raw materials of palm shell, EFB, and mesocarp fiber

The IR spectra of palm shell, EFB, and mesocarp fiber are shown in Figure 3.2. The typical functional groups and the IR signals are listed in Table 3.3, along with a list of the possible compounds that may be responsible for each signal as a reference (Leng et al., 2011; Yang et al., 2006; Yang et al., 2007). The spectra of both EFB and mesocarp fiber are similar with respect to their shapes and their intensities. The infrared spectra of palm oil shell exhibited weaker IR absorbances compared to those of mesocarp fiber and EFB, which may reflect its lower volatiles content (Yang et al., 2006). This result is in good agreement with the proximate analysis results (Table 3.1).

Table 3.3: The main functional groups of palm shell, EFB, and mesocarp fiber

	Wavenumber (cm^{-1})	**Functional groups**	**Compounds**
1	3600–3100 (s)	O–H stretching vibration	Acid, methanol
	1108 (m)	O–H association	C–OH
	1333 (m)	O–H bending	
	1440–1400 (m)	OH bending	Acid
2	2860–2970 (m)	C–H_n stretching vibration	Alkyl, aliphatic, aromatic
	700–900 (m)	C–H	Aromatic hydrogen
	1402 (m)	C–H bending	
3	1700–1730 (m), 1510–1560 (m)	C=O stretching	Ketone and carbonyl
	1279-1060 (s)	C–O stretching vibration	Phenol
	1232 (s)	C–O–C stretching	Aryl-alkyl ether linkage
	1170 (s), 1082 (s)	C–O–C stretching vibration	Pyranose ring skeletal
4	1632 (w)	C=C	Benzene stretching ring
	1613 (w), 1450 (w)	C=C stretching	Aromatic skeletal mode
5	1470–1430 (m)	O–CH_3	Methoxyl–O–CH_3
	1060 (w)	C–O stretching and C–O deformation	C–O-C (ethers)
	700–400 (w)	C–C stretching	

The most significant band in the spectra in Figure 3.2 occurred at 1060 cm^{-1}; this band, which exhibits the highest IR absorbance, may be due to the presence of ethers (C–O-C). Mesocarp fiber and palm shell showed the highest and the lowest IR adsorption intensities, respectively, at this absorbance value. The high intensities of the bands in the spectra at 1613 cm^{-1} and 1450 cm^{-1} were mentioned by Yang et al. as possibly being due to an aromatic skeletal mode that is significantly intensified by the presence of oxygen-containing polar substitutes (Yang et al., 2006).

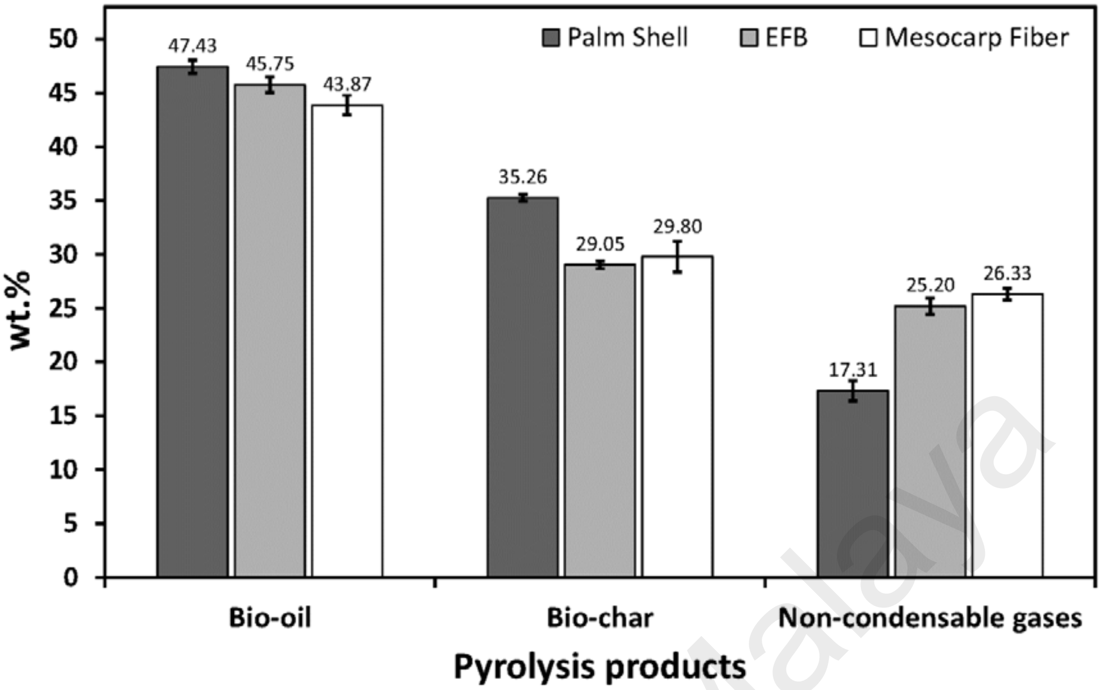


Figure 3.3: Yield of pyrolysis products from different palm oil wastes

3.3.2 Bio-oils

3.3.2.1 Yield of bio-oils

As evident from the results in Figure 3.3, the conversion of raw material through pyrolysis yielded more bio-oil than bio-char or non-condensable gases. The same tendencies were found by Mullen et.al for the fast pyrolysis of two corn residues, corn cobs, and corn stover (Mullen et al., 2010). The high oil yield may be due to the raw materials containing a high fraction of volatiles and low fraction of ash, as shown in Table 3.1. Biomass with low ash fraction favors high oil yields (Bridgwater, 2012), and a high fraction of volatiles also favors a higher oil yield (Asadullah et al., 2008). The yields of bio-oils obtained were approximately 47.43 wt%, 45.75 wt%, and 43.87 wt% for palm shell, EFB, and mesocarp fiber, respectively. In addition, the amount of bottom layer obtained after the centrifugation process was similar for all the samples and was in the range of 3-8 wt% of the total oil.

3.3.2.2 Physicochemical properties of bio-oils

The physicochemical properties of bio-oils produced from several palm oil wastes are presented in Table 3.4. The bio-oils produced in this study were shown to contain a large amount of water. The presence of water in the oil arises from the exothermic dehydration reaction during the initial stage of pyrolysis (100-300 °C). The highest water content of 68% was obtained for bio-oil from mesocarp fiber, and the lowest water content of 41% was obtained for bio-oil from EFB. Similar tendencies have been observed for products from the pyrolysis of pine sawdust and mesquite sawdust (Bertero et al., 2012).

Table 3.4: Physicochemical properties of bio-oils

Type of bio-oils	Properties			
	Water content (wt%)	pH	Density (kg/m^3)	Viscosity at 50 °C (cP)
Palm shell	53	2.5	1051	1.9
EFB	41	3.1	1032	1.7
Mesocarp fiber	68	2.5	1039	1.5

The bio-oils from the pyrolysis of palm oil wastes exhibited low pH values that varied from 2.5-3.1. The low pH values indicated that the oils contain high concentrations of acidic compounds. As described in the literature, a high concentration of acidic compounds may result from the degradation of hemicellulose and lignin during pyrolysis (Sınağ et al., 2011). A low pH in bio-oil causes corrosion in storage and piping systems in fluidization.

Density and viscosity are properties related to the liquid mass flow rate, which significantly affects the performance of fluid atomizers. The densities of the bio-oils were similar and in the range of 1032 to 1051 kg/m^3. The oils are denser than heavy fuel oil, which typically has a density of approximately 855 kg/m^3. All the bio-oils showed similar viscosities in the range of 1.5-1.9 cP when measured at 50 °C. Inconsistent with the results of a previous study (Abnisa et al., 2011), the bio-oil derived from palm shell showed a lower viscosity after centrifugation because the bottom layer was separated from the bio-oil.

The ultimate analysis results of the upper layer of bio-oils are given in Table 3.5. The analyses showed that all of the bio-oils contained high levels of oxygen (greater than 70%). In general, the pyrolysis of biomass results in a high oxygen content in the oil product; however, the oxygen content in the oils investigated in this study were higher than that previously reported in literature. Zheng (2007) studied the production of bio-oil from the fast pyrolysis of rice husk, and the results showed that the oxygen content in the oil was approximately 50.3 wt%. In another study, Zheng (2008) reported that the oxygen content was approximately 47.5 wt% in bio-oil produced from the fast pyrolysis of maize stalk. To investigate the trend of oxygen content in this study, additional ultimate analyses were performed on the bottom layer products. As evident from the results in Table 3.5, the results showed that bottom layer in all of the bio-oils contained less oxygen than did the upper layer. The high level of carbon content in the bottom layer may explain why the oil exhibited a high oxygen content. A similar trend was also observed by Sulaiman and Abdullah (2011), where they found that the bottom layer from fast pyrolysis of EFB contained 69.35 wt% of carbon and 20.02 wt% of oxygen. Mahmood et al. (2012) described that the bottom layer contains the heavy condensable phase, which are mainly tars, and the upper layer is the light condensable phase mainly comprising of water. However, the high oxygen content causes the oils to have a low calorific value.

Table 3.5: Ultimate analysis and HHV results

Type of products	Type of palm oil waste		
	Palm shell	EFB	Mesocarp fiber
Bio-oil (upper layer)			
C (wt%)	15.10	14.97	15.29
H (wt%)	9.08	12.03	10.18
N (wt%)	0.15	0.72	0.54
O^a (wt%)	75.68	72.30	74.01
HHV (MJ/kg)	10.49	14.78	12.18
Bio-char			
C (wt%)	79.40	64.93	67.70
H (wt%)	3.18	2.55	2.43
N (wt%)	0.82	1.12	0.65
O^a (wt%)	16.61	31.41	29.23
HHV (MJ/kg)	28.85	21.34	29.06
Bio-oil (bottom layer)			
C (wt%)	61.15	66.75	58.93
H (wt%)	9.07	9.32	8.67
N (wt%)	1.09	1.71	0.69
O^a (wt%)	28.70	22.23	31.73
HHV (MJ/kg)	29.61	32.6	27.97

Calorific value is an important parameter in the characterization of bio-oil as a fuel. In this study, the calorific values are given in Table 3.5 and are represented by HHV. The HHV of the upper layer products, which was calculated using Eq. 2, were approximately 10.49 MJ/kg, 14.78 MJ/kg, and 12.18 MJ/kg for palm shell, EFB, and mesocarp fiber, respectively. The results were lower than the HHV of bottom layer. The high carbon content detected in the bottom layer products contributed to the elevated HHV values. Nevertheless, the upper layer products have slightly higher hydrogen contents than the bottom layer products. Hydrogen is the most important parameter with respect to elevation of the HHV because it has the highest heating value among known fuels (I. Ali & Basit, 1993).

In this study, a FTIR instrument was used to identify the types of chemical bonds (functional groups) in the upper layer of bio-oils. The FTIR spectra of the bio-oils obtained from the pyrolysis of palm oil wastes are shown in Figure 3.4a. The wavelengths of the absorbed light indicated that the characteristics of the chemical bonds in the different bio-oils were similar. For all the bio-oils, the strong absorption bands observed between 3200 and 3600 cm^{-1} (characteristic of O-H stretching) indicate the presence of phenols and alcohols. The absorption bands between 1650 and 1750 cm^{-1}, which are related to C=O stretching, indicate the presence of ketones, carboxylic acids, and aldehydes. The –C–H bending vibrations between 1350 and 1480 cm^{-1} that indicate the presence of alkanes were observed for all of the bio-oils. The presence of acid compounds was indicated by the observation of absorptions due to C–O stretching within the range of 1210 to 1320 cm^{-1}. The bands between 970 and 1250 cm^{-1}, which are assigned to the C–O stretching of alcohols and phenols, were detected in all of the oils. Finally, the presence of aromatic compounds in the bio-oils was indicated by absorption bands between 650 and 900 cm^{-1}.

3.3.3 Bio-chars

3.3.3.1 Yield of bio-chars

Palm shell and mesocarp fiber were identified as biomass wastes that produced greater amounts of bio-char (35.26 wt% and 29.80 wt%, respectively) compared with the pyrolysis of EFB, which produced 29.05 wt% bio-char. The weight loss or yield of bio-char may be attributed to either a more extensive primary decomposition of the raw material at higher temperatures or to secondary decomposition of the solid product; as a result of these processes, the pyrolysis conversion was increased (Şensöz & Kaynar, 2006; Williams & Nugranad, 2000; Williams & Reed, 2003). Additionally, a great difference in the pyrolysis behavior among the three main components of biomass (cellulose, hemicelluloses and lignin) plays an important role in the bio-char yield (Yang et al., 2007). Yang et al. (2007) have reported that cellulose, hemicelluloses and lignin exhibit the highest to the lowest decomposition rates, respectively, in the pyrolysis process. When the temperature is increased to more than 400 °C, almost all of the cellulose will be pyrolyzed with a very small amount of solid residue. According to the lignocellulosic contents of palm oil wastes (Table 3.2), the EFB contains the greatest amount of cellulose among the investigated biomasses. Therefore, the low production yield of EFB bio-char can be attributed to the high cellulose content of raw EFB. However, mesocarp fiber contains a large amount of hemicelluloses compared to the other studied biomasses, especially palm shell. The higher hemicellulose content of mesocarp fiber makes the yield of these bio-chars lower than that of palm shell bio-char. Finally, palm shell, which contains low levels of cellulose and hemicelluloses and a high level of lignin, shows the highest yield of bio-char because, among the three components, lignin is the most difficult to decompose.

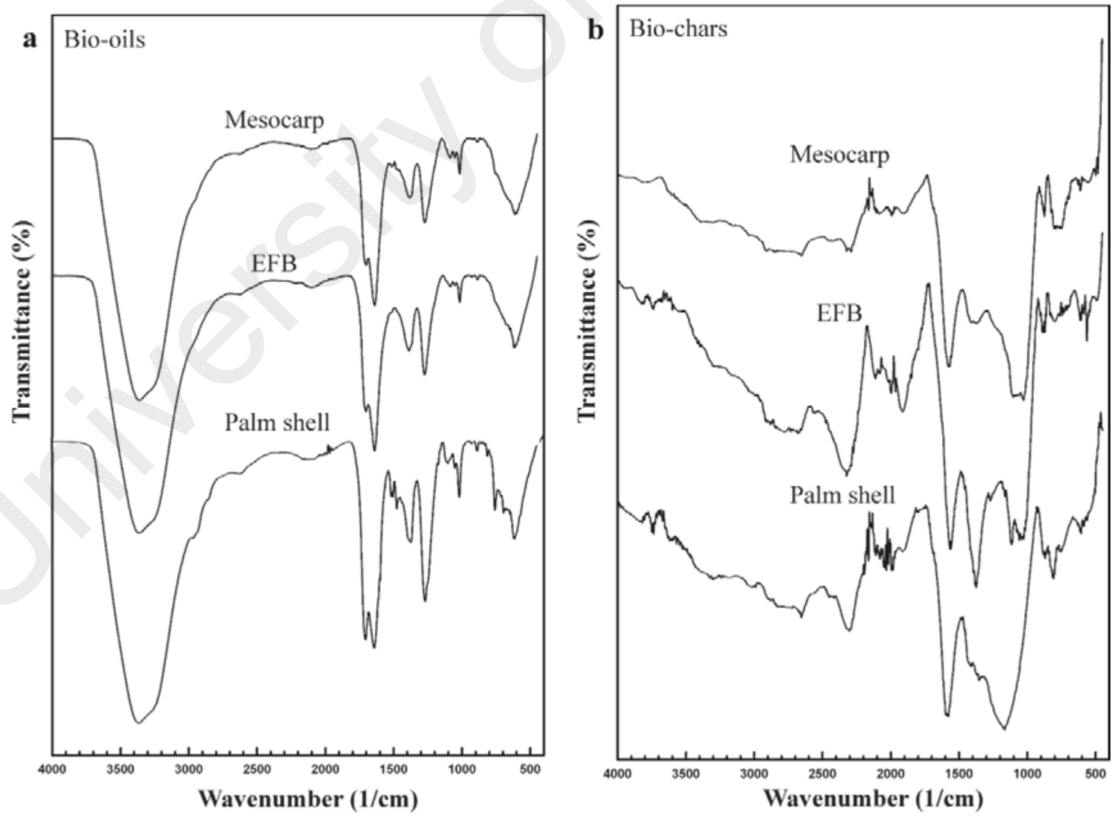


Figure 3.4: FTIR spectra of (a) bio-oils obtained from pyrolysis of palm oil wastes and (b) bio-chars obtained from pyrolysis of palm oil wastes

As evident from the results in Table 3.1, EFB shows the highest volatile percentage compare with the other two biomasses. Although, mesocarp fiber (Table 3.6) shows the highest volatile value after pyrolysis, the high volatiles (40%) and ash contents of EFB (12%) may be responsible for its high yield compared to that of mesocarp fiber. A comparison of the proximate analysis of biomasses and their chars (see Tables 3.1 & 3.6), shows that palm shell exhibited the highest reduction of volatiles (from 73.5% to 18%) during pyrolysis among the investigated biomasses, which is in accordance with its lowest yield percentage among the bio-chars. The high fixed carbon and very low ash contents of palm shell indicate that this bio-char is suitable for use in the production of adsorbents, such as activated carbon.

Table 3.6: Proximate analysis of bio-chars

Type of bio-chars	Moisture (wt%)	Volatile (wt%)	Fixed carbon (wt%)	Ash (wt%)
Palm shell	6.5	18	72.5	2
EFB	5.4	40.1	41.7	12.8
Mesocarp fiber	12.1	52	30.6	4.3

From this study, mesocarp fiber was identified as the waste that produced the highest amount of gas (26.33 wt %) among the investigated biomasses. The high yield of gas can be attributed to a high content of hemicellulose in the mesocarp fiber. This finding is in accordance with that reported in the literature (Prabir, 2010).

3.3.3.2 Physicochemical properties of bio-chars

The infrared spectra of the carbonaceous materials are shown in Figure 3.4b. Although the spectra of biomass chars are almost similar in shape and in intensity, different oxygen-containing surface groups (C=O, C–O, –OH) and other groups (olefins, –CH_2, –CH_3, aromatic rings) differentiate them from the infrared spectra of the raw materials.

The intensity of the band attributed to carboxyl groups at 1718 cm^{-1} decreased, which is attributed to the degradation of cellulose components during the conversion of biomass into char. Yang et al. suggested that the decrease in intensity of the OH absorbance may be due to the dehydration of biomass combined with the release of a large amount of water (Yang et al., 2006). A decrease in the intensity of the band associated with alkene (C-H) groups in all three biomasses can be explained by the breaking of the weak bonds between C and H of the alkyl groups, which results in an increase in the CH_4 and C_2 hydrocarbon content in the gaseous products.

A comparison of the FTIR spectral data reveals that the intensity of the C≡C (alkynes) absorbance (2313-2330 cm^{-1}) increased in carbonaceous chars, possibly because of dehydrogenation. In addition, the intensities of the bands at 1586.33–1571.62 cm^{-1} and 877.04–779.19 cm^{-1} for aromatic C=C and adjacent H deformation were significantly higher for the chars than for the raw materials, which indicated the cracking of volatiles and the conversion of aliphatic compounds into aromatic compounds in the char. This conversion can be attributed to the substantial decrease in the intensities of the OH and CH alkyl peaks (Yang et al., 2006).

The char produced from palm shell, EFB and mesocarp fiber have similar chemical groups; however, the spectrum of the EFB char shows a higher concentration of OH groups (greater intensity of the band at 1374.94 cm^{-1}) and a lower concentration of aromatic C=C (decreased intensity in the bands at 877.04–779.19 cm^{-1}) compared to the two other bio-chars. These results are attributed to the higher level of oxygen in EFB bio-char as a result of the higher level of volatiles in EFB (Table 3.1). The FTIR spectral data indicate that the char produced from mesocarp fiber exhibit a decreased IR absorbance at 2313-2330 cm^{-1} (C≡C) compared to the spectra of the two other bio-chars.

Due to the various thermal cracking of organic functional groups on the surface of the mentioned palm oil wastes and evolution of volatiles, changes in the elemental composition (C, H, O and N) of the bio-chars are expectable. A CHN/O analyzer was used to study the chemical composition (C, H, O and N) of the bio-chars, and the results are listed in Table 3.5. Carbon, as the main element in all of the produced bio-chars (65-80 wt%), is present in significantly greater amounts in the bio-chars than in the dried biomasses (see Table 3.1). In accordance with the FTIR results (Figures 3.2 and 3.4b), the O and H contents significantly decreased, especially in palm shell, because of the dehydration and decarbonylation/decarboxylation reactions. In the next step of pyrolysis, the aromatization of the bio-char led to the evolution of H_2 and to the formation of light molecular hydrocarbons (CH_4 and C_2); thus, the H content in the bio-chars decreased (Yang et al., 2007).

In addition to their use as soil amendments or in production of porous adsorbents, such as activated carbon, an alternative use for the produced bio-chars is as a renewable solid fuel. The HHV values for bio-chars from palm wastes (Table 3.5) were 28.85 MJ/ kg, 21.34 and 29.06 MJ/kg, respectively for palm shell, EFB, and mesocarp fiber. These values are comparable to those of some coals (Akkaya, 2009; Bilgen & Kaygusuz, 2008). The nitrogen levels in the bio-char were between 0.5–1.5%, which is important information for predicting the NO_x emissions from combustion of the bio-chars.

Figures 3.5a, 3.5c, and 3.5e show the scanning electron microscopy (SEM) images of palm shell, EFB, and mesocarp fiber, respectively. A comparison of the SEM micrographs of the raw biomasses and bio-chars allows interesting conclusions to be drawn about morphological changes after the devolatilization step. As evident from these figures, few pores were present on the surface of the precursors. However, after carbonization, the creation of some pores is evidenced in Figures 3.5b, 3.5d and 3.5f, which display images of the bio-chars of palm shell, EFB, and mesocarp fiber, respectively. These SEM micrographs show that residual palm oil wastes porosity and morphology remain in the bio-chars, so it can be said that the short heating time of the pyrolysis process has not totally destroyed the original palm shell, EFB, and mesocarp fiber cell morphological structure originally present. Instead, chemical decomposition has occurred with loss of water and organic fragments which reduces the total mass.

3.4 Conclusion

The results of analysis of the lignocellulosic contents of palm oil wastes showed that palm shell has a high content of lignin (44%), that EFB has a high content of cellulose (51.2%), and that mesocarp fiber has a high content of hemicellulose (30.5%). The volatiles contents of all the palm oil wastes were high, which is favorable to produce more bio-oil. The experimental data showed that more than 40 wt% of palm oil wastes can be converted into bio-oil through the pyrolysis process under the following conditions: a temperature of 500 ºC, a nitrogen flow rate of 2 L/min and reaction time of 60 min. All of the bio-oils contained high levels of oxygen (greater than 70 wt%). The compounds identified in all of the bio-oils by FTIR analyses include phenols, alcohols, ketones, carboxylic acids, aldehydes, alkanes, and aromatic compounds.

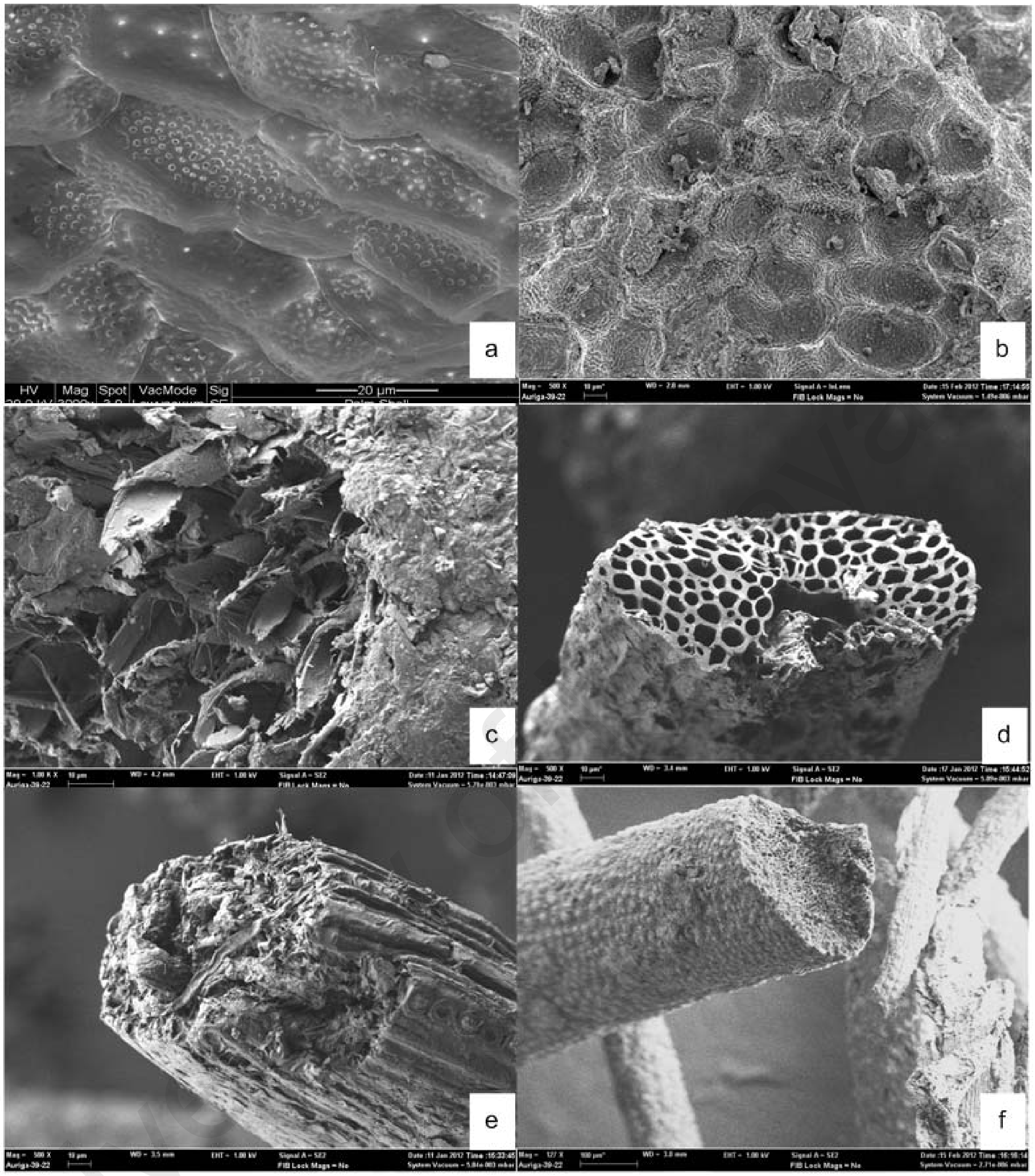


Figure 3.5: SEM photographs of (a) palm shell, (b) palm shell bio-char, (c) EFB, (d) EFB bio-char, (e) mesocarp fiber, and (f) mesocarp fiber bio-char

Palm shell and mesocarp fiber were identified as biomass wastes that produced higher amounts of bio-char compared to the pyrolysis of EFB waste. A significant difference between the pyrolysis behaviors of the three main components of biomass (cellulose, hemicelluloses and lignin) was observed to play an important role in the bio-char yield. Therefore, palm shell, which contains the greatest amount of lignin, exhibited the highest yield of bio-char because, among the three components, lignin is the most difficult to decompose. The infrared spectra of the biomass chars were similar in shape and in intensity, whereas different oxygen-containing surface groups (C=O, C–O, –OH) and other groups (olefins, $–CH_2$, $–CH_3$, aromatic rings) differentiated the spectra of the chars from those of the raw materials. The HHV values of bio-chars from palm wastes were 28.85 MJ/kg, 21.34 MJ/kg and 29.06 MJ/kg, respectively, for palm shell, EFB, and mesocarp fiber. These values are comparable to those of some coals.

Based on this study, we recommend that pyrolysis is a valid technique that can increase the value of palm oil wastes by producing bio-oil and bio-char. The oil can be used as a fuel in several applications to generate heat energy, and the EFB is the best material for this purpose since it has high calorific value. As a byproduct from pyrolysis, the produced mesocarp fiber based bio-char has the highest calorific value and it potentially can be used for any application that uses coal. Besides, it also can be noted that the utilization of palm oil waste as bioenergy is able to enhance the energy security in Malaysia.

CHAPTER IV

UTILIZATION OF OIL PALM TREE RESIDUES TO PRODUCE BIO-OIL AND BIO-CHAR VIA PYROLYSIS

4.1 Introduction

Malaysia is a tropical and humid country located in the central part of Southeast Asia with a total landmass of 329,847 km^2. Approximately 24% of the nation's landmass is used by the agricultural sector, which means the land is categorized as arable, under permanent crops, and under permanent pastures (World Bank, 2012). Most of the land is planted with oil palm. The expansion of oil palm plantations has occurred each year over the last three decades at a real growth rate of 0.36% per year (Department of statistics Malaysia, 2011). In 2010, it is estimated that approximately 48,537 km^2 (4,853,766 hectares), or 14.72% of the total landmass, was used for oil palm plantations (Department of statistics Malaysia, 2011), with approximately 135 - 145 trees planted per hectare (Asma et al. 2010). Each of the trees produces approximately 10% of palm oil, while the remaining 90% is biomass residue (Hon & Joseph, 2010). The different types of residues are produced by the mill and plantation activities. The palm kernel shells (PKS), mesocarp fibers (MF), and empty fruit bunches (EFB) are the main residues produced during the milling process, while the fronds and trunks are the major residues obtained from the plantation during felling. The fronds are also obtained during harvesting and pruning. The sources and types of residues are shown in Table 4.1. The volume and type of oil palm residues are expected to rapidly increase and will become a serious problem in the future.

Currently, the residues of the oil palm are the main contributors to biomass waste in Malaysia, and these wastes require extra attention with respect to handling. A survey of the literature indicates that most of them are handled with unsatisfactory practices that negatively impact the environment. Most of the residues from the plantations are incinerated or dumped as organic fertilizer to decompose naturally, and only 40% of the trunks are used in plywood manufacturing (Asma et al.). In palm oil mills, the PKS, EFB, and MF residues are generally sent to the boiler to be burned as fuel for steam generation (Mahlia et al., 2001). Although burning the residues as fuel reduces the diesel consumption, this approach is not an environmentally friendly approach because it produces smoke and dust emissions due to incomplete combustion.

Table 4.1: Sources and types of oil palm residues

Source of residue	Type of residue	Weight of the total source (%)	Quantity per hectare (ton/ha)
Fresh fruit bunch (from palm oil mill)	Palm kernel shell	5.5	1.10
	Empty fruit bunch	22	4.42
	Mesocarp fiber	13.5	2.71
Oil palm tree at felling (from plantation)	Trunk[a]	70	41.07
	Frond	20.5	16
	Leaf	6.53	7.69
	Other	2.97	19.44
Oil palm tree at pruning (from plantation)	Frond[b]	27.03	10.40

[a] Palm trunks felled once every 25-30 years.
[b] Consists of the leaf and measured in dry weight.

The abundant amount of biomass residue from oil palm can potentially be used as a renewable energy source through conversion into other energy products such as biofuel. The use of biomass in other forms of energy products is more beneficial than the direct burning of biomass because it releases many pollutants into the air. One potential technique for alleviating these environmental concerns is to convert oil palm residues into bio-oil and bio-char via pyrolysis. According to the literature, pyrolysis has been recommended as an environmentally friendly method because no wastes are produced during the process. Pyrolysis is the thermal decomposition of organic material at elevated temperatures in an inert environment, and the products of this process include bio-oil, bio-char, and syngas.

Bio-oil is the main product from pyrolysis because it is typically obtained in higher yields than the other products. The oil is formed from vapor condensation (Zheng & Kong, 2010), and for biomass pyrolysis, the vapors are generally released at a temperature of 400-500 °C (Gerçel, 2011; Yang et al., 2006). The oil obtained from the condensation process is dark brown in color and free-flowing and also has a strong acrid smell. Some advantages of bio-oil include ease of storage and transportation and use in the production of renewable energy and chemical feedstocks. According to Zheng, the energy density of bio-oil is four to five times higher than that of the original precursor, which offers important logistical advantages (Zheng, 2008). For chemical applications, the oil can be used to produce useful chemicals by taking advantage of its most abundant functional groups, such as carbonyl, carboxyl, and phenolic groups, through reaction or separation techniques (Czernik & Bridgwater, 2004; Žilnik & Jazbinšek, 2012).

In addition to liquid fuel, the stored solar energy of biomass can be converted into solid and gaseous fuels with high calorific values through pyrolysis and used for industrial combustion purposes (Lim & Alimuddin, 2008). The produced bio-char can be used as a highly efficient fuel in boilers either alone or as a mixture with biomass. In our previous study, we have shown that the bio-chars produced from the pyrolysis of palm oil wastes have high heating values of approximately 20-30 MJ/kg, which is comparable to those of some coals (Abnisa et al., 2013a). This value-added product is beneficial for soil amendment and prevents water contamination and soil erosion. Due to the high adsorption capacity of bio-char, it can adsorb moisture and nutrients and slowly release them to soil (Laird, 2008; Mullen et al., 2010). Bio-char can be used as a stable, renewable and inexpensive catalyst for biogas reforming and the conversion of greenhouse gases (CO_2 and CH_4) to value-added products (Domínguez et al., 2007; Dufour et al., 2008; Muradov et al., 2012). Another application of bio-char is its use as an adsorbent in water treatment to remove heavy metals such as lead, cadmium, arsenic and chromium (Mohan et al., 2007; Mohan et al., 2011).

In the present work, the oil palm residues were characterized and then pyrolyzed in a fixed-bed reactor. The scope of this paper is limited only to residues from plantation activities, while the residues from mill activities were discussed previously (Abnisa et al., 2013a). All of the experiments were conducted at the same pyrolysis conditions to obtain the yields of bio-oil and bio-char. Furthermore, the chemical and physical properties of the products were characterized using several laboratory techniques.

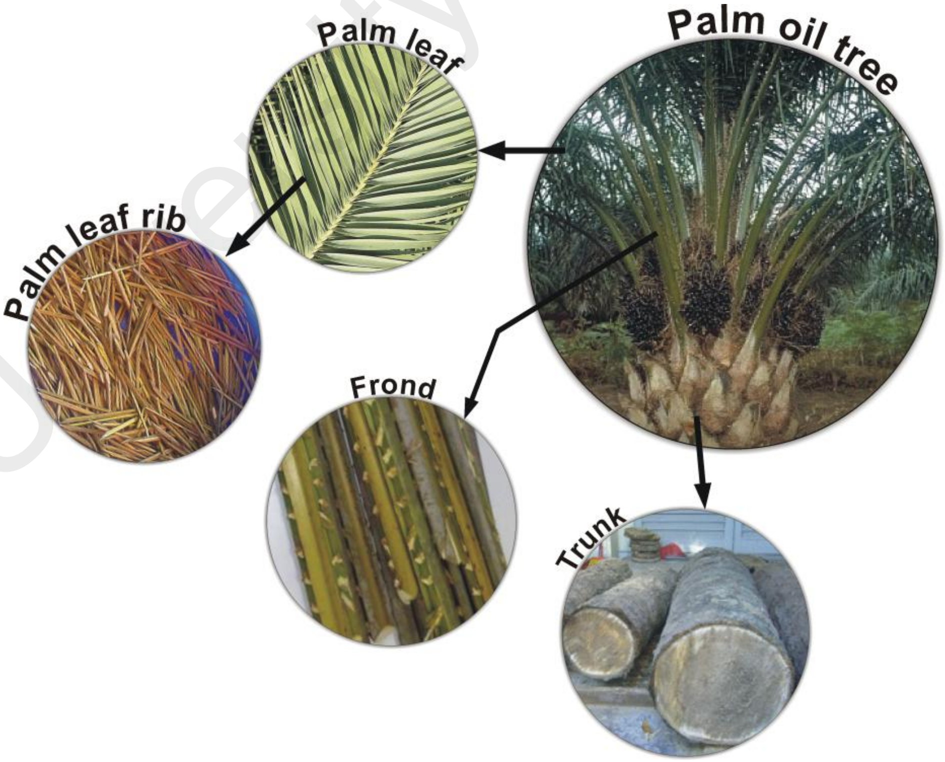


Figure 4.1: The residues generated from oil palm trees

4.2 Materials and methods

4.2.1 Raw materials

The oil palm wastes were obtained from Sime Darby Plantation in Selangor Dahrul Ehsan, Malaysia. The waste was separated into four samples categorized as trunk, frond, palm leaf, and palm leaf rib. Figure 4.1 shows the wastes generated from oil palm trees. The samples were initially treated by washing and subsequent drying in the sun for one day. The dried samples were ground and screened to obtain particle sizes that ranged from 1.0 to 2.0 mm. Prior to use in the experiments, the samples were dried again in an oven at 105 °C for 24 hours to remove the moisture.

4.2.2 Pyrolysis experiments

Approximately 200 g of the sample was placed in a stainless steel reactor with a length of 127 cm and an internal diameter of 2.5 cm. The fixed-bed reactor was selected in this study because it is relatively inexpensive, simple, and reliable (Bridgwater, 2003). An electric furnace was used to heat the reactor, and the temperature was monitored using a K-type thermocouple placed inside the reactor. A detailed design of the pyrolysis apparatus is shown schematically in Figure 4.2. Nitrogen gas (N_2) was used as an inert gas to purge air from inside the reactor. Moreover, N_2 was also employed to sweep the vapor products from the reactor into the condensation traps. The purging with N_2 was performed throughout the entyre procedure. The condensable products, specifically the bio-oils, were collected in a series of condensers and stored at 0.5 °C. They were subsequently weighed to obtain the mass of bio-oil. The bio-char was collected from the inside of the reactor and weighed. The final yields of bio-oil and bio-char were calculated using the equations below:

$$Y_{OP} = \frac{X_1}{X_2} \times 100\% \qquad (4.1)$$

where Y_{OP} is the product yield, X_1 is the mass of the desired product, and X_2 is the initial mass of the raw material. The gas yield was determined by difference: gas yield = 100 – (bio-oil yield + bio-char yield).

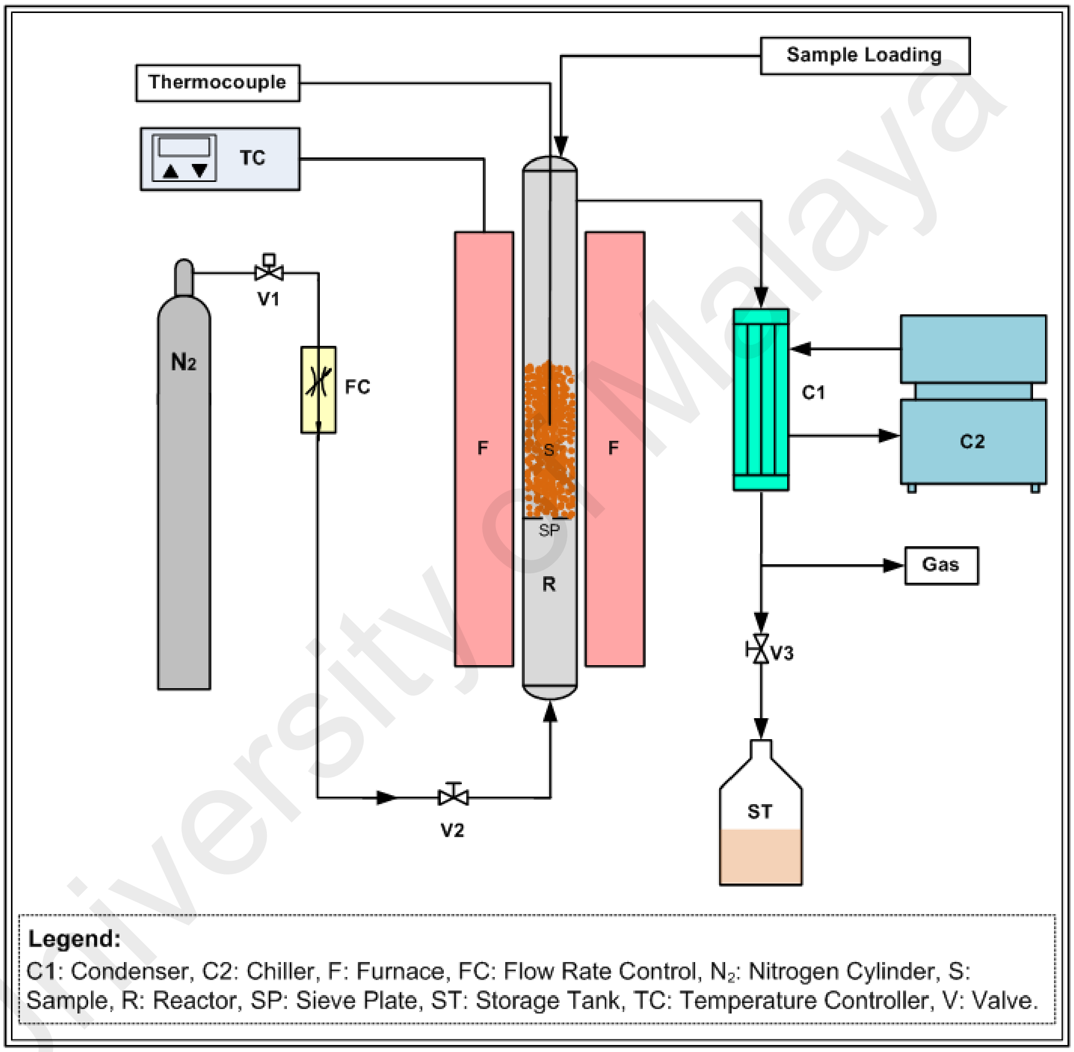


Figure 4.2: Schematic diagram of experimental setup

In this study, the same parameters were employed for all of the experiments. Pyrolysis parameters were selected according to literature studies (Bridgwater, 1999; Yang et al., 2006) and the results from our previous study (Abnisa et al., 2011). The experiments were conducted using a pyrolysis temperature of 500 °C, a particle size of 1 - 2 mm, a reaction time of 60 min, and an N_2 flow rate of 2 L/min. The heating rate was 10 °C/min. To validate the experimental data, each experiment was repeated with 3 - 5 replicates, and the average result was used as the final yield. The reactor, condenser, and piping system were sterilized between each set of experiments to avoid contamination of the samples.

4.2.3 Characterization

Prior to characterization, all feedstock were dried in an oven at a temperature of 105 °C for 24 hours. The pyrolysis products from the experiments were collected in three different groups, bio-oil, bio-char, and syngas. Bio-oil and bio-char were collected and weighted directly after the production process and the amount of non-condensable gases were calculated by mass balance in the system. Before analysis, the bio-oil was separated into two fractions by a centrifugation process based on a procedure developed by Bertero et al. (2012). The process entailed centrifugation at 3200 rpm for 8 min, and the fractions after centrifugation are referred to as upper-layer bio-oil and bottom-layer bio-oil. In addition, in order to reduce the margin of error and to produce more reliable data, the analysis of each product from all experiments was repeated three times, and the results were averaged.

4.2.3.1 Physical characterization

The viscosity of the bio-oil was determined using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer made in USA, model DV-II+Pro EXTRA). The measurement, which required approximately 7 mL of the sample, was taken at 50 ºC. A 25 mL pycnometer was used to determine the density of the bio-oil. The measurement was performed by carefully filling the pycnometer with the oil and then measuring the mass. The density was determined by dividing the mass of the bio-oil by the empty volume of the pycnometer. The analysis was conducted at 24 ºC. Scanning electron microscopy (SEM) experiments were conducted to study the physical morphology of the surfaces. A JSM-6390LV (JEOL, Japan) operating at a 3 kV accelerating voltage was used to characterize the morphology of the precursor and the bio-chars, which were dried overnight at approximately 105 °C under vacuum before SEM analysis. No conductive coating was applied to prepare the samples for SEM.

4.2.3.2 Chemical characterization

A Metrohm 827 pH meter (Switzerland) was used to analyze the pH of the bio-oils, and the measurements were performed at room temperature. The water content of the bio-oil was measured using a Karl Fischer 737 KF coulometer from Metrohm. Approximately 80 mL of Hydranal-Coulomat AG was used as the anolyte reagent, and 5 mL of Hydranal-Coulomat CG was used as the catholyte reagent. Approximately 2 - 6 mg of the pyrolytic liquid was injected through a titration cell into a flask.

The proximate analysis of both the precursors and the products were conducted according to ASTM D 7582-10 using thermal gravimetric analysis (TGA), and the results were expressed in terms of moisture, volatile matter, fixed-carbon and ash contents. The ultimate analysis was performed using a Model 2400 Series II CHNO/S analyzer (Perkin-Elmer, USA) to determine the C, H, and N contents. A CHN combustion tube and reduction tube were used for this measurement. As reported in literature (Abnisa et al., 2011; Sulaiman & Abdullah, 2011), oil palm wastes have very low sulfur content (around 0.1 wt%), thus, the value of it was not determined in this study. The oxygen content was determined by difference as following: O = 100 – (C+H+N). The lignocellulosic contents of oil palm residues were determined using a method developed by Omar et al. (2011). In this method, three different analyses, namely acid detergent fiber (ADF), neutral detergent fiber (NDF), and acid detergent lignin (ADL), were performed. The final ADF, NDF, and ADL values were then used to calculate the percentage of cellulose, hemicellulose and lignin using the equations below (Omar et al., 2011):

$$\text{Cellulose (\%)} = \text{ADF} - \text{ADL} \tag{4.2}$$

$$\text{Hemicellulose (\%)} = \text{NDF} - \text{ADF} \tag{4.3}$$

$$\text{Lignin (\%)} = \text{ADL} \tag{4.4}$$

The data obtained from the ultimate analysis were also used to calculate the high heating value (HHV). Eq. (4.5) was used to calculate the HHV because the oxygen content in the precursors and the products was found to be greater than 15% (Buckley, 1991).

$$\text{HHV(MJ/kg)} = 0.336\text{C} + 1.418\text{H} - \left(0.153 - 0.000720\text{O}\right)\text{O} + 0.0941\text{S} \tag{4.5}$$

To analyze the functional group compositions of the raw materials, bio-oils, and bio-chars, a FTIR spectrometer (Spectrum 400, Perkin-Elmer, USA) was used to collect the infrared (IR) spectra of the samples. The samples were scanned over the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. For the FTIR analysis, the raw materials and bio-chars were prepared using the following method. The sample (0.1 g) was mixed with 1 g of spectroscopy grade KBr in a porcelain mortar. The mixed sample was converted into a solid disc, which was placed in an oven at 105 °C for 4 hours to avoid any interference with any existing water vapor or carbon dioxide molecules. A solid disc of pure KBr was used as a reference sample for background measurements.

Table 4.2: The lignocellulosic contents of oil palm tree residues

Type of oil palm wastes	ADF	NDF	ADL	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Trunk	70.33	94.27	35.89	34.44	23.94	35.89
Frond	72.03	95.21	21.7	50.33	23.18	21.7
Palm leaf	58.49	81.46	26	32.49	22.97	26
Palm leaf rib	75.41	98.58	29.31	46.1	23.17	29.31

4.3 Results and discussion

4.3.1 Characterization of the feedstock

The major components of the residues include cellulose, hemicellulose, and lignin; therefore, the thermal effect of the decomposition of these components plays an important role in the pyrolysis process to produce bio-oil and bio-char. Table 4.2 shows the lignocellulosic contents of the trunk, frond, palm leaf, and palm leaf rib, which were analyzed using the ADF, NDF, and ADL approaches. The three components decomposed at different rates and within distinct temperature ranges during the pyrolysis. According to Ishak et al. (2012), hemicellulose decomposes first, and the decomposition of cellulose and then lignin follows. These phases were identified as the temperature increased during the pyrolysis. The hemicellulose usually starts to decompose near 220 °C, and the process is mostly complete by the time the temperature reaches 315 °C (Yang et al., 2007). When hemicellulose had completely decomposed, cellulose then undergoes decomposition, which normally starts at a temperature of 315 °C and is completed at 400 °C. This temperature range can also be assigned to the second phase of the lignocellulosic decomposition. In this study, the frond had the highest cellulose content, while the trunk had the highest hemicellulose content. Both the cellulose and hemicellulose contributed significantly to the bio-oil yield (Akhtar & Amin, 2012).

The thermal behavior of lignin was found to be considerably different than that of hemicellulose or cellulose. Naturally, lignin has a more complex chemical composition; therefore, high-temperature conditions are necessary to decompose the lignin. The decomposition of lignin occurred slowly, starting at ambient temperature and proceeding up to a temperature of 900 °C (Yang et al., 2007). In agreement with the literature, the lignin is responsible for the major portion of the bio-char product (Akhtar & Amin, 2012; Zabaniotou et al., 2008). According to the results listed in Table 4.2, the trunk material had the highest lignin content in this study.

The proximate and ultimate analysis results for the different residues of oil palm waste are presented in Table 4.3. In this study, the proximate analysis has been used to quantify the relative proportions of moisture, volatiles, fixed carbon and ash in all the residues. The moisture content, which can be easily removed by drying the residue at a temperature of 105 °C overnight in an oven, was observed to be the highest for the frond residue. The percentage of volatile matter was found to be high for the frond and trunk, while the palm leaf and palm leaf rib were observed to have lower amounts. In contrast to the results for the volatile matter, the trunk and frond contained lower amounts of fixed carbon, 4.97 wt% and 3.22 wt%, respectively, than the palm leaf (11.92 wt%) and palm leaf rib (11.79 wt%). During pyrolysis, the presence of volatiles favors the production of a large amount of bio-oil. According to Omar et al. (2011), the high volatiles content results in high volatility and reactivity, which are favorable for liquid fuel production. The temperature and heating rate significantly affected the volatile matter yield (Guldogan, 2000). In addition, ash also plays an important role in determining the proportions of the products of biomass pyrolysis. An increase in the ash content contributes to a decrease in the bio-oil yield, and as consequence, the bio-char and non-condensable gases are produced in higher yields (Venderbosch & Prins, 2010b). The effect of ash was clearly observed for the palm leaf, which had higher product yields of bio-char and non-condensable gases than that of bio-oil.

Table 4.3: Proximate and ultimate analyses of oil palm tree residues

Type of palm oil wastes	Proximate analysis (wt%)				Ultimate analysis (wt%)			
	Moisture	Volatiles	Fixed carbon	Ash	C	H	N	O[a]
Trunk	7.16	82.60	4.97	5.27	42.72	5.61	0.44	51.24
Frond	13.84	82.70	3.22	0.24	42.76	5.99	0.39	50.88
Palm leaf	9.00	66.76	11.92	12.32	40.40	5.58	1.94	52.09
Palm leaf rib	8.01	75.94	11.79	4.26	43.76	6.30	0.38	49.57

[a] By difference

As listed in Table 4.3, the results from the ultimate analysis showed that all the materials contain similar amounts of C, H, N, and O. The C, H, N, and O contents of the oil palm residues varied as follows: carbon 40.40 - 43.76 wt%, hydrogen 5.58 - 6.30 wt%, nitrogen 0.38 - 1.94 wt%, and oxygen 49.57 - 52.09 wt%. The oxygen content was found to be higher than the C, H, and N contents of the oil palm residues, and the palm leaf has been confirmed to have the highest oxygen content of all the materials.

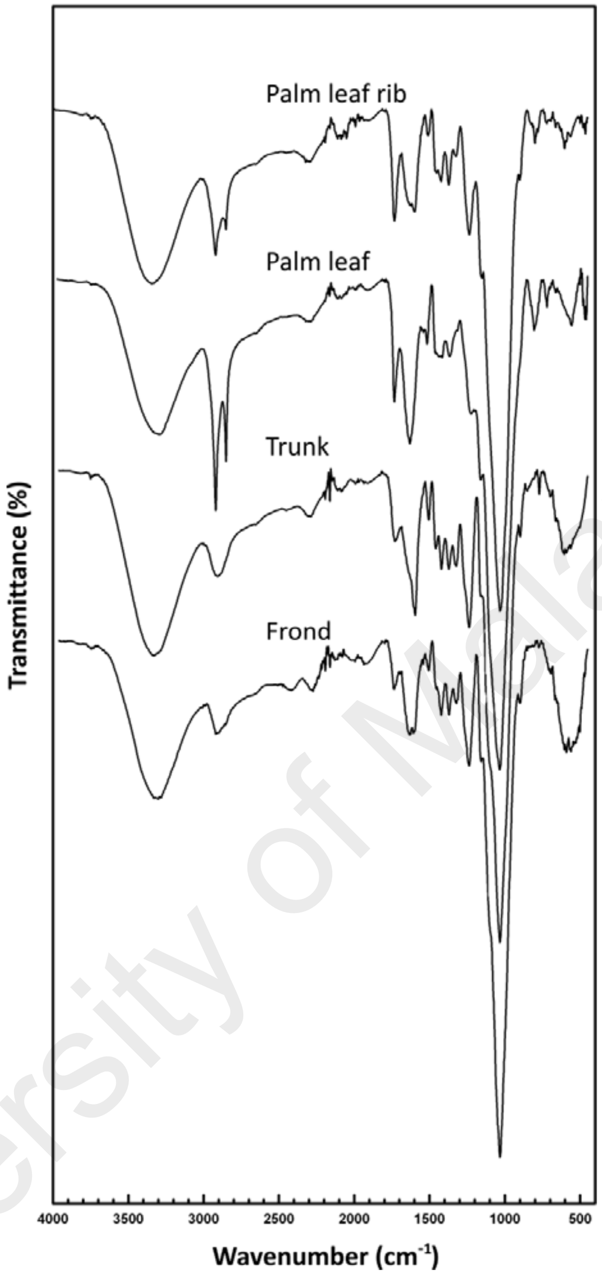


Figure 4.3: FTIR spectra of oil palm residues

The infrared spectra of the raw materials are presented in Figure 4.3. Various bands in the spectra were identified, including 1) O-H stretching vibrations at 3600-3100, 1333, and 1108 cm^{-1} and O-H bending at 1440-1400 cm^{-1} from acid and methanol compounds; 2) aromatic CH$_n$ vibrations at 2970-2860, 1402, and 900-700 cm^{-1}; 3) C=O stretching at 1730-1700 and 1560-1510 cm^{-1}, C-O stretching at 1279-1060 cm^{-1}, aryl-alkyl ether linkage (1232 cm^{-1}) and pyranose ring skeletal C-O-C stretching (1170 and 1082 cm^{-1});

4) benzene stretching of the ring C=C at 4632 cm^{-1} and aromatic C=C at 1613 and 1450 cm^{-1}; 5) other groups such as C-O stretching at 1060 cm^{-1} and C-C stretching at 700-400 cm^{-1} (Omar et al., 2011; Yang et al., 2006; Yang et al., 2007). The spectra of all the biomasses have similar shapes and intensities, although there are some small differences in their spectra. Just as for palm oil wastes, these biomasses also exhibit a significant IR absorbance at 1060 cm^{-1}, which might result from the presence of ethanol in their structures (Abnisa et al., 2013a).

4.3.2 Bio-oil

4.3.2.1 Bio-oil yield

The results for the pyrolysis products listed in Table 4.4 show that the non-condensable gases are found in higher quantities than the bio-oils in the palm leaf and palm leaf rib. The lower oil yield is due to high ash content in the raw materials as shown in Table 4.3. The same trend also can be observed in the work published by Fahmi et al. (2008). They recognized that the presence of ash (alkali metals) decreases the yield of organic liquids and tends to increase char and gas yields. Moreover, the volatile matter also significantly affects the proportion of the bio-oil product. Asadullah et al. (2008) noted that the volatile matter is usually converted to bio-oil upon condensation. Thus, it can be assumed that the smaller amount of volatile matter found in the palm leaf and palm leaf rib is responsible for the decrease in the amount of bio-oils. The smallest amount of bio-oil obtained was approximately 16.58 wt% for the palm leaf, which was composed of 66.76 wt% volatile matter and 12.32 wt% ash content.

Table 4.4: Product distributions from the pyrolysis of oil palm tree residues at a temperature of 500 °C, a particle size of 1 - 2 mm, a reaction time of 60 min, and an N_2 flow rate of 2 L/min

Type of oil palm wastes	Pyrolysis products (wt%)		
	Bio-oil	Biochar	Non-condensable gases[a]
Trunk	40.87	33.60	25.53
Frond	43.50	30.24	26.26
Palm leaf	16.58	36.75	46.67
Palm leaf rib	29.02	28.63	42.35

[a] By difference

The lignocellulosic nature of biomass is an important factor that affects the bio-oil yield. As shown in Table 4.4, a high oil yield was only observed for the trunk (40.87 wt%) and frond (43.50 wt%) samples. The higher bio-oil yield might be due to the fact that both samples have high cellulose and hemicellulose contents. Cellulose and hemicellulose promote the production of bio-oil because they are highly volatile. According to Qu et al. (2011), cellulose is more volatile than hemicellulose. Therefore, the material with the largest amount of cellulose should have the most volatile matter, leading to an increase in the oil yield. In this study, the frond had the most cellulose (50.33%). The frond material also produced the most oil and had the largest amount of volatile matter (43.50 wt% and 82.70 wt%, respectively). The same tendencies were found by Mullen et.al for the fast pyrolysis of two corn residues, corn cobs, and corn stover (Mullen et al., 2010). Their research concluded that the highest bio-oil yield was observed for corn stover material, which has the highest cellulose content. In addition, the amount of the bottom-layer oil obtained from the centrifugation process was similar for all the samples and was in the range of 3-8 wt% of the total oil.

The result from our previous study (Abnisa et al., 2013a) showed that the yields of bio-oils obtained were approximately 47.43 wt%, 45.75 wt%, and 43.87 wt% for palm shell, empty fruit bunches, and mesocarp fiber, respectively. Therefore, it can be concluded that the yields of bio-oils from the residues of palm oil mill activities is more attractive than those of residues from plantation activities.

4.3.2.2 Characterization of the bio-oils

The bio-oil properties are summarized in Table 4.5. From Table 4.5, it can be observed that the measured water contents were high, ranging from 52 to 66 wt%, for all bio-oils. This result is consistent with the results reported by Bertero et al. (2012). In their research, sawdust pine, mesquite trees, and wheat shell were pyrolyzed at a temperature of 550 °C for 60 min, and the water contents were determined to be within the range of 49.60–84.40 wt%. Wasterhof et al. (2007) have studied how to control the water content of biomass fast-pyrolysis oil, and they have concluded that drying the feedstock to obtain very low moisture levels (approaching zero) leads to a decrease in the water content. On the other hand, Garcia-Perez et al. (2008) stated that the biomass particle size has a significant effect on the water content of bio-oil. Generally, a smaller particle size increases the water content. While a high water content decreases the viscosity of bio-oil, which is helpful for pumping purposes, water is an undesirable component of bio-oil because it can be detrimental for the ignition performance.

The viscosities of the bio-oils were found to range from 1.23 to 1.99 cP at 50 °C. In this study, the viscosity exhibited a negative linear relationship with the water content. As shown in Table 4.5, an increase in the water content reduces the oil viscosity. These results are in agreement with the work of Nolte and Liberatore (2010), which investigated the viscosity of biomass pyrolysis oils from various feedstocks. Furthermore, the viscosity of oil can increase during the storage time. According to Diebold and Czernik (1997), the viscosity of an oil increases because of the polymerization of the reactive species, and as consequence, it might become unstable and separate into two phases (a viscous bottom portion and a fluid aqueous upper portion) (Oasmaa & Kuoppala, 2003).

Table 4.5: Properties of bio-oils produced via the pyrolysis of oil palm tree residues

Type of bio-oil	Properties			
	Water content (wt%)	Viscosity at 50 °C (cP)	Density (kg/m^3)	pH
Trunk	52	1.99	1053	3.1
Frond	53	1.88	1045	2.1
Palm leaf	59	1.75	1040	3.8
Palm leaf rib	66	1.23	1034	4.6

The presence of water in bio-oil also affects the density. Typically, a high water content leads to a decrease in the bio-oil density (Oasmaa et al. 1997). This trend is clearly observed in this study where the oil produced from palm leaf rib has the highest water content and the lowest density compared to the other bio-oil samples. Several researchers have supported this finding with studies using various biomass pyrolysis process conditions. Salehi et al. (2009) found that the density of bio-oil obtained from the pyrolysis of sawdust in a fixed-bed system is 1050 kg/m^3 at a water content of 39%. Lu et al. (2008) studied the chemical and physical properties of bio-oil produced via the fast pyrolysis of rice husk, and they measured an oil density of 1140 kg/m^3 at 28% water content. Zheng et al. (2008) obtained an oil density of 1160 kg/m^3 at a water content of 24.2%. The oil was produced from the fast pyrolysis of cotton stalk at a temperature of 510 °C in a fluidized bed reactor.

The pH values for all bio-oils obtained from the pyrolysis of oil palm residues were in the range of 2.1 - 4.6. In general, the low pH is due to the high concentration of acidic compounds in bio-oil. According to Sınağ et al. (2011), a high concentration of acidic compounds might result from the degradation of hemicellulose and lignin during pyrolysis. The low pH makes the oil highly unstable and corrosive. Therefore, careful material selection is needed in the design of storage and piping systems.

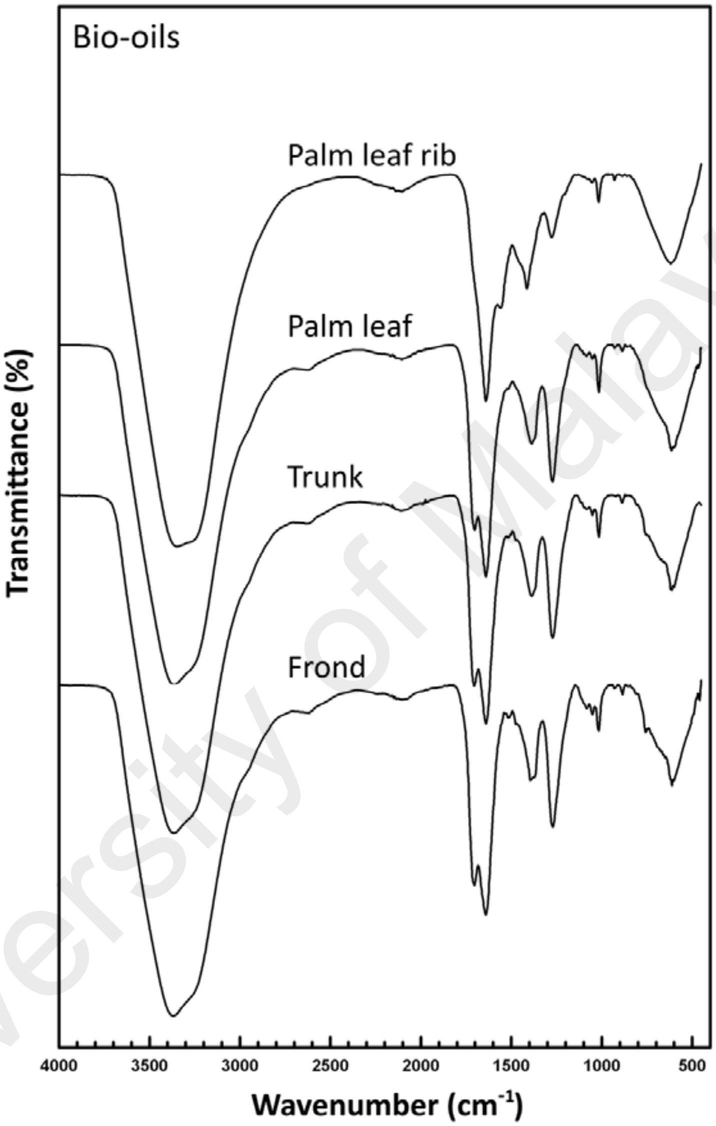


Figure 4.4a: FTIR spectra of bio-oils

Figure 4.4a shows the bio-oil spectra from the FTIR analysis. The results showed that all the bio-oils have similar types of chemical bonds (functional groups). The strong absorption peaks observed between 3200 and 3600 cm^{-1} indicate that phenols and alcohols are present. On the other hand, the peaks are also considered to result from the presence of water impurities (Das et al., 2004). This finding is consistent with the results in Table 4.5, namely that the water content of the bio-oils was found to be large in this study. The absorption peaks in the range of 1650-1750 cm^{-1}, which are related to C=O stretching, indicate the presence of ketones, carboxylic acids, and aldehydes. However, only the oil produced from palm leaf rib does not exhibit obvious peaks in this range. The –C–H bending vibrations between 1350 cm^{-1} and 1480 cm^{-1}, which indicate the presence of alkanes, were observed for all of the bio-oils. Moreover, the acid compounds are represented by the C−O stretching peaks observed between 1210 cm^{-1} and 1320 cm^{-1}. From Figure 4.4a, it can be seen that the oils from the trunk, frond, and palm leaf exhibited stronger peaks, indicating that they are more acidic than the oil produced from the palm leaf rib. This finding is in good agreement with the pH analysis results listed in Table 4.5. The C−O stretching vibrations in the range of 970-1150 cm^{-1} were assigned to alcohol and phenolic groups. The peaks in the range of 600-700 cm^{-1} showed that alkynes, which are represented by the C−H bending vibration, were present.

Table 4.6 presents the ultimate analysis results for the upper-layer bio-oils. The results showed that more than 70% of the oxygen was detected in the upper layer of the bio-oils. The high level of oxygen is generally found in bio-oils produced from the pyrolysis of biomass. Several authors have reported the oxygen content in varying types of biomass to range from 35 to 60 wt% (Czernik & Bridgwater, 2004; Lu et al., 2009; Zhang et al., 2007). However, the oils produced in this work have a higher oxygen content than has been previously reported in the literature. In this case, additional ultimate analyses were performed on the bottom-layer products in order to further investigate the behavior of the oxygen content. As shown in Table 4.6, the bottom-layer bio-oil products have less oxygen than the upper-layer products. The bottom-layer product of the palm leaf rib residue has the highest oxygen content of 49.16 wt%. In contrast to the upper-layer products, a high carbon content was measured for all bottom-layer products. A similar trend was also observed in the study conducted by Chen et al. (2011), where they found that the bottom-layer bio-oil has high carbon and low oxygen contents, while the opposite was observed for the upper layer. This finding is supported by Samanya et al. (2012), who noted that the upper layer contained lighter organic fractions, while the bottom layer contained tar fractions originating from wood. Of the four elements studied in the ultimate analysis, nitrogen was detected in the smallest quantities in the upper and bottom layers of the bio-oil.

Table 4.6: Ultimate analysis and HHV results

Type of product	**Type of oil palm residue**			
	Trunk	**Frond**	**Palm leaf**	**Palm leaf rib**
Bio-oil (upper layer)				
C (wt%)	16.88	17.93	15.16	10.34
H (wt%)	11.64	11.69	11.70	9.60
N (wt%)	0.64	0.33	0.65	1.64
O[a] (wt%)	70.85	70.07	72.48	78.42
HHV (MJ/kg)	14.94	15.41	14.38	9.52
Bio-oil (bottom layer)				
C (wt%)	50.56	54.57	55.54	39.66
H (wt%)	9.82	9.03	7.69	7.13
N (wt%)	1.07	0.63	3.60	4.06
O[a] (wt%)	38.56	35.77	33.17	49.16
HHV (MJ/kg)	24.31	25.03	23.90	14.83
Biochar				
C (wt%)	63.68	65.33	71.79	49.60
H (wt%)	2.28	2.56	2.41	2.14
N (wt%)	0.63	0.75	1.27	2.74
O[a] (wt%)	33.43	31.37	24.54	45.53
HHV (MJ/kg)	18.79	20.12	23.32	11.64

[a] By difference

The HHV of the bio-oil are listed in Table 4.6. The HHV of the upper-layer products, which were calculated using Eq. 4.5, were approximately 14.94 MJ/kg, 15.41 MJ/kg, 14.38 MJ/kg, and 9.52 MJ/kg for the trunk, frond, palm leaf, and palm leaf rib, respectively. However, these values are much lower than those reported by Czernik and Bridgwater (2004), who measured HHV of approximately 16-19 MJ/kg. The high water and oxygen contents are mainly responsible for the low bio-oil HHV. Moreover, the results in Table 4.6 clearly showed that the HHV of the bottom-layer products were higher than those of the upper-layer products. The different carbon contents between the upper and bottom layers might explain the difference in the HHV listed in Table 4.6. Nevertheless, the hydrogen content in the upper layer of the bio-oil was similar to that of heavy fuel oil reported in the literature (Czernik & Bridgwater, 2004). Hydrogen is the most important component with respect to increasing the HHV because it has the highest heating value among known fuels and is typically measured to be approximately 141 MJ/kg (Ali & Basit, 1993).

4.3.3 Bio-char

4.3.3.1 Bio-char yields

The product distributions from the biomass pyrolysis at 500˚C are shown in Table 4.4. The palm leaf had the highest bio-char product yield, followed by the trunk, frond and finally palm leaf rib. The different behavior of the hemicellulose, cellulose and lignin components at the pyrolysis temperature affects the product yields. Hemicellulose starts to decompose over a low temperature range of 220-315 ˚C (Yang et al., 2007); therefore, most of it decomposes at the pyrolysis conditions of this study. In addition, the hemicellulose content of all the precursors is similar (Table 4.2). Thus, the hemicellulose contents cannot be an important factor in the bio-char and non-condensable product yields. Lignin, which is composed of aromatic rings with various branches, decomposes over a wide range of low to very high temperatures with a very low mass loss rate (Yang et al., 2007). Therefore, the samples with higher lignin content might have relatively higher bio-char yields (Dong et al., 2012), which is true in the case of the trunk sample. Although lignin content is an important parameter, cellulose content can be considered to be the most significant factor in determining the bio-char yield. We observed this effect in our last study where the biomass sample with the highest cellulose content, the EFB sample, had a high bio-char yield (Abnisa et al., 2013a). Due to a faster mass loss rate of cellulose (6.5 wt%/˚C) than of other components, almost all of it would decompose at the pyrolysis temperature of this study. Therefore, the samples with high cellulose content will lose a large portion of their mass during pyrolysis, which might explain the lower bio-char yields of 30.24 and 28.63% for the frond and palm leaf rib samples, respectively, although they had the highest cellulose contents (46.1% for the frond and 50.33% for the palm leaf rib).

On the other hand, the palm leaf and trunk had very high carbon-based and volatile matter contents, respectively, in the precursor and bio-char samples (Table 4.3 and Figure 4.5). The very high amount of fixed carbon in the palm leaf samples (raw material and bio-char) can explain the high bio-char yield. In the case of the trunk-based bio-char, which was the second highest yield, the low decomposition of the volatile content during the pyrolysis process in addition to a high lignin content can contribute to its high yield.

The sweeping gas removes the products of secondary reactions, such as thermal cracking, repolymerization, and recondensation, from the hot zone (Ertaş & Hakkı Alma, 2010). The part of this pyrolysis vapor that is condensed in the cooling apparatus is called bio-oil, and the other part is a non-condensable gas mixture that contains CO, CO_2, H_2, and CH_4. The gas product yields of the oil palm wastes are listed in Table 4.4. The palm leaf and palm leaf rib had the highest product yields of 46.7 and 42.3%, respectively. It was reported in the literature that a high gas yield can be attributed to a high hemicellulose content in the precursor (Abnisa et al., 2013a; Basu, 2010;). However, the hemicellulose content of the precursors are similar in this study. As shown by the proximate analysis results for the produced bio-chars in Figure 4.5, the bio-chars with fewer volatile residuals have higher non-condensable gas product yields. Both the palm leaf and palm leaf rib had the lowest volatiles content of 28.7% in the produced bio-chars and the highest non-condensable gas product yields. Conversely, the samples with high volatile matter content in their bio-char (trunk) had the lowest non-condensable gas product yields. Thus, it can be concluded that the samples with the highest decomposition of volatile matter have higher gas product yields.

4.3.3.2 Characterization of bio-chars

The FTIR spectra of the trunk, frond, palm leaf and leaf rib bio-chars are shown in Figure 4.4b. Compared to the infrared spectra of the raw biomasses in section 3.1, the spectra of these carbonaceous materials show that different oxygen-containing surface groups (C=O, C–O, –OH) and other groups (olefins, $–CH_2$, $–CH_3$, aromatic rings) are present. The O-H stretching vibrations at 3600-3100 cm^{-1} in the FTIR spectra of the produced bio-chars were nearly absent after the carbonization process, probably due to the dehydration of the biomass together with the release of a large amount of water (Yang et al., 2006). A decrease in the intensity of the alkene (C-H) group vibrations in all three biomasses could be explained by the breaking of the weak alkyl C-H bonds, which would increase the CH_4 and C_2 hydrocarbon content in the gas products. However, in the case of the trunk-based bio-chars, a small IR absorption peak that is consistent with the proximate analysis data in Table 4.3 showing that the trunk samples contain a high level of volatiles after carbonization is observed. The next band in the spectra of the raw materials occurring at 2860 - 2970 cm^{-1}, which can be assigned to the

CH alkyl functional groups, were also absent in the spectra of the biomass chars. The CH aromatic bands at 877 - 779 cm^{-1} were also weaker due to the deformation of the adjacent H. In addition, the intensity of the carboxyl group band at 1718 cm^{-1} decreased in all the bio-char samples, possibly due to the degradation of the cellulose components during pyrolysis.

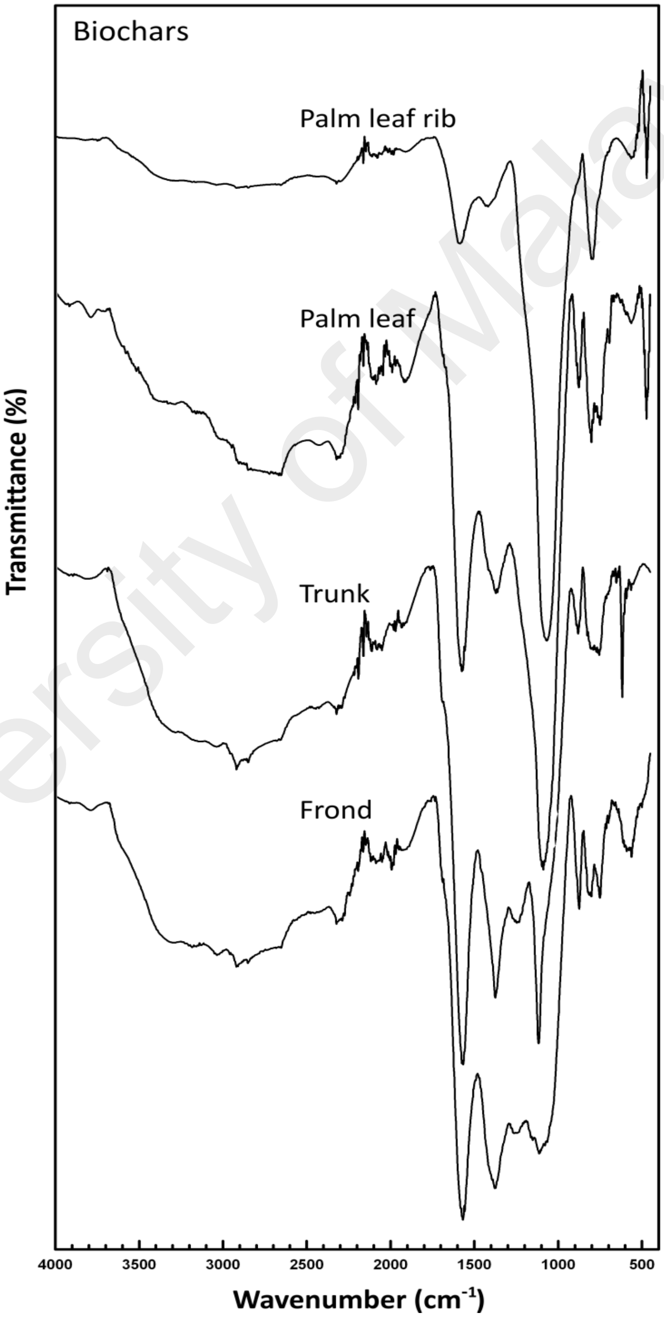


Figure 4.4b: FTIR spectra of bio-char

On the other hand, the FTIR spectral data indicate that the IR peaks of the produced chars at 2313 - 2330 cm^{-1} ($C\equiv C$) and 1586 - 1571.62 cm^{-1} (aromatic C=C) increased in intensity relative to those of the raw biomasses after the carbonization process. The cracking of volatiles (decrease in the OH and CH alkyl peaks) and the conversion of the aliphatic compounds into aromatic compounds in the char structure can explain these bands.

The proximate analysis of the produced bio-chars was performed according to ASTMD7582-10, and the results are summarized in Figure 4.5. The moisture, volatiles, fixed-carbon and ash contents can be derived from the mass losses of the carboneous samples over the process time shown in Figure 4.5. It can be seen that all the samples undergo three main mass losses. The first occurs during heating from room temperature to 110 $^{\circ}$C under a nitrogen atmosphere, which leads to complete dehydration and thus allows for the determination of the moisture content (up to 2300 s). Then the temperature is increased rapidly to 950 $^{\circ}$C to determine the amount of volatile matter by measuring the mass loss after dehydration (between 2300 and 4700 s). Finally, the temperature was decreased to 650 $^{\circ}$C, and the atmosphere was changed to oxygen gas to measure the mass loss during the oxidation stage, which corresponds to the carbon content (rapid decrease in the mass of all the samples). Ash constituted the mass remaining at the end of the analysis. Based on this figure, the trunk-based char has the highest volatile content, followed by the frond, palm leaf and rib samples. However, the last two had similar volatile matter contents. Thus, it can be concluded that a higher carbonization temperature is needed in the case of the trunk-based bio-char to improve the devolatilization. The leaf char sample had the highest fixed-carbon content, which was similar to that of the frond-based sample, while the rib and trunk samples had much lower fixed-carbon contents. The ash content of all the samples is similarly low except in the case of the rib sample, which contained a very high amount of ash after carbonization.

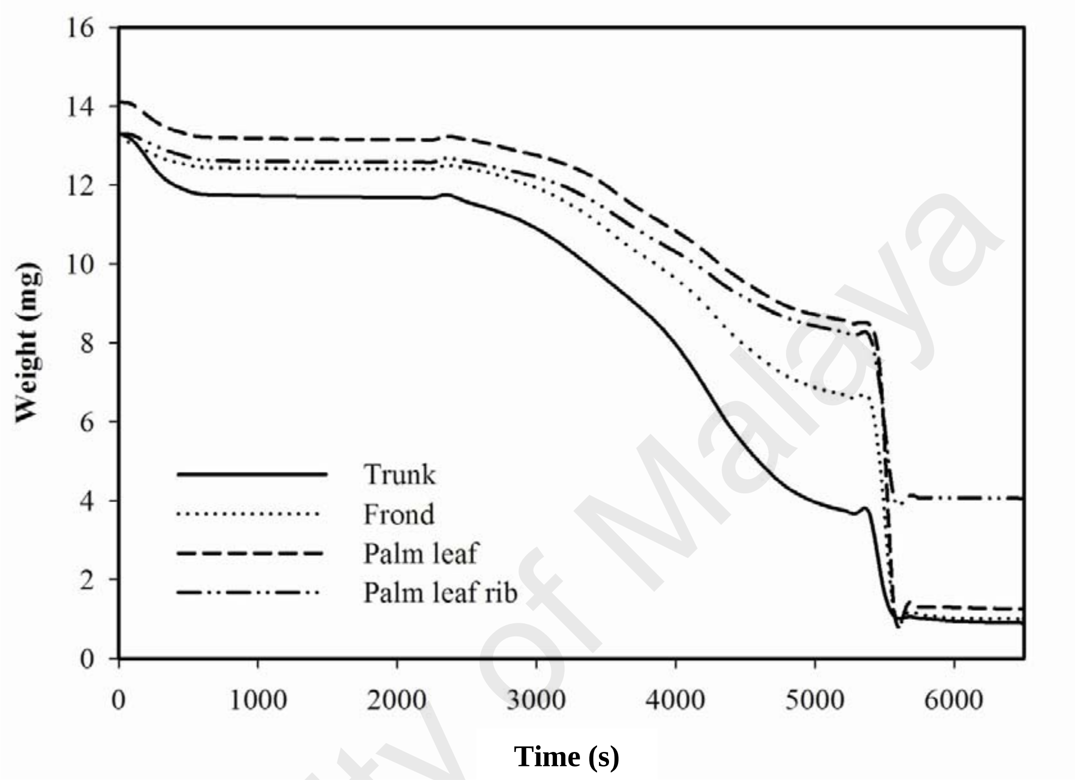


Figure 4.5: Mass loss behavior of the produced bio-chars over time under nitrogen and then oxygen heating

The results of ultimate analysis of bio-char are listed in Table 4.6. The HHV of the produced bio-chars are also given in this table. Carbon, as the main element in all of the produced bio-chars (49-72 wt%), is present in significantly greater amounts in the bio-chars than in the dried biomasses, except for the palm leaf sample, which had similar amounts of carbon and oxygen before and after pyrolysis (see Table 4.3). In comparison to the raw biomasses, the O and H contents decrease in all the bio-char samples due to dehydration and decarbonylation/decarboxylation reactions, which is consistent with the FTIR results (Figure 4.4b). The largest decrease in the O and H contents is observed for the palm leaf sample, which was found to have the second highest devolatilization percentage (approximately 57%) in the proximate analysis. Although the palm leaf rib exhibited the highest devolatilization (approximately 62%) during pyrolysis, possibly due to its high ash content in the produced bio-char, the amount of carbon and oxygen did not change considerably. The hydrogen content decreases in all the samples, probably due to the aromatization of the bio-char and evolution of H_2 as light molecular hydrocarbons (CH_4 and C_2) were formed during the pyrolysis process (Yang et al., 2007).

The HHV of the bio-char samples calculated using Eq. 4.5 is highly dependent on the hydrogen and carbon contents of the samples. As long as all the bio-char samples have similar hydrogen contents (2-3%), the amount of carbon plays an important role in the determination of HHV. Thus, similarly to the carbon content, HHV also follows the order of palm leaf > frond > trunk > palm leaf rib. With the exception of the palm leaf rib sample with a low HHV, the other bio-char samples have HHV values comparable to those of some coals and are therefore acceptable for use as a renewable solid fuel (Akkaya, 2009; Bilgen & Kaygusuz, 2008). The low level of nitrogen content in the bio-char samples also indicates that these samples produce low levels of NO_x emissions during the combustion process.

Figure 4.6 presents the SEM pictures of the raw biomasses and their bio-chars obtained after pyrolysis. It is clear in all the images that the pyrolysis of the biomasses allows the evolved volatile compounds to escape from the inside of the raw materials. Consequently, more void space and higher porosity are detectable on the surface of the bio-chars, which have higher surface areas than the raw materials. The images of the bio-chars show the heterogeneity of their surfaces with mesopores that can be useful in many liquid-solid adsorption processes (Mohan et al., 2011). As shown in Figure 4.6, the primary surface structures changed during the carbonization and devolatilization processes.

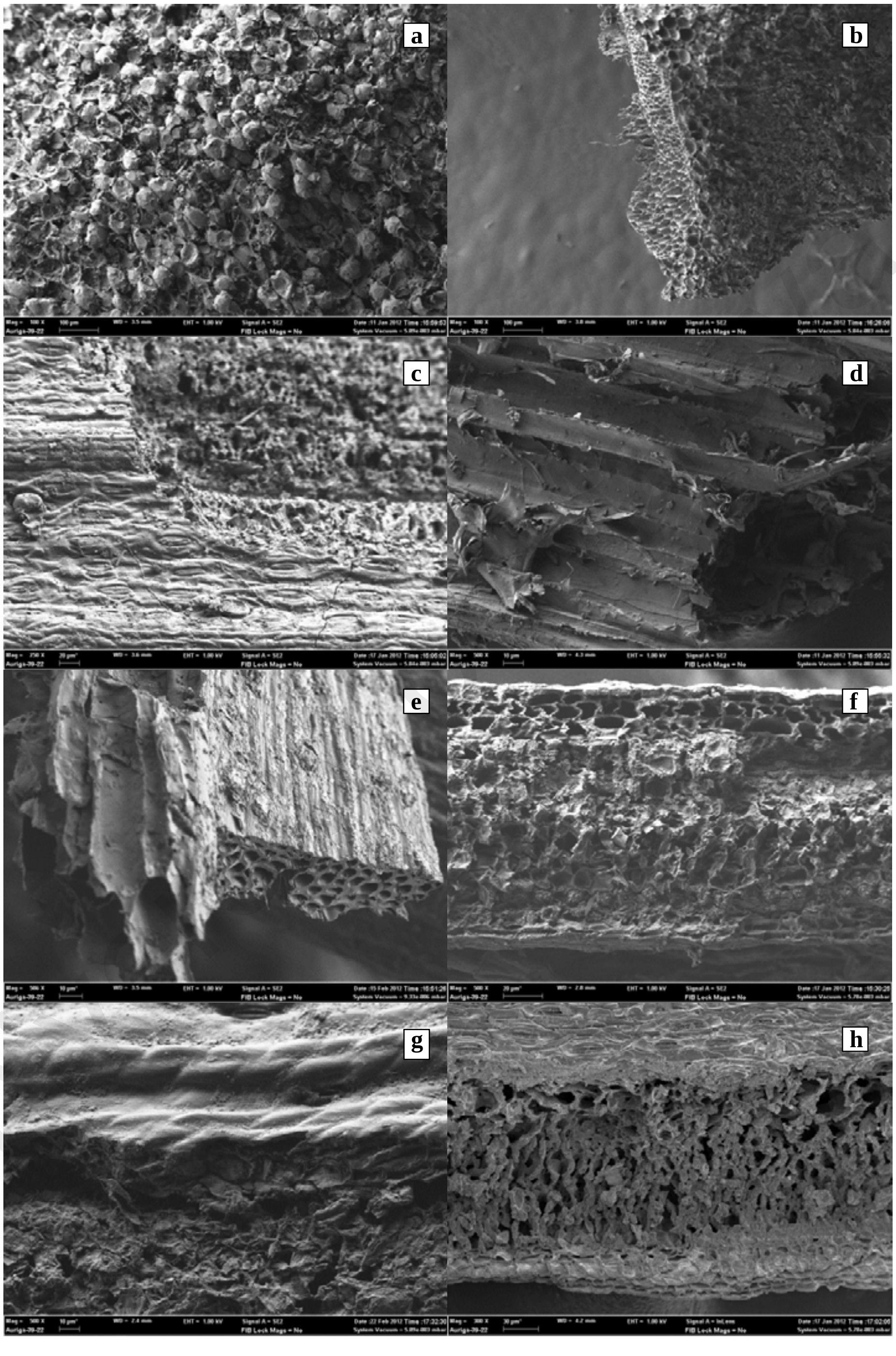


Figure 4.6: SEM photographs of a. trunk, b. trunk bio-char, c. frond, d. frond bio-char, e. leaf, f. leaf bio-char, g. rib, h. rib bio-char

Spherical structures on the surface of the trunk (Figure 4.6a) were transformed into open cells after carbonization (Figure 4.6b), while the amorphous structure of the frond (Figure 4.6c) allowed for the formation of open channels after devolatilization (Figure 4.6d). Partly open channels and larger pores in the palm leaf and palm leaf rib bio-chars (Figures 4.6f and 4.6h) are also observed after pyrolysis of the amorphous raw biomasses (Figures 4.6e and 4.6g).

4.4 Conclusions

All of the residues that came from oil palm plantation activities have been successfully pyrolyzed to produce bio-oil and bio-char using a reaction temperature of 500 °C, a nitrogen flow rate of 2 L/min and a reaction time of 60 min. Different proportions of the products have been clearly observed in this study and are mainly caused by the different amounts of cellulose, hemicellulose, lignin, volatile matter, fixed carbon, and ash in the samples. The HHV of the upper layer of the bio-oils was found to range from 9.52 to 15.41 MJ/kg, while the HHV of the bottom layer was higher (approximately 14.83 - 25.03 MJ/kg). However, further efforts to improve the quality of the bio-oil must be performed prior to its use as an alternative fuel. The improvement can be performed through the catalytic cracking or hydrodeoxygenation process. Furthermore, most of the bio-char samples have HHV that are comparable to those of some coals and are thus acceptable for use as a renewable solid fuel. They also have low levels of NO_x emissions during the combustion process. In addition, the SEM images showed that the pyrolysis of the biomasses allows the evolved volatile compounds to escape from the inside of the raw materials and consequently increases the porosity of the surface of the produced bio-chars.

CHAPTER V

PYROLYSIS OF MIXTURES OF PALM SHELL AND POLYSTYRENE: AN OPTIONAL METHOD TO PRODUCE A HIGH-GRADE OF PYROLYSIS OIL

5.1 Introduction

The decrease in non-renewable energy resources such as coal, petroleum, and natural gas has encouraged research to develop new approaches to find or create renewable fuel from biomass. The biomass can be converted into a liquid product that can potentially be used for fuel through pyrolysis, gasification, and combustion. Amongst them, pyrolysis was selected as the most appropriate technology because it is able to convert 75 wt% of the total biomass into liquid form (Bridgwater, 2006). Unlike fossil fuels, use of this liquid has received positive comments as being a more environment-friendly fuel because it contributes minimally to the emission of greenhouse gases (Vitolo et al., 1999). However, the liquid or pyrolysis oil contains high levels of oxygen, which causes low caloric value, corrosion problems and instability (Lu et al., 2009).

Many studies have been undertaken to obtain a high-grade of pyrolysis oil that has low oxygen content and high caloric value. Catalytic cracking and hydrodeoxygenation (HDO) are the methods commonly used, which can cost more than the oil itself. Catalytic cracking is a method that involves the addition of a catalyst to the pyrolysis process. This method can be divided into two options: off-line catalytic cracking (using bio-oil as raw material) and on-line catalytic cracking (using pyrolysis vapors as raw material) (Hew et al., 2010). Zhang et al. (2007) have determined that catalytic cracking is a cheaper method than hydrodeoxgenation, but the results do not seem promising because of high coke production during the process (8–25 wt%) and the poor quality of the fuels obtained. Furthermore, HDO is an upgrading method suitable for converting low-grade pyrolysis oil into hydrocarbons (Toba et al., 2011). This process has received a lot of attention because of the significant increase in hydrocarbon fuel obtained (Joshi & Lawal, 2012). However, the method is complex and costly because of the complicated equipment, need to add catalysts, and the high-pressure requirement for reaction. Thus, a new approach is necessary to overcome this cost.

Simplicity and effectiveness are especially important in developing a method. The idea of biomass pyrolysis mixed with plastic waste is an optional method that shows promise of meeting these two criteria. In the pyrolysis process, the yield of oil obtained from incorporating plastic waste was higher than that obtained with biomass alone and it also had a higher caloric value, which comes from hydrocarbon polymers consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable gas with a high calorie value (Panda et al., 2010). Therefore, the presence of plastic waste in biomass pyrolysis can make a positive contribution to the heating value and yield of oil through synergy.

The main benefit of using this method is the volume of waste can be reduced significantly because more waste is consumed as feedstock. It also has the added benefits of reducing the landfill needed, decreasing the cost for waste treatment, and solving some environmental problems. Since disposing of the waste in landfill is becoming undesirable (Garforth et al., 2004), this method could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and enhance energy security.

Malaysia is a humid tropical country located in the central part of Southeast Asia with a total landmass of 329,847 km^2 (Manaf et al., 2009). In 2007, about 20.32 % of the landmass was being used for agriculture including oil palm, rubber, cocoa, paddy, coconut, pepper, flowers, coffee, sugarcane, tea, vegetables, tobacco and fruits (Goh et al., 2010; Mekhilef et al., 2011). During that year, about 93,598 ktons of biomass waste were produced, mostly from oil palm. Currently, the utilization of biomass waste generated from oil palm is not efficient. It is incinerated or dumped as organic fertilizer through natural decomposition (Qin Ng et al., 2012) or used to cover road surfaces in the plantation area (Abnisa et al., 2011), and only a fraction of it is burned for steam generation (Yang et al., 2004). Unsatisfactory practices also occur in the management of municipal solid waste (MSW). Currently, landfilling is the only method used to dispose of MSW in Malaysia (Manaf et al., 2009). This method results in leached contamination to the surface and groundwater, pest infestation and the emission of landfill gases such as methane (40–50%), and carbon dioxide (50%) (Fauziah & Agamuthu, 2012). In 2001, the quantity of MSW was about 16,200 tons/day, which increased sharply up to 19,100 tons/day in 2005 and is projected to be 30,000 tons/day in 2020 (Siwar, 2008). One study reported that about 24% of total MSW is plastic waste (Manaf et al., 2009). Improved management is necessary if the volume of waste in landfill sites is to be reduced. This need makes biomass pyrolysis mixed with plastic an attractive alternative way to solve the problems faced.

In this work, pyrolysis of biomass and biomass mixed with plastic was carried out to produce pyrolysis oil. Palm shell was selected as representative of biomass and polystyrene was selected as representative of plastic waste. The collected results were compared to determine whether there was improvement in the quantity and quality of the oil product produced.

5.2 Materials and experimental procedure

5.2.1 Materials

Palm shell was selected for this work because it is one of the most plentiful biomass wastes available in Malaysia (5.2 million tons/year) (Mohammed et al., 2011). Polystyrene was selected as the plastic material because pyrolysis of polystyrene results in high oil yield with a quality close to that of petroleum-based oil (Ayhan, 2004; Kiran et al., 2000). Each year over 280,000 tons of this waste are generated in Malaysia (Mohammed, 2010). Palm shell was collected from a local processing plant in Kuala Lumpur; polystyrene waste was obtained from a local rubbish collection point. The palm shell was oven-dried at 105ºC for 24 h; the polystyrene was dried under the sun for several days. Then, both materials were ground and sieved to obtain the desired particle size of 1–2 mm.

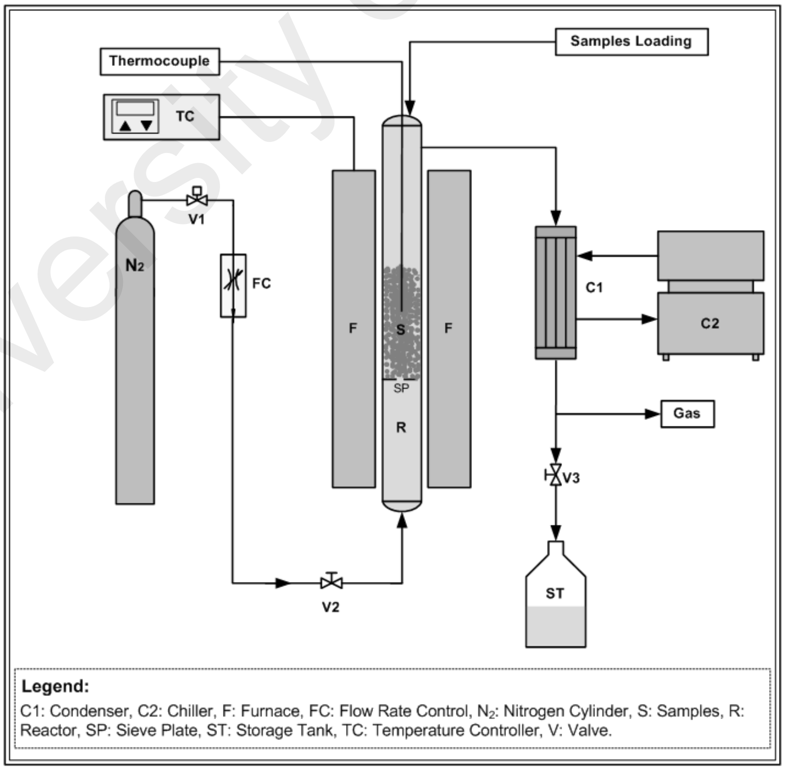


Figure 5.1: Schematic diagram of experimental setup for pyrolysis oil production

5.2.2 Experimental setup and procedures

All pyrolysis experiments were conducted using a fixed-bed reactor made from stainless steel with an internal diameter of 5.0 cm and a length of 127 cm. The reactor was heated by an external vertical furnace. A series of condensers that maintained furnace temperature at the desired level ± 0.5ºC was installed to obtain the oil through gas condensation. The experimental setup is shown in Figure 5.1.

The study was divided into two parts. The first part was pyrolysis of palm shell alone. About 150 g of palm shell was loaded into the reactor and pyrolyzed at 500ºC with a heating rate of 10 ºC/min. The reaction time of pyrolysis was maintained at 60 min. To minimize secondary reactions of vapors that cause decreases in oil yield (Açıkalın et al., 2012), a 2 L/min nitrogen flow was applied. The second part was pyrolysis of palm shell mixed with polystyrene. The ratio of sample materials was set at 1:1. The processing parameters (temperature, nitrogen flow, and reaction time) were the same as in the previous experiment. Each experiment was repeated three times and the results were averaged. The oil yield of the resulting product was then calculated using Eq. (5.1). The equation can also be used to estimate the char produced as a byproduct resulting from the pyrolysis process.

$$\text{Yield of product} = \frac{\text{Desired product}}{\text{Total feed}} \times 100\ \% \qquad (5.1)$$

5.2.3 Characterizations

5.2.3.1 Characterization of raw materials

Proximate analysis included moisture, fixed carbon, volatile matter, and ash in palm shell and polystyrene. In this study, the procedure for obtaining a proximate analysis was carried out according to ASTM standards described in the literature (Kalanatarifard

& Yang, 2012). The ultimate analysis of palm shell and polystyrene followed ASTM D-5291 using a Model 2400 Perkin-Elmer Series II CHNS/O Analyzer. The amount of carbon, hydrogen, and nitrogen was determined using this method; the oxygen content was calculated by difference.

5.2.3.2 Characterization of pyrolysis oil

The pyrolysis oils were analyzed for viscosity, density, pH, water content, elemental analysis, FTIR, and GCMS. Viscosity was measured using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer model DVII+ Pro EXTRA). A 25 mL pycnometer was used to determine the density of the pyrolysis oil. The pH was measured using a Methrom pH meter series 827 at 25ºC. Then, the water content of the pyrolysis oil was measured using a Karl Fischer 737 KF Coulometer from Metrohm. The elemental analysis was carried out using a Model 2400 Perkin-Elmer Series II CHNO/S Analyzer to determine C, H, and N. The oxygen content was determined by a difference. The obtained data from the elemental analysis were also used to calculate the high heating value (HHV). Eq. (5.2) was used to calculate the HHV of the pyrolysis oil produced from palm shell because the oxygen content in the oil was found to be greater than 15% (Buckley, 1991). The HHV of the pyrolysis oil derived from mixtures of palm shell and polystyrene was obtained by using Eq. (5.3).

$$\mathrm{HHV\ (MJ/kg)} = 0.336\,\mathrm{C} + 1.418\,\mathrm{H} - (0.153 - 0.000720\,\mathrm{O})\mathrm{O} + 0.0941\,\mathrm{S} \tag{5.2}$$

$$\mathrm{HHV\ (MJ/kg)} = \frac{338.2\mathrm{C} + 1442.8\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right)}{1000} \tag{5.3}$$

A Perkin Elmer FTIR spectrometer (Spectrum 400) was used to obtain an infrared absorption spectrum of the pyrolysis oil. The chemical compositions were determined by gas chromatography/mass spectroscopy (GCMS). The analysis was performed with an Agilent Technologies 7890A gas chromatograph equipped with an Agilent 5975C mass-selective detector (mass spectrometer). High purity helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The Agilent HP-5 50 m column with an inner diameter of 0.32 mm and a film thickness of 0.25 μm was used in the GCMS. The analysis was started by heating the column at 50 °C and kept isothermal for 1 min, then ramped to 270°C at a rate of 7 °C/min. This condition was held for 10 min. The volume of sample injected was about 1 μL.

Table 5.1: Proximate and ultimate analyses of palm shell and polystyrene

Characteristics	**Palm shell**	**Polystyrene**
Proximate analysis (wt%)		
Moisture	4.7	0.25
Fixed carbon	13.2	0.12
Volatile	73.5	99.63
Ash	8.6	0.00
Ultimate analysis (wt%)		
C	49.74	91.34
H	5.32	7.80
N	0.08	0.34
O (by difference)	44.86	0.52
S	0.16	0

5.3 Results and discussion

5.3.1 Characteristics of the raw materials

The proximate and ultimate analyses of the palm shell and polystyrene are given in Table 5.1. The result of the proximate analysis showed that the level of volatile compounds was high in both materials (73.5 wt% for palm shell and 99.63 wt% for polystyrene). Unlike palm shell, moisture and fixed carbon were very low in polystyrene. In addition, palm shell contained a small amount of ash while no ash was detected in the polystyrene. For the ultimate analysis, the oxygen content of the palm shell was determined to be 44.86 wt%, significantly higher than that of the polystyrene (0.52 wt%). The higher oxygen content indicated that the palm shell had a lower caloric value.

The TGA thermographs of palm shell and polystyrene at a heating rate 20 ºC/min are shown in Figure 5.2a. In this study, the TGA analysis helped to define the temperature at which degradation starts for each sample. The result showed that a temperature in the range of 350–430 ºC was effective for pyrolysis of polystyrene. Approximately 99% of the total weight was lost in this range. For the palm shell, a weight loss of more than 60% was observed when temperatures reached 500 ºC. In this case the initial decomposition represents the degradation of hemicellulose and cellulose occurring at temperatures of 200–260 °C and 240–350 °C, respectively. Lignin was reported to be the most difficult component to decompose. Lignin decomposed slowly throughout the whole temperature range from 280 °C to 900 °C (Mahanim et al., 2011; Mohan et al., 2006). These thermographs indicate that the pyrolysis process should occur above 300 °C to gain the thermal degradation of the polystyrene and palm shell. In addition, as can be seen in Figure 5.2b, the DTG graph for the palm shell showed two distinct peaks between 250 °C and 450 °C, indicating that two main groups of reaction occur during the decomposition process. The first peak indicated the decomposition of hemicellulose and some of the lignin, while the second peak corresponded to the decomposition of cellulose and the remaining lignin (Font et al., 1991; Tsamba et al., 2006).

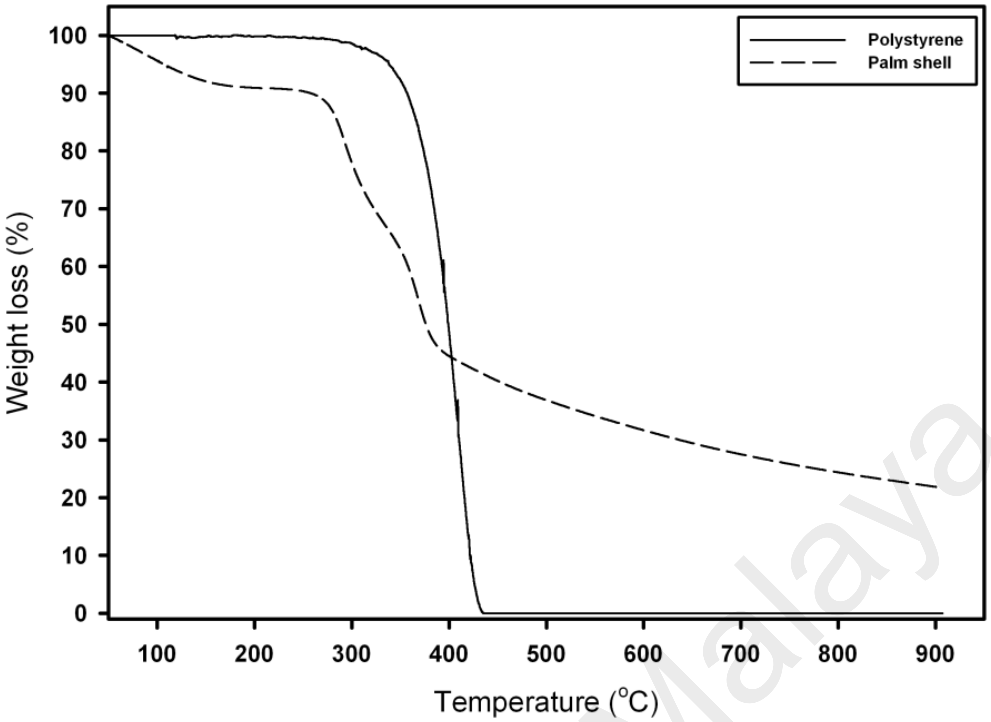


Figure 5.2a: TGA thermographs of palm shell and polystyrene

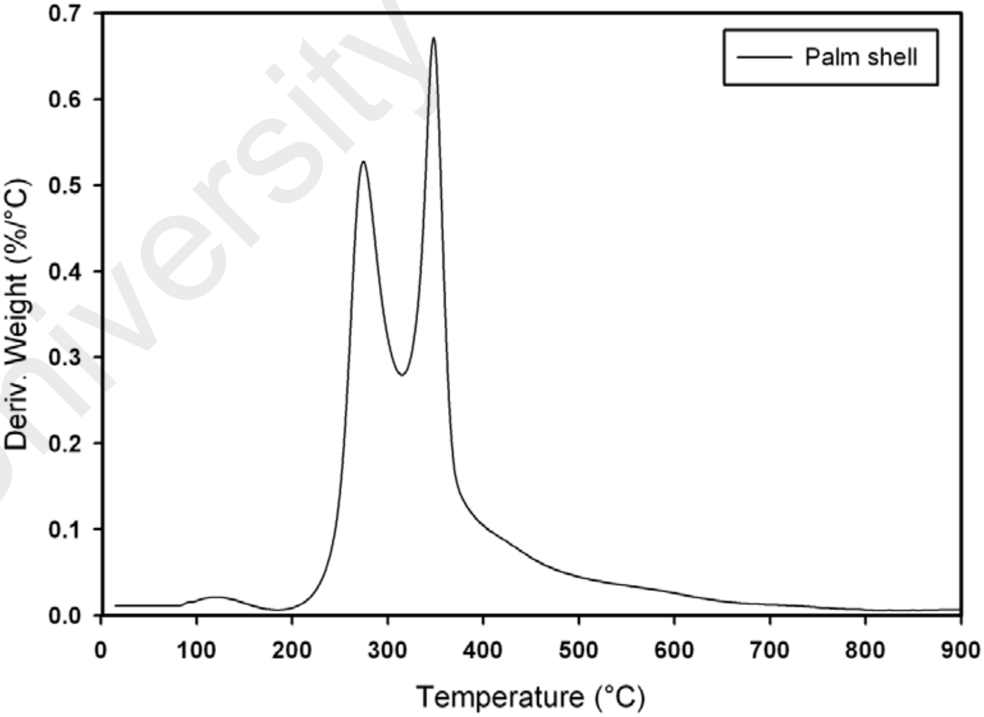


Figure 5.2b: DTG graph of palm shell

5.3.2 Pyrolysis yields

Figure 5.3 shows the product yields from pyrolysis of palm shell alone or palm shell mixed with polystyrene at 500ºC, a nitrogen flow rate of 2 L/min, and a reaction time of 60 min. The amount of oil obtained was higher than the volume of the other products (char and non-condensable gases) in all of the pyrolysis experiments. This could be explained by the volatile content being high in both samples. This finding is in good agreement with the studies of Omar et al. and Islam et al., which stated that the high volatile content is favorable for the oil yield (Islam et al., 2008; Omar et al., 2011). Furthermore, the pyrolysis of palm shell mixed with polystyrene yielded about 15 wt% more oil than pyrolysis of palm shell alone, which also resulted in a decrease in char product as a consequence.

Table 5.2: Distribution of products from co-pyrolysis of palm shell and polystyrene at different ratios

Polystyrene in feed (%)	Pyrolysis oil (wt%)	Char (wt%)	Non-condensable gases [a] (wt%)
20	47.73	27.81	24.46
30	49.93	23.22	26.85
40	59.13	20.18	20.69

[a] Calculated by difference

To obtain a more accurate description of the effect of polystyrene on the oil yield in palm shell pyrolysis, some additional experiments were performed. The experiments included: pyrolysis of polystyrene alone and co-pyrolysis of palm shell mixed with polystyrene at ratios of 80:20, 70:30, and 60:40 (palm shell to polystyrene). The results showed that the pyrolysis of pure polystyrene produced oil, residue and non-condensable gases in proportions of about 88.63 wt%, 9.22wt%, and 2.15 wt%, respectively. For comparison purpose, the product yields from co-pyrolysis of palm shell mixed with polystyrene are given in Table 5.2. As can be seen in the table, the decrease in char yield was obvious when the mass weight of palm shell was reduced in the feed. In this regard, the lignin content of palm shell can be a reason for the char generated during pyrolysis. Mohan et al. noted that the presence of lignin in biomass favors the production of a high amount of char (Mohan et al., 2006).

Unlike char production, reducing the palm shell in the feed resulted in an incremental increase in the yield of pyrolysis oil. In this case, the addition of polystyrene is playing an important role in the rise of oil production. As described in the literature, a synthetic polymer such as polystyrene is an excellent hydrogen source; hence, it could provide hydrogen during thermal co-processing with wood biomass, which can lead to an increase in liquid production (Brebu et al., 2010). Most of the liquid (about 60%) produced during the pyrolysis of polystyrene is contributed by the styrene compound (Karaduman, 2002), while cellulose is the major component responsible for liquid production in woody biomass (Qu et al., 2011).

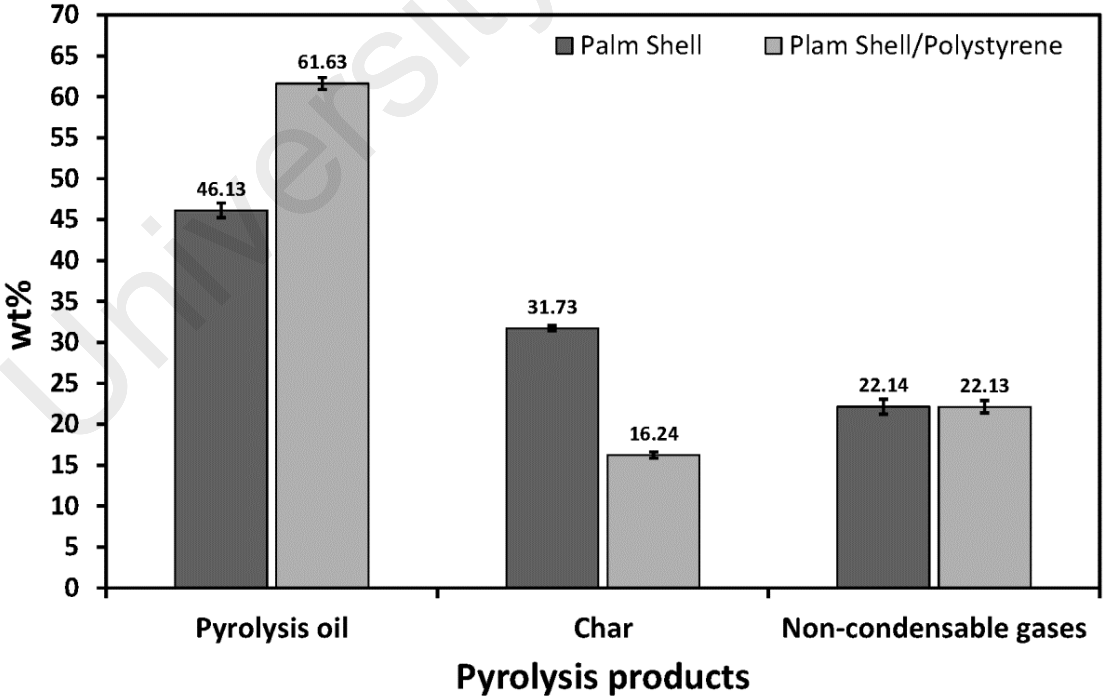


Figure 5.3: Product yields of pyrolysis

From this study, it can be seen that the addition of polystyrene during pyrolysis of palm shell has a significant influence on elevating the oil yield. The same trends during co-pyrolysis of cellulose with polystyrene were observed by Rutkowski and Kubacki (2006). Their study reported that a significant enhancement in the liquid product generated was observed when the polystyrene content was at a higher ratio than the cellulose content. Their experiment was performed at a temperature of 500ºC, the heating rate was 5 ºC/min, and the reaction time was 60 min.

In addition, the waste from tyre manufacture can also be used as an alternative mixing material with biomass to increase the oil fraction. Research into co-pyrolysis of sawdust mixed with tyre waste showed that the oil yield reached 45.0 wt%, 46.2 wt%, 47.0 wt% and 47.2 wt.% when tyre mass occupied 0%, 40%, 60% and 100% of the mixture, respectively. This work was done at 500ºC with a heating rate of 20 ºC/min and a 3.5 h reaction time (Cao et al., 2009).

5.3.3 The properties and compositions of pyrolysis oil

The physical and chemical properties of the pyrolysis oils are presented in Table 5.3, together with the properties of diesel oil, which were studied from literatures (Dmytryshyn et al., 2004; Ikura et al., 2003; Imam & Capareda, 2012). In this study, the measurements of viscosity shown are dynamic viscosity. The results indicated that the viscosity of the oil generated from pyrolysis of palm shell was lower than that of the blend. The high water content may be responsible for reducing the viscosity of the oil. Nolte and Liberatore (2010) carried out a study to observe how water content affected viscosity and acidity. According to their results, the water content in the oil was found to have a stronger effect on viscosity than acidity; thus, oils with greater water content had lower viscosities, making them easier to pump and atomize.

The analysis results show that the oils obtained in this study are acidic, with pH of 2.5 and 2.7. The acidity is most likely caused by the presence of carboxylic acid, acetic acid, and formic acid (Pollard et al., 2012). The acidity makes the oil corrosive and difficult to use in engines, boilers, and refinery processing equipment. Aubin and Roy (1990) observed that the pyrolytic oil produced from wood was extremely corrosive at 45 ºC, showing high contents of acid (17.5 %) and water (55.7 wt%). Nevertheless, the acid compounds can be reduced to a very low level by using a hydrocracking process, as described by Elliott et al. (2009).

Table 5.3: Physical and chemical properties of pyrolysis oils

Properties	Value			Unit
	Palm shell	Palm Shell/ polystyrene (50:50)	Diesel	
Viscosity	3.20 at 50°C	6.71 at 50°C	3.50 at 40°C	cP
pH	2.5	2.7	-	-
Density	1051 at 24°C	1070 at 24°C	853 at 20°C	kg/m^3
Elemental composition:				
C	19.48	84.02	86.6	wt%
H	8.92	7.63	13.1	wt%
N	0.2	0.53	0.004	wt%
O (by differences)	71.40	7.82	1.8	wt%
S	0.04	0.61	0.11	
High Heating Value (HHV)	11.94	38.01	45.5	MJ/kg
Water content	53	2.4	<0.1	wt%

The density of pyrolysis oil produced from pyrolysis of palm shell mixed with polystyrene (1070 kg/m^3) was higher than that of oil produced from palm shell alone (1051 kg/m^3). The densities of the obtained oils are higher than diesel by about 1.2-fold. Before pyrolysis, the original densities of the polystyrene and palm shell were shown to be about 1050 and 1462 kg/m^3, respectively. It was noted that the conversion of palm shell and polystyrene mixtures into pyrolysis oil reduced the density of the wastes. This means that the area needed for liquid storage is less than the area needed for a landfill site for the solid waste.

The water content of each pyrolysis oil was obtained by using the Karl Fischer titration method. The results are presented in Table 5.3. A water content of approximately 53 wt% was observed for pyrolysis oil from palm shell. High water content has also been observed for pyrolysis of pine sawdust (49.60 wt%), mesquite sawdust (67.60 wt%), and wheat shell (84.40 wt%) as reported by Bertero et al. (2012). Generally, pyrolysis of biomass results in a high water content in the liquid product. The high water content is undesirable because it could be detrimental to ignition and can cause the formation of rust in engines. Czernik et al. (1994) found that the water concentration can also be increased by long periods of time in storage. Their study showed that high temperature (60 ºC) was a suitable condition to increase water content during storage. In contrast, pyrolysis of palm shell mixed with polystyrene showed a significant reduction in water content (2.4 %) in this study. This reduction in water content was consistent with the results reported by Rotliwala & Parikh (2011). In that study, the co-pyrolysis of a deoiled cake of jatropha and waste commercial polyolefins resulted in a very low water content in the pyrolysis oil.

Elemental analyses of the pyrolysis oils are shown in Table 5.3. The analyses showed that the contents of the two oils were very different. The pyrolysis oil from palm shell was found to be highly oxygenated (71.40 wt%). This high oxygen content reduced its energy density below that of the conventional fuel. Imam & Capareda (2012) reported that the oxygen content of diesel oil is very low, around 1.8 wt%. Furthermore, the amount of oxygen in the oil showed a linear relationship to the water content. The amount of oxygen can be easily predicted (low or high) once the amount of water has been measured. Different researchers have tried several methods to eliminate the oxygen content and thus elevate the energy density of pyrolysis oil. In pyrolysis oil upgraded by high pressure thermal treatment, Mercader et al. (2010) showed that the 51 wt% of oxygen in pine wood pyrolysis oil was reduced to 20 wt% using a continuous tubular reactor at a temperature of 350 ºC, a pressure of 240 bar, and residence time of 3.4 min. Zhang et al. (2005) tried to eliminate oxygen in pyrolysis oil using a 500 mL autoclave filled with a sulfide Co–Mo–P catalyst and a solvent (tetralin as a hydrogen donor solvent). Their study showed that the pyrolysis oil yield obtained was about 59.59 wt% and the oxygen content was significantly reduced from 41.8 wt% to 3 wt% under optimum conditions (temperature of 360 ºC, cold hydrogen pressure of 2.0 MPa, and reaction time of 30 min). However, both the study by Mercader et al. and that by Zhang et al. yielded results that are not economical and require additional work to prepare the catalyst. In this study, the co-pyrolysis of palm shell and polystyrene waste mixtures showed a significant reduction in oxygen, to about 7.82 wt%. This result was obtained with high oil yield and without additional hydrogen pressure, catalysts or solvents.

The low oxygen content contributed to an elevated HHV (see Table 5.3). The HHV of the oil from pyrolysis of palm shell mixed with polystyrene was more than triple that from pyrolysis of palm shell alone. The HHV result proved that the oil from pyrolysis of palm shell mixed with polystyrene is close to that of conventional fuel oil (about 42–44 MJ/kg). Also, it should be noted the oil has an energy content about 83.5% that of diesel oil, which is higher than the typical value of oil from the pyrolysis of woody biomass (40%) that has been reported in the literature (Bridgwater & Peacocke, 2000).

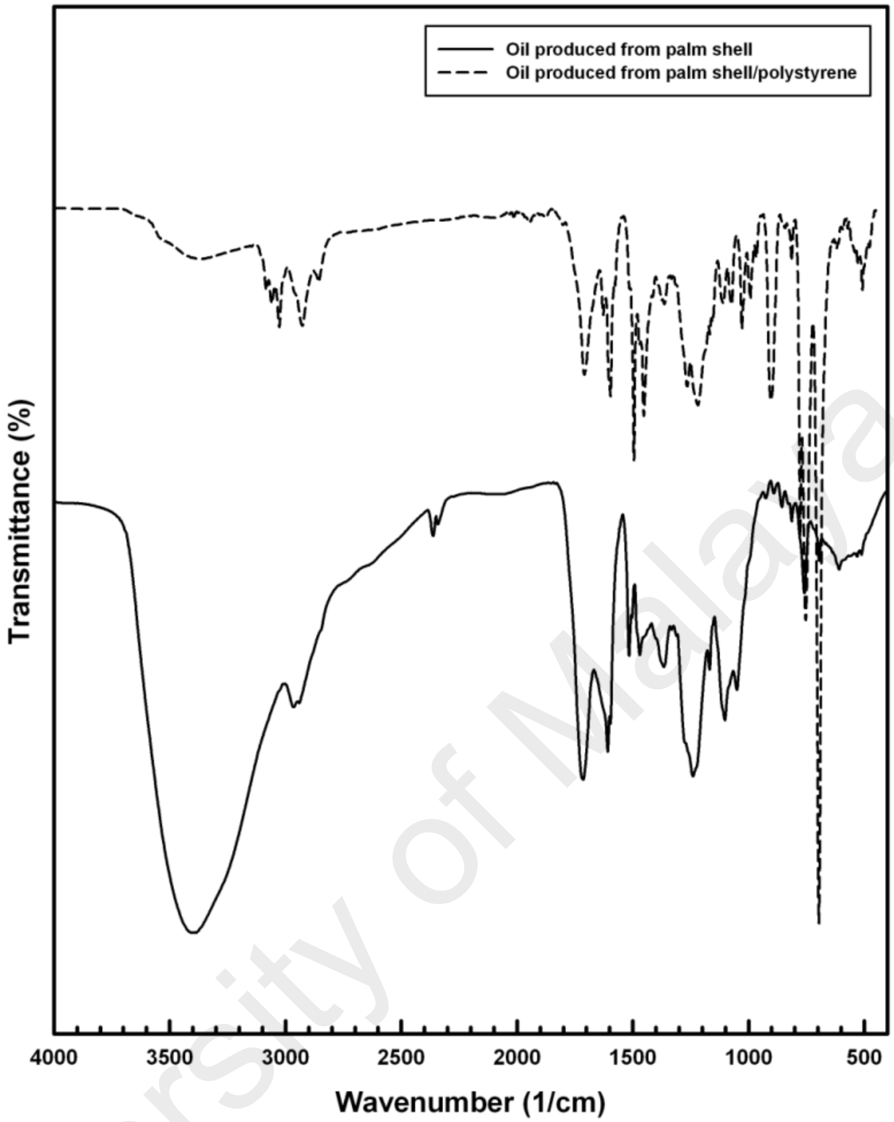


Figure 5.4: IR spectra of the oils produced from pyrolysis of palm shell alone and palm shell/polystyrene

Figure 5.4 shows the spectra of pyrolysis oils from FTIR analysis. The significant difference between the two oils was clearly observed for peaks in the range of 3200 and 3600 cm^{-1}, which indicated the presence of phenols and alcohols. The peaks also show the presence of oxygen in the oil, representative of O-H stretching vibrations. However, the peaks were observed clearly in the pyrolysis oil produced from palm shell. The strong peaks in the 730–770 cm^{-1} and 690–710 cm^{-1} ranges showed the presence of aromatic compounds, represented by C-H bending vibrations. These peaks were observed in the oil produced from the blend of materials.

Table 5.4 Compounds detected in obtained oil from pyrolysis of palm shell

No.	Compound	Area %	Group	Formula
1	Benzoic acid, 4-hydroxy-	2.59	Acid	$C_7H_6O_3$
2	Benzoic acid, 4-hydroxy-3-methoxy-	3.96	Acid	$C_8H_8O_4$
3	Hexadecanoic acid, methyl ester	0.25	Acid	$C_{17}H_{34}O_2$
4	Furfural	3.61	Furan	$C_5H_4O_2$
5	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.19	Ketone	$C_{10}H_{12}O_3$
6	Phenol	47.53	Phenol	C_6H_6O
7	Phenol, 2,6-dimethoxy-	11.24	Phenol	$C_8H_{10}O_3$
8	Phenol, 2-methoxy-	5.24	Phenol	$C_7H_8O_2$
9	Phenol, 2-methoxy-4-methyl-	5.45	Phenol	$C_8H_{10}O_2$
10	Phenol, 4-ethyl-2-methoxy-	3.18	Phenol	$C_9H_{12}O_2$
11	Vanillin	0.15	Phenol	$C_8H_8O_3$
12	.beta.-D-Glucopyranose, 1,6-anhydro-	0.73	Sugar	$C_6H_{10}O_5$
13	D-Allose	2.51	Sugar	$C_6H_{12}O_6$

The main purpose of GCMS analysis is to get an idea of the nature and types of compounds in the obtained oils. In this study, the detected compounds were identified by searching the MS library database; the results are listed in Table 5.4 and Table 5.5. However, since more than 100 peaks were detected, only the peaks with a high degree of probability (≥ 70%) and peak areas around or greater than 0.1% are included in the list. As can be seen in Table 5.4, the main chemical groups in the pyrolysis oil produced from palm shell include phenol, acid, sugar, ketone, and furan, which are typically the main primary products generated from biomass pyrolysis (Bertero et al., 2012; Lu et al., 2009). Amongst them, the proportion of phenol was found to be the highest in the oil, accounting for about 72.79% of the total. The high level of phenol typically found in pyrolysis oils from woody biomass is mostly contributed by lignin contained in the material (Mohan et al., 2006). In this study, the lignin component was found to be higher (around 44%) than that of cellulose (27.7%) or hemicellulose (21.6%).

Table 5.5: Compounds detected in obtained oil from pyrolysis of mixtures of palm shell and polystyrene

No.	Compound	Area %	Group	Formula
1	1,1'-Biphenyl, 3-methyl-	0.19	Aromatics	$C_{13}H_{12}$
2	1,1'-Biphenyl, 4-pentyl-	0.26	Aromatics	$C_{14}H_{12}F_2$
3	1H-Cyclopropa[l]phenanthrene,1a,9b-dihydro-	0.22	Aromatics	$C_{15}H_{12}$
4	3-Methyl-1-phenyl-1H-indene	1.49	Aromatics	$C_{16}H_{14}$
5	5H-Dibenzo[a,d]cyclohepten-5-one, 10,11-dihydro-	16.61	Aromatics	$C_{15}H_{14}$
6	6,7,8,9-Benzo[b]fluorene	1.14	Aromatics	$C_{17}H_{16}$
7	7-Isopropenyl-1,4a-dimethyl-4,4a,5,6,7,8-hexahydro-3H-naphthalen-2-one	1.42	Aromatics	$C_{15}H_{22}O$
8	9,10-Dimethylanthracene	0.41	Aromatics	$C_{16}H_{14}$
9	Anthracene	1.08	Aromatics	$C_{14}H_{10}$
10	Anthracene, 9,10-dihydro-	0.57	Aromatics	$C_{14}H_{12}$
11	Anthracene, 9-ethyl-9,10-dihydro-10-methyl-	0.86	Aromatics	$C_{17}H_{18}$
12	Bibenzyl	5.86	Aromatics	$C_{14}H_{14}$
13	Biphenyl	0.59	Aromatics	$C_{12}H_{10}$
14	Naphthalene	0.36	Aromatics	$C_{10}H_8$
15	Naphthalene, 1-methyl-	0.16	Aromatics	$C_{11}H_{10}$
16	Naphthalene, 2-phenyl-	7.07	Aromatics	$C_{16}H_{12}$
17	Phenanthrene, 1,2-dihydro-	0.28	Aromatics	$C_{14}H_{12}$
18	p-Terphenyl	0.81	Aromatics	$C_{18}H_{14}$
19	Pyrene, 1-methyl-	0.21	Aromatics	$C_{17}H_{12}$
20	.alpha.-Methylstyrene	1.51	Benzene	C_9H_{10}
21	1,2-Diphenylcyclopropane	5.11	Benzene	$C_{15}H_{14}$
22	1,3-Butadiene, 1,4-diphenyl-, (E,E)-	2.62	Benzene	$C_{16}H_{14}$
23	1H-Indene, 2-phenyl-	1.09	Benzene	$C_{15}H_{12}$
24	2,5-Diphenyl-1,5-hexadiene	4.31	Benzene	$C_{18}H_{18}$
25	3,5-Cyclohexadiene-1,2-dione, 3,4,5,6-tetrachloro-	0.24	Benzene	$C_6Cl_4O_2$
26	4-Ethylbiphenyl	0.20	Benzene	$C_{14}H_{14}$
27	Benzaldehyde	0.14	Benzene	C_7H_6O
28	Benzene, (1-methylene-2-propenyl)-	0.22	Benzene	$C_{10}H_{10}$
29	Benzene, (1-methylenebutyl)-	0.16	Benzene	$C_{11}H_{14}$
30	Benzene, (1-methylenepropyl)-	0.63	Benzene	$C_{10}H_{12}$
31	Benzene, (2-methylene-1-phenylcyclopropyl)-	0.42	Benzene	$C_{16}H_{14}$
32	Benzene, 1,1'-(1,3-butadienylidene)bis-	1.49	Benzene	$C_{16}H_{14}$
33	Benzene, 1,1'-(1,3-propanediyl)bis-	2.96	Benzene	$C_{15}H_{16}$

34	Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis-	3.19	Benzene	$C_{15}H_{16}$
35	Bicyclo[4.2.0]octa-1,3,5-triene	0.17	Benzene	C_8H_8
36	Dibenzo[a,e]cyclooctene	1.28	Benzene	$C_{16}H_{12}$
37	Ethylene, 1,1-diphenyl-	0.54	Benzene	$C_{14}H_{12}$
38	Styrene	6.13	Benzene	C_8H_8
39	Diphenylmethane	0.59	Benzene	$C_{13}H_{12}$
40	Benzhydryl isothiocyanate	0.10	Benzhydryl	$C_{14}H_{11}NS$
41	Bis(2-ethylhexyl) phthalate	0.20	Ester	$C_{24}H_{38}O_4$
42	Di-n-octyl phthalate	0.11	Ester	$C_{24}H_{38}O_4$
43	Furfural	0.52	Furan	$C_5H_4O_2$
44	2',6'-Dihydroxyacetophenone	0.27	Ketone	$C_8H_8O_3$
45	Phenol	5.37	Phenol	C_6H_6O
46	Phenol, 2,6-dimethoxy-	0.67	Phenol	$C_8H_{10}O_3$
47	Phenol, 2-methoxy-	0.55	Phenol	$C_7H_8O_2$
48	Phenol, 2-methoxy-4-methyl-	0.51	Phenol	$C_8H_{10}O_2$
49	Phenol, 2-methyl-	0.36	Phenol	C_7H_8O
50	Phenol, 4-ethyl-2-methoxy-	0.30	Phenol	$C_9H_{12}O_2$
51	Phenol, 4-methyl-	0.51	Phenol	C_7H_8O
52	Ethisterone	8.62	Progestogen	$C_{21}H_{28}O_2$

Furthermore, the results of GCMS analysis for the oil produced from blend materials are presented in Table 5.5. The results show that the quantity of phenol groups in the oil was reduced (around 8.27%), while compounds consisting entyrely of hydrogen and carbon were identified as abundant in the oil. This indicates that the oil can potentially be used as a combustible fuel source. The hydrocarbon groups in the oil were mostly found in the form of aromatics and benzene, with percent areas of 39.59% and 32.99%, respectively. In addition, the finding by GCMS analysis is in good agreement with the result of FTIR analysis.

5.4 The energy potential from pyrolysis oils

The energy potential was calculated based on the total amount of polystyrene waste available in Malaysia (280,000 tons/year). The amount of the waste was established as a

50% ratio. So, the total quantity of wastes that can be used for production of pyrolysis oil is:

Total feedstock (A) = 50% ratio of polystyrene + 50% ratio of palm shell

= 280,000 + 280,000 = 560,000 tons/year

As shown in Figure 5.3, the oil obtained by pyrolysis of palm shell mixed with polystyrene accounted for 61.63 wt% of the raw materials. Therefore, the total pyrolysis oil that can be produced per year through the pyrolysis process is:

Total of pyrolysis oil yield (B) = A × 61.63 wt%

= 560,000 × 61.63 wt% = 345,128 tons/year

As shown in Table 5.3, the oil from pyrolysis of palm shell mixed with polystyrene has a HHV of 38.01 MJ/kg. The total amount of pyrolysis oil is equal to 345,128,000 kg/year. Hence, the total energy contained in the oil is:

Energy contained in oil = B x HHV of oil

= 345,128,000 x 38.01 = 13,118,315,280 MJ/year

= 13.12 PJ/year

A comparison of potential energies from different pyrolysis oils is given in Table 5.6. The use of palm shell waste as a source of biomass energy by producing pyrolysis oil has the potential to contribute 3.08 PJ/year to Malaysia's energy supply. This number increases to 13.12 PJ/year when polystyrene waste is included in the palm shell pyrolysis.

Table 5.6: Projection of energy potential from pyrolysis oils

Type of sample	Feedstock (tons/year)	Liquid Yield (kg/year)	HHV (MJ/year)	HHV (PJ/year)
Palm shell	560,000	258,328,000	3,084,436,320	3.08
Palm shell/polystyrene	560,000	345,128,000	13,118,315,280	13.12

5.5 Conclusions

This study has shown that pyrolysis of palm shell mixed with polystyrene waste has the potential to be a suitable method for producing high-grade pyrolysis oil that has a high liquid yield (61.63 wt%). This quantity of oil was obtained with a process temperature of 500 ºC, a reaction time of 60 min, a N_2 flow rate of 2 L/min, and without any catalysts or solvents. The oxygen content was significantly changed from 71.40 wt% to 7.82 wt% without any change in parameter settings and free of hydrogen pressure. The synergistic effect in the pyrolysis of the palm shell/polystyrene mixtures also plays an important role in increasing the HHV of the liquid. Therefore, this method can be considered a simple, cheap, and effective procedure to obtain high-grade pyrolysis oil. In addition, by using this method, the volume of palm shell and polystyrene wastes is easy to control. Using these wastes to produce pyrolysis oil could contribute to reducing the landfill needed, decreasing the cost for waste treatment, and solving some environmental problems. Furthermore, it can also be noted that this is an optional solution to increase energy security in Malaysia.

CHAPTER VI

CO-PYROLYSIS OF PALM SHELL AND POLYSTYRENE WASTE MIXTURES TO SYNTHESIS LIQUID FUEL: AN OPTIMIZATION STUDY

6.1 Introduction

The use of palm shell and polystyrene wastes for recovery of liquid fuel by co-pyrolysis is the key to overcoming environmental problems stemming from the high volume of palm shell waste generated by the oil palm industry. In 2007, a study reported that the amount is about 4.7 million tons (Sumathi et al., 2008) and then sharply increased up to 5.2 million tons in 2009 as reported by Mohammed et al (2011). Most often it is left to decompose naturally, with only a fraction of it used to cover road surfaces in the plantation area or burned for steam generation (Abnisa et al., 2011; Yang et al., 2004).

Furthermore, a study estimated that well over 280,000 tons of waste polystyrene is produced annually in Malaysia, most of it by food packagers (Mohammed, 2010). The volume of polyethylene waste has increased as the product gets wider use because of its light weight, durability, and low cost (Panda et al., 2010). Currently most of this waste is dumped in landfill sites, which will pose environmental and social problems as volumes accumulate (Manaf et al., 2009). Because polystyrene waste is not biodegradable, dumping in the landfill site is not an environmentally friendly option. This study investigates the possibility of producing liquid fuel by co-pyrolysis of this waste material with the palm shell waste that is also causing environmental concerns.

Pyrolysis is one method used to recover potential energy in biomass and plastic wastes. This method is useful to break down the waste materials into three products; char, liquid, and gas in an inert environment. Pyrolysis is known to be an environmentally friendly method because no wastes are produced during the process.

The liquid is attractive because its properties show its potential for use as chemical feedstock or fuel. A number of studies of liquid fuel production have been reported at various scales and with varying success (Ali & Siddiqui, 2005; Luo et al., 2004; Singh & Shadangi, 2011).

The yield of liquid from co-pyrolysis depends on the relationship of parameters set in the process. An optimization study was needed to adjust the parameters to maximize the production of liquid. One of the methods used to solve the optimization problem is to apply response surface methodology (RSM). The method is a statistical approach to analysis of the relationship between several selected variables and one or more defined responses (Baş & Boyacı, 2007). RSM can include designing experiments from the collection of statistical techniques, building models, evaluating the effects of variables, and searching for the optimum conditions of variables for desirable responses (Su et al., 2009). The RSM has been widely used in optimization of pyrolysis process variables for several purposes (Abnisa et al., 2011; Arami-Niya et al., 2011; Ellens & Brown, 2012; Isa et al., 2011; Tan et al., 2008).

In general, plastic has been recognized by many researchers as a good material to produce liquid fuel. Some studies showed that the pyrolysis of plastic resulted in high oil yield, particularly with polystyrene (Ayhan, 2004; Kaminsky et al., 2004; Kiran et al., 2000; Liu et al., 2000; López et al., 2011b). The authors also reported that the quality of the oil was acceptable for use as a fuel. It mainly consisted of aliphatic and aromatic hydrocarbons. Aliphatic hydrocarbons include alkadienes, alkenes (paraffin, olefins) and alkanes (methane, ethane, heptane, octane, propane). Aromatic hydrocarbons include styrene, toluene, benzene, cumene, ethylbenzene, monocyclic aromatics (alkyl benzenes, alkyl toluene) and polycyclic aromatics (naphthalene, methylnaphthalene and ethylnaphthalene). On the other hand, the oil produced from biomass is found to contain high amounts of oxygen (35-40 wt%) and water (15-50 wt%) (Bridgwater, 2012), which causes the liquid to have a low high heating value (HHV). Typically, the HHV of oil from biomass has been approximately 17 MJ/kg. In comparison, the oil produced from plastics has shown a HHV in the range of 37-40 MJ/kg (Onwudili et al., 2009).

In this work, co-pyrolysis of palm shell mixed with polystyrene waste was carried out to evaluate the yield and quality of liquid produced. The mass ratio between palm shell and polystyrene waste, temperature, and reaction time were chosen as independent variables. The process was optimized by using response surface methodology with the aim of maximizing liquid yield. The liquid obtained was tested for pH, density, viscosity, water content, elemental analysis, and Fourier transform infrared (FTIR).

6.2 Materials and Experimental

6.2.1 Materials

The palm shell was collected from a local processing plant in Kuala Lumpur. The polystyrene waste was obtained from a local rubbish collection point. The palm shells were oven-dried at 105 ºC for 24 h; the polystyrene was dried under the sun for several days. Then, both materials were ground to the desired size of 1-2 mm.

6.2.2 Experimental

The experiment was carried out by charging 100 g of feed into a stainless steel tubular reactor with an internal diameter of 5.0 cm and a length of 127 cm. The reactor was heated by an external vertical furnace. The temperature was monitored using a K-type thermocouple located inside the reactor. To minimize secondary reactions during the process, 2 L/min of nitrogen flow was applied for all experiments. The process flow of experimental work was presented in Figure 6.1.

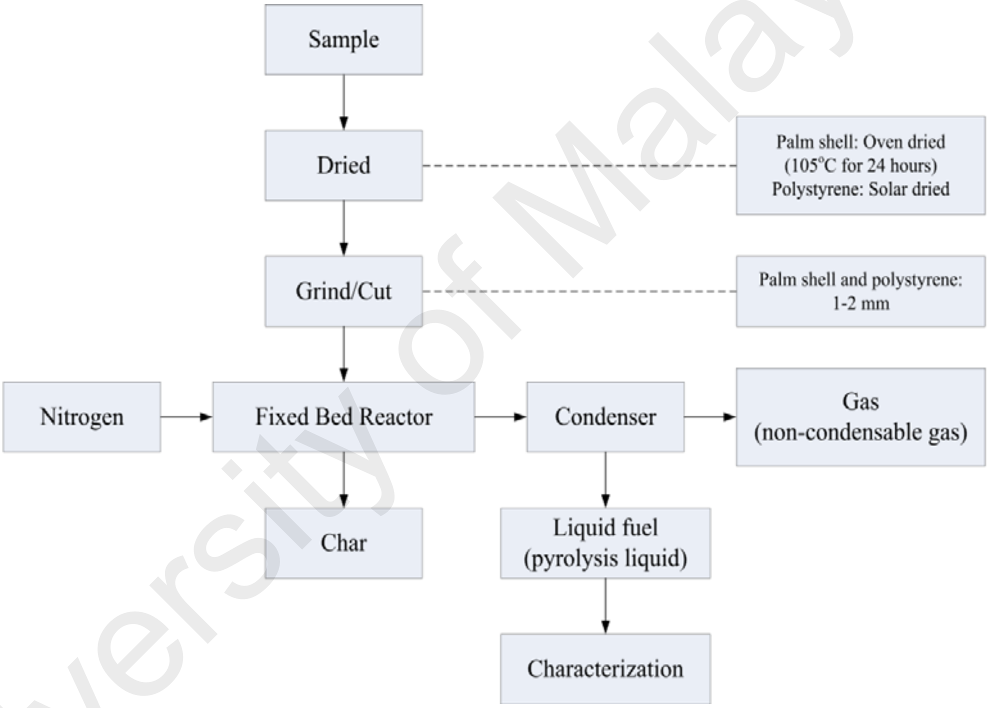


Figure 6.1: Process flow for the recovery of liquid fuel by co-pyrolysis of palm shell and polystyrene waste mixtures

6.2.2.1 Screening point of parameters

The aims of the screening study were to obtain the reference data that were used later for the optimization study and also to observe the effect of each parameter on production of the liquid during co-pyrolysis. Three effective parameters were applied in this study with each parameter being evaluated at five different points. Each point was investigated to select the points that produced the largest volume of pyrolytic liquid.

Table 6.1: Specification of variables and the experimental domain

Variables	Experimental domain		
	(-1)-level	0-level	(+1)-level
A: Temperature (ºC)	400	500	600
B: Ratio of palm shell/polystyrene (%)	60:40	50:50	40:60
C: Reaction time (min)	15	30	45

Table 6.2: The CCD matrix of experimental and yield response

Run	Actual variables			Coded levels			Response
	Temperature (°C)	Ratio (palm shell: polystyrene)	Reaction time (min)	A	B	C	Liquid Yield (wt%)
1[a]	500	50:50	30	0	0	0	61.2
2[b]	400	40:60	15	-1	1	-1	60.8
3[b]	600	60:40	45	1	-1	1	57.2
4[c]	500	60:40	30	0	-1	0	56.6
5[a]	500	50:50	30	0	0	0	61.2
6[b]	400	60:40	15	-1	-1	-1	50.2
7[b]	600	40:60	45	1	1	1	68.3
8[c]	400	50:50	30	-1	0	0	60.8
9[c]	500	50:50	45	0	0	1	61.3
10[b]	400	40:60	45	-1	1	1	62.9
11[a]	500	50:50	30	0	0	0	61.1
12[a]	500	50:50	30	0	0	0	61.3
13[a]	500	50:50	30	0	0	0	61.3
14[c]	500	40:60	30	0	1	0	64.1
15[a]	500	50:50	30	0	0	0	61.3
16[b]	600	60:40	15	1	-1	-1	55.2
17[b]	400	60:40	45	-1	-1	1	55.3
18[c]	500	50:50	15	0	0	-1	56.9
19[c]	600	50:50	30	1	0	0	62.2
20[b]	600	40:60	15	1	1	-1	64.1

The different markings in run order mean (a) center point, (b) factorial design, and (c) axial point.

The study was divided into several parts. The first part was to study the influence of reaction time on co-pyrolysis yields by applying the fixed parameters of feed ratio (50:50) and temperature (400 ºC). The reaction times were varied from 15 to 75 min.

The second stage was to obtain the temperature effect. With the feed ratio fixed at 50:50 and reaction time constant at 30 min, the temperatures were varied in 100 °C increments from 300, to 700 ºC.

The same procedure was followed to study the effect of feed ratio. The ratios of palm shell waste to polystyrene chosen were 80:20, 70:30, 60:40, 50:50 and 40:60. The yields of pyrolytic liquid, char, and non-condensable gas for all the experiments were calculated using Eq. 6.1.

$$\text{Yield of product} = \frac{\text{Desired product}}{\text{Total feed}} \times 100\,\% \tag{6.1}$$

6.2.2.2 Optimization study

The three points of each parameter that produced the highest yield of pyrolytic liquid were chosen for the optimization study. This study was designed to identify the variables that have the largest influence on the process and then develop the variables in the polynomial model. Therefore, RSM was used to determine the optimum and experimental design matrix in this study specified according to the central composite design (CCD) method. The variables and the experimental domain in this design are specified in Table 6.1. The CCD consists of axial points (2n), the number of independent variables (2^n) and replications of center points (n_c). Thus, the CCD in this study consists of 2n = 6, $2^n = 8$ and $n_c = 6$, resulting in 20 experiments. The CCD matrix for varying 3 variables was constructed in Table 6.2. All experiments were performed randomly to reduce the effect of unexplainable variance in the observed response caused by unrelated variables. After running the experiments, the results were fitted to a quadratic polynomial model to predict the system response as given in Eq. 6.2.

$$Y = \beta_O + \sum_{i=1}^{n} \beta_i \times X_i + \sum_{i=1}^{n} \beta_{ii} \times X_i^{\,2} + \sum_{i=1}^{n} \sum_{j>1}^{n} \beta_{ij} \times X_i X_j \qquad (6.2)$$

where Y is the predicted response; n is the number of experiments; β_o, β_i, β_{ii} and β_{ij} are regression coefficients for the constant, linear, quadratic and interaction coefficients, respectively; and X_i and X_j are the coded independent factors.

In this study, Design Expert software Version 8.0.0 (Stat-Ease, Inc., Minneapolis, USA) was used to design the experiments, do the analysis of variance (ANOVA) which includes the development of the quadratic model, and do the regression analysis and graphical analysis (three-dimensional response surface).

6.2.2.3 Characterization of pyrolytic liquid

The liquid products were produced with the optimum parameters conditions were characterized for viscosity, density, pH, water content, elemental analysis, and FTIR.

Viscosity is an important property in chemical process design. Viscosity data are essential for various heat transfer considerations, calculating pressure drop, distillation calculations and mixing system considerations. For fuels, viscosity data are used to evaluate the effect on pumping and injecting. In this study, measurement of viscosity was determined using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer model DV-II+Pro EXTRA). The measurement was taken at 50 ºC with about 7 ml of sample required for the test.

One of the important physical characteristic of a material is density. Density describes the quantity of mass material divided by its volume. In this study, a 25 ml pycnometer was used to determine the density of the pyrolytic liquid. The measurement was started by carefully filling the liquid into the pycnometer and then measuring the mass. The density was determined by dividing the mass of pyrolytic liquid by the empty volume of the pycnometer. The analysis was conducted at 24 ºC. The density calculation can be expressed by Eq. 6.3 where ρ is density, m is the mass of sample, and V is the volume.

$$\rho = m / V \tag{6.3}$$

The testing of acidity or basicity in the pyrolytic liquid was indicated through pH measurement. The pH measurement is necessary in many chemical processes such as for adjustment of the chemical reaction and to avoid corrosion problems. In this study, the pH was measured using a Metrohm pH meter series 827 at 25 ºC.

Water content is one of the unexpected presences in the pyrolytic liquid. The water content of the pyrolytic liquid was measured using a Karl Fischer 737 KF Coulometer from Metrohm. About 80 ml of Hydranal-coulomat AG was used as anolyte reagent and 5 ml of Hydranal-coulomat CG was used as catholyte reagent. Approximately 2-6 mg of pyrolytic liquid was injected trough a titration cell into a flask. When the titration is completed, the instrument beeps 1 time and shows water content as either a percentage (%) or in ppm of water on the display panel.

Elemental analysis is a combustion analysis technique to determine the mass fractions of carbon, hydrogen, nitrogen, and heteroatoms of a sample. The data analysis is helpful in identifying unknown compounds or to verify the structure and purity of a synthesized compound. The elemental analysis were carried out using a Model 2400 Perkin-Elmer Series II CHNS/O Analyzer to determine C, H, N, and S. The oxygen content was determined by a difference.

The data obtained from elemental analysis were also used for calculating the HHV. HHV describes the quantity of energy that is released as heat by complete combustion of a compound, assuming the water contained in the sample and that generated from the combined hydrogen remains in liquid form (Añón et al., 1995). In this study, the HHV of pyrolytic liquid was calculated from elemental analysis using the equation given by Friedl et al. (2005) that specifically designed for biomass fuels.

$$\mathrm{HHV\,(kJ/kg)} = 3.55\mathrm{C}^2 - 232\mathrm{C} - 2230\mathrm{H} + 51.2\mathrm{C}\times\mathrm{H} + 131\mathrm{N} + 20{,}600 \qquad (6.4)$$

A Perkin Elmer FTIR spectrometer (Spectrum 400) was used to obtain an infrared spectrum of absorption in the pyrolytic liquid. The samples were scanned in the range of 400 to 4000 $\mathrm{cm^{-1}}$ with a resolution of 4 $\mathrm{cm^{-1}}$. FTIR analysis is a technique that is useful for characterization of organic (including polymer) and inorganic compounds. The result of FTIR provides information about the types of chemical bonds (functional groups) and molecular structure.

6.3 Results and Discussion

6.3.1 Screening study on parameter process

6.3.1.1 Influence of reaction time on oil yield.

Reaction times of 15, 30, 45, 60, and 75 min at temperature 400 °C and a 50:50 ratio of palm shell waste to polystyrene were studied in this experiment. The effect of using different reaction times on the yield of the liquid from co-pyrolysis of palm shell and polystyrene is represented in Figure 6.2a. The maximum oil yield of 61.6 wt% was obtained at a reaction time of 45 min. This liquid yield is greater than that obtained from a previous study in which the oil yield was 46.1 wt% at 500 °C and a reaction time of 60 min for the pyrolysis of palm shell alone (Abnisa et al., 2011). The initial weight of liquid was 56.1 wt%, obtained at a reaction time of 15 min. This percentage increased as reaction time was increased to 45 min. Further increment of reaction time caused a decrease in the yield of liquid product. Non-condensable gas output, however, increased slightly with increasing reaction time. These variations in the liquid and non-condensable gas yields can be explained due to the secondary reactions of pyrolysis vapors generating lower-molecular-weight non-condensable gaseous products as the reaction time increases (Açıkalın et al., 2012). These results are in agreement with the work of Paradela et al. (2009), who studied the slow batch pyrolysis of mixtures of plastics, tyres, and forestry biomass wastes.

6.3.1.2 Influence of temperature on oil yield.

The temperatures of 300, 400, 500, 600 and 700 °C were studied with reaction time fixed at 30 min and a 50:50 ratio of palm shell waste to polystyrene. Figure 6.2b shows the maximum oil yield at different temperatures.

This study suggests that no significant decomposition occurred at 300 °C. The oil yield shows a significant increase after the pyrolysis temperature reached 400 °C and beyond. This may be explained trough thermal decomposition of the polystyrene. As mentioned by R.S. Chauhan et al. (2008), the decomposition of polystyrene occurred at temperatures of 350 °C and above. From this, we concluded that the contribution of polystyrene in co-pyrolysis of biomass can be achieved above 350 °C.

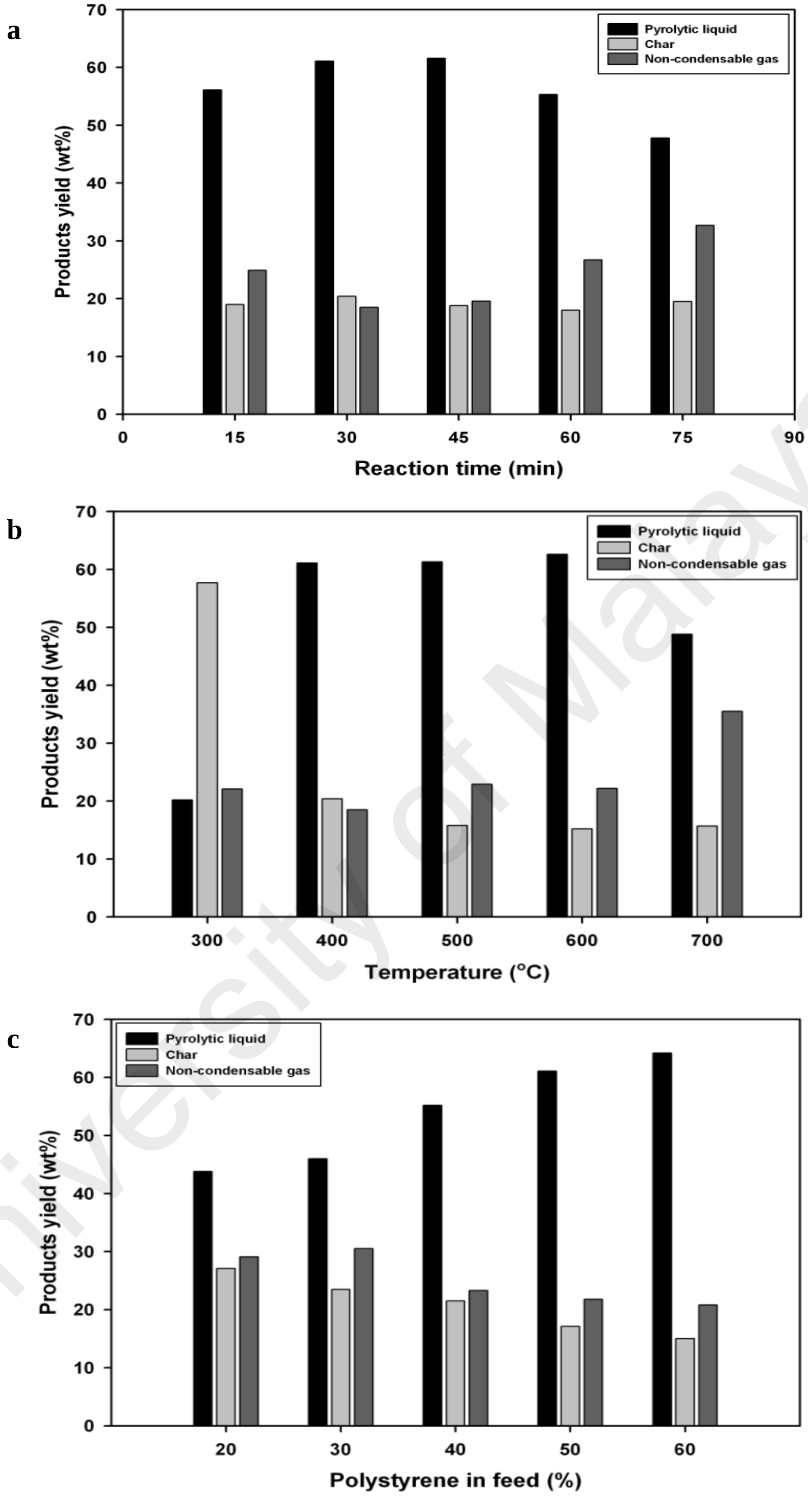


Figure 6.2: The product yields with respect to (a) different reaction time at constant temperature of 400°C and 50:50 palm shell to polystyrene ratio, (b) different temperature with 30 min reaction time and 50:50 palm shell to polystyrene ratio, (c) different polystyrene percentage in feed at constant temperature of 400°C and reaction time of 30 min

Unlike polystyrene, the thermal decomposition of palm shell starts above 220 °C. The material components start to decompose at 220–320 °C for hemicellulose, 320–370 °C for cellulose, and 320–500 °C for lignin (Hardy et al., 2012). As described in the literature, the decomposition of hemicellulose and cellulose mostly contributed to the formation of liquid (Akhtar & Amin, 2012), while the decomposition of lignin is found to be the main contributor to the final char weight (Williams & Besler, 1993). In this study, the palm shell composes of 27.7 % cellulose, 21.6 % hemicellulose, and 44 % lignin.

6.3.1.3 Influence of palm shell waste to polystyrene ratio on oil yield.

The ratio of palm shell to polystyrene waste in the feed were varied at 80:20, 70:30, 60:40, 50:50 and 40:60 with both temperature and reaction time kept constant at 400 °C and 30 min, respectively. Figure 6.2c show that a higher percentage of polystyrene in the feed resulted in a higher oil yield. The oil yield increases with the decrease of the gaseous product. The maximum oil yield obtained was 64.2 wt% at the 40:60 palm shell to polystyrene waste ratio. The presence of polystyrene could provide more hydrocarbons during co-pyrolysis with palm shell and can lead to an increase of liquid production.

6.3.2 Optimization study on parameter process

6.3.2.1 Development and evaluation of model

The results from the screening study showed that the high liquid yields were obtained in the temperature range of 400 to 600°C, reaction time of 15 to 45 min and palm shell/polystyrene ratio of 40:60 to 60:40. All of the result data were input to the Design Expert software to generate the 20-experiment design matrix for the optimization study. The results from 20 experiments showed that the liquid yield varied from 50.2 wt% to

68.3 wt%. Then, all results were used to develop a coded factor model of the pyrolytic liquid yield. The coded factor model developed to fit a polynomial model is represented in Eq. 6.5, where Y is yield of pyrolytic liquid, A is temperature, B is ratio, and C is reaction time.

Table 6.3: ANOVA for response surface quadratic model

Source	Sum of Squares (SS)	Degree of Freedom (df)	Mean Square	F-Value	*p*-value Prob > F	Remarks
Model	289.234	9	32.137	38.758	< 0.0001	significant
A-Temperature	28.900	1	28.900	34.854	0.0002	
B-Ratio	208.849	1	208.849	251.874	< 0.0001	
C-Reaction Time	31.684	1	31.684	38.211	0.0001	
AB	0.405	1	0.405	0.488	0.5006	
AC	0.125	1	0.125	0.151	0.7060	
BC	0.080	1	0.080	0.096	0.7625	
A^2	0.818	1	0.818	0.987	0.3440	
B^2	1.005	1	1.005	1.212	0.2967	
C^2	9.458	1	9.458	11.407	0.0070	
Residual	8.292	10	0.829			
Lack of Fit	8.258	5	1.652	247.755	< 0.0001	significant
Pure Error	0.033	5	0.007			
Cor Total	297.526	19				

R^2 = 0.972; Adjusted R^2 = 0.947; Q^2 = 0.610; Adeq Precision = 25.004; *PRESS* = 116.01.

$$\begin{aligned} \mathrm{Y} = {} & 61.12 + 1.70(\mathrm{A}) + 4.57(\mathrm{B}) + 1.78(\mathrm{C}) + 0.22(\mathrm{A})(\mathrm{B}) \\ & - 0.12(\mathrm{A})(\mathrm{C}) - 0.100(\mathrm{B})(\mathrm{C}) + 0.55(\mathrm{A}^2) \\ & - 0.60(\mathrm{B}^2) - 1.85(\mathrm{C}^2) \end{aligned} \tag{6.5}$$

The results of ANOVA were summarized in Table 6.3. The analysis showed that the *p*-value (less than 0.05) as a statistic test indicated that the model terms are significant. In this case, A, B, C, and C^2 are significant model terms. The parameter having the most significant effect on pyrolytic liquid yield is the ratio (B) since the *p*-value of B is the smallest in value compared to other conditions. The results obtained in the screening study support this finding. Yield increased from 43.8 wt% at the palm shell to polystyrene waste ratio of 80:20 to 64.2 wt% at the 40:60 ratio. The same trends also occurred at flash co-pyrolysis of the mixtures of willow-Salix and polyhydroxybutyrate (PHB) that were studied by Cornelissen et al (2008a). Their study reported that the significant enhancement of liquid product was observed when PHB was at a higher ratio than willow. Furthermore, the model developed also shows a high determination coefficient of R^2 (0.972), indicating a close fit of the model to the actual data. R^2 can be calculated using Eq. 6.6. The actual value represents the response data from the experiment; the predicted value represents the value obtained from the model.

$$R^2 = 1 - SS_{resid} /(SS_{\mathrm{mod}\,el} - SS_{resid}) \tag{6.6}$$

Another analysis to evaluate the fit of a model is Q^2. The Q^2 describes how well the response can be predicted in the model. The Q^2 can be calculated using *PRESS* (the prediction residual sum of squares) following Eq. 6.7. In this study, Q^2 was 0.610. Generally, a $Q^2 > 0.5$ is regarded as good and a $Q^2 > 0.9$ as excellent (Eriksson et al., 2006).

$$Q^2 = 1 - (PRESS/(SS_{\mathrm{mod}\,el} + SS_{resid})) \tag{6.7}$$

6.3.2.3 Three-dimensional response surfaces and interpretation of optimization plot.

Based on the ANOVA, the effect of the three parameters studied (ratio, reaction time, and temperature) were found to be significant on the liquid fuel yield, and a three-dimensional response surface was developed. Three-dimensional response surfaces plotted for the yield of pyrolytic liquid from variation of the palm oil and polystyrene ratio and temperature are shown in Figure 6.3. The figure shows that both an increase in the ratio of polystyrene and increasing temperature improved the yield of liquid. The highest yield was obtained when variables of ratio and temperature reached the maximum point, which was a reaction time set constant at 30 min.

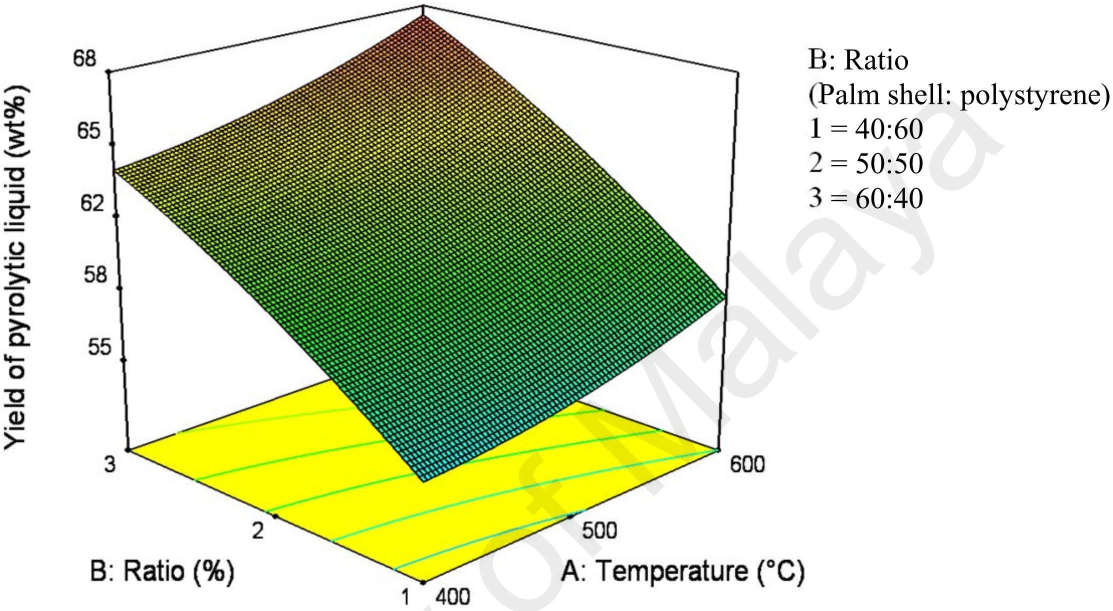


Figure 6.3: Three-dimensional response surfaces plot of pyrolytic liquid yield with the combined effect of feed ratio and temperature (at constant reaction time of 30 min)

Figure 6.4 shows the three-dimensional response surface plot for the yield of pyrolytic liquid from variation of reaction time and temperature. The maximum yield of 63 wt% was obtained at the optimal condition of a 30 min reaction time and the temperature at 600°C with a feed ratio of 50:50.

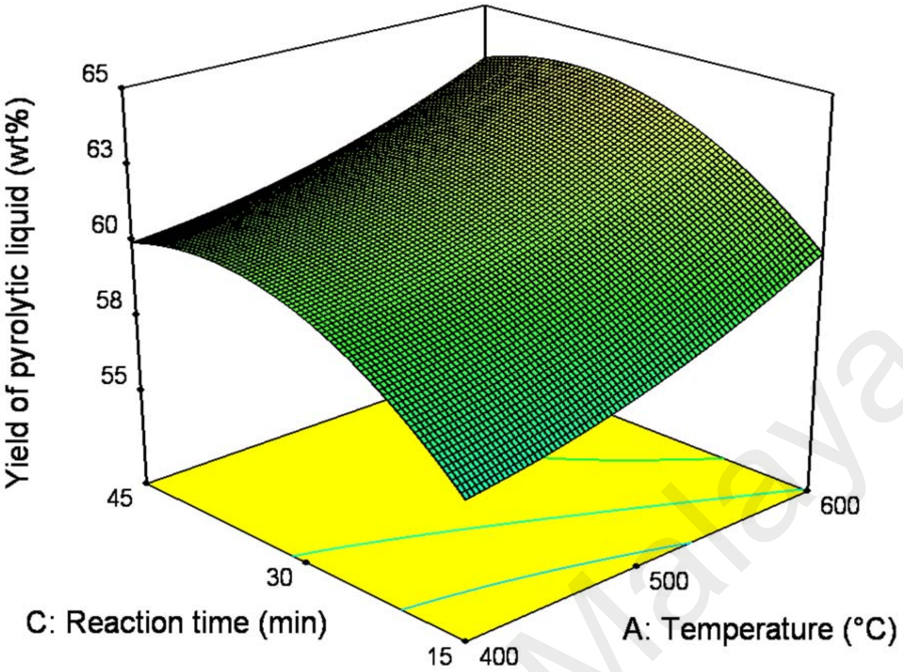


Figure 6.4: Three-dimensional response surfaces plot of pyrolytic liquid yield with the combined effect of reaction time and temperature (at constant ratio of 50:50)

The three-dimensional response surface plot for the yield of pyrolytic liquid from variation of the palm shell waste to polystyrene ratio and reaction time is shown in Figure 6.5. In Figure 6.5, the optimum conditions of a palm shell waste and polystyrene ratio of 40:60 and reaction time of 30 min were obtained for maximum liquid yield of 65 wt%. The temperature was kept constant at 500°C.

One of advantages of optimization plots is their help in getting a predicted response with a higher desirability score (Hasan et al., 2009). In this study, the quadratic model presented in Eq. 6.5 was used to optimize the yield of pyrolytic liquid. The model predicted that for a temperature of 600°C, a ratio at 40:60 (palm shell:polystyrene), and 45 min of reaction time, pyrolytic liquid production would be at a maximum of about 67.3 wt%. To validate the model prediction, one additional experiment with three repetitions were needed using the variables the model predicted. The final result showed that the liquid was at a maximum of about 68.3 wt% with a deviation error of 1.48 %. The correlation of results from the experiments with the model prediction proved that the model is suitable for predicting the optimization of pyrolytic liquid with variables of temperature, ratio, and reaction time.

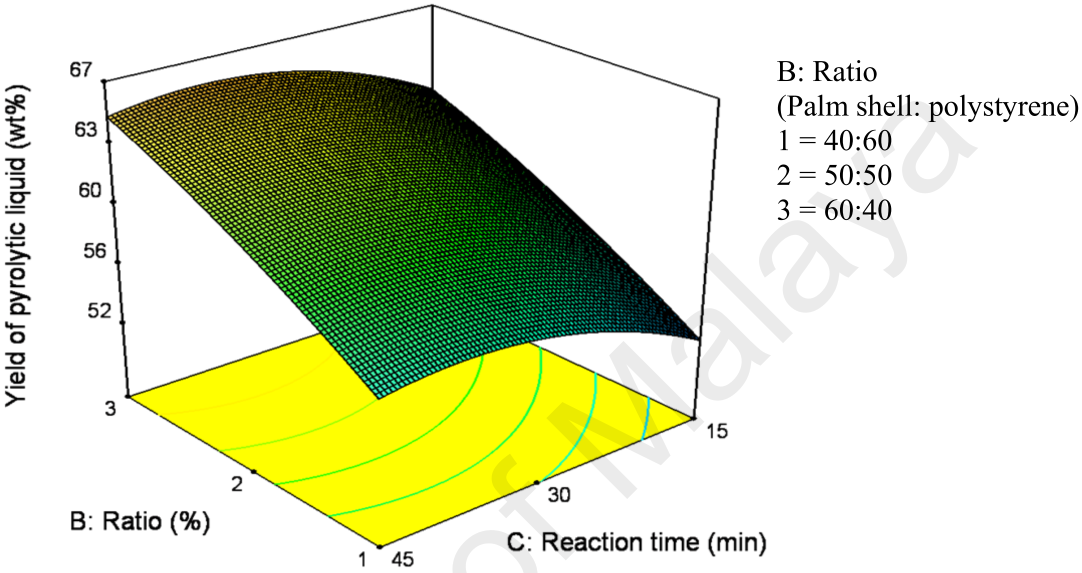


Figure 6.5: Three-dimensional response surfaces plot of pyrolytic liquid yield with the combined effect of feed ratio and reaction time (at constant temperature of 500°C)

6.3.3 Characterization of pyrolytic liquid

The pyrolytic liquid was obtained under optimum conditions (temperature of 600 °C, ratio of palm shell/polystyrene of 40:60, and reaction time of 45 min) was used for characterization of physical and chemical properties. The summary of this characterization is given in Table 6.4. The viscosity of the pyrolytic liquid was 8.28 cP. The liquid from co-pyrolysis of palm shell and polystyrene mixtures showed higher viscosity compared to pyrolysis of palm shell alone as described in a previous study (Abnisa et al., 2011). The decomposition of inorganic material in polystyrene may have contributed to the higher viscosity.

Table 6.4: Physical and chemical properties of pyrolytic liquid

Properties	Value	Unit
Viscosity at 50 °C	8.28	cP
pH	2.8	
Density at 24 °C	1058	kg/m^3
Elemental composition (wet basis)		
C	81.34	wt%
H	7.79	wt%
N	0.38	wt%
O (by differences)	10.50	wt%
High Heating Value (HHV)	40.34	MJ/kg
Water content	1.9	%

The densities of polystyrene and palm shell were shown to be about 1110 kg/m^3 (Rutkowski & Kubacki, 2006) and 1051 kg/m^3 (Abnisa et al., 2011), respectively. After co-pyrolysis, the liquid from the mixture of wastes was about 1058 kg/m^3 at 24°C. It was noted that the conversion of palm shell and polystyrene mixtures into pyrolytic liquid reduced the density of the wastes. It means that the area needed for liquid storage is smaller than the area needed for a landfill site of waste.

The pH value of liquid from this study was 2.8. The result is in good agreement with the results in the literature (Lu et al., 2009). The pH value in the range of 2 to 4 indicated the presence of organic acid such as acetic acid and formic acid. The acidity of pyrolytic liquid thus can lead to corrosion problems in both vessels and piping systems.

The average water content shown by the Karl Fischer method was about 1.9 %. Compared to a previous study, the mixture of palm shell and polystyrene feed resulted in a significant decrease in water content, which results in an increased HHV in the pyrolytic liquid. This reduction in water content was consistent with the results reported by Rotliwala & Parikh (2011). In that study, the co-pyrolysis of deoiled cake of jatropha and waste commercial polyolefins resulted in very low water content in the pyrolytic liquid.

As can be seen in Table 6.4, the results from an elemental analysis of the pyrolytic liquid show a high percentage of carbon (86.57 wt%). The oxygen in the liquid was found to be about 4.24 wt%. The low value of oxygen contributed to the high HHV of about 40.34 MJ/kg determined using Eq. 6.4. In addition, the HHV of the pyrolytic liquid from this study is very close to that of conventional fuel oil (about 42 to 44 MJ/kg) that were reported in the literature (Bridgwater & Peacocke, 2000).

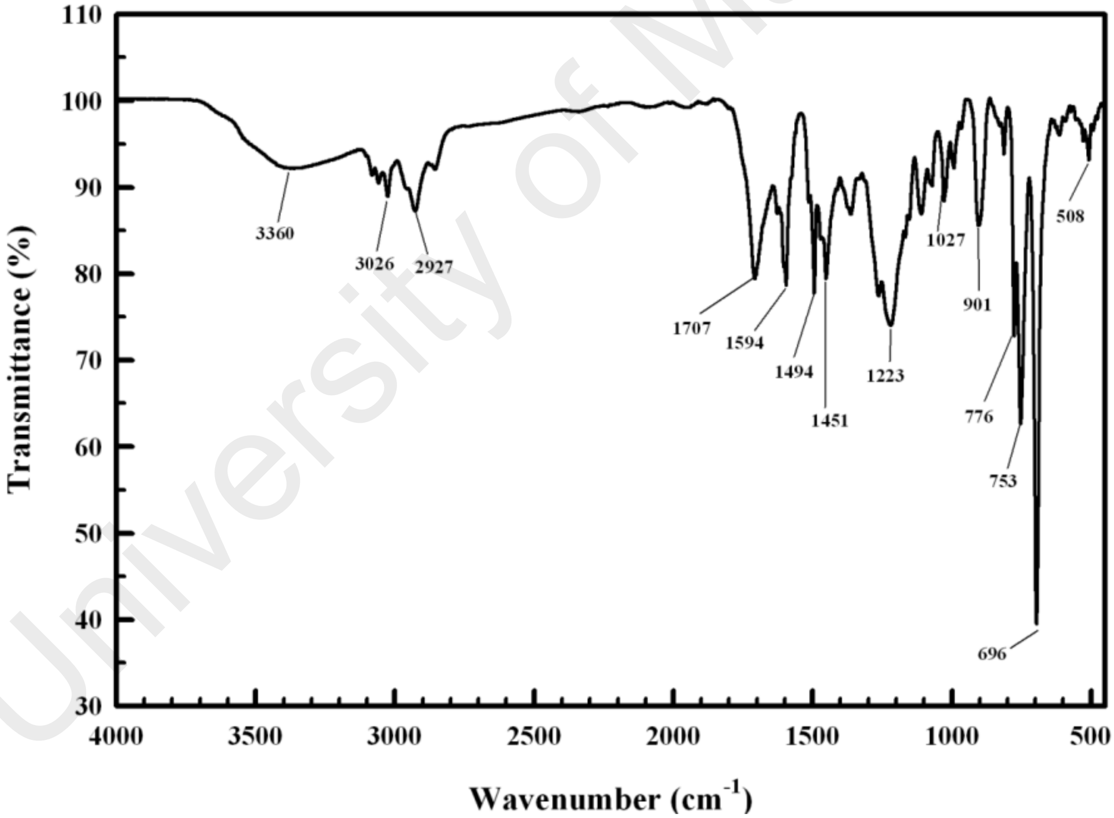


Figure 6.6: FTIR spectrum of pyrolytic liquid obtained at conditions temperature of 600°C, ratio of palm shell/polystyrene of 40:60, and reaction time of 45 min

Figure 6.6 shows the spectrum result of pyrolytic liquid from the FTIR analysis. The result showed that the liquid produced from the mixture of palm shell and polystyrene was dominated by aliphatic hydrocarbons. Aliphatic hydrocarbon such as alkenes and alkanes were detected at absorption peaks in the range of 3100 to 3010 cm^{-1} and 3000 to 2850 cm^{-1}, respectively. The strong peaks in the range of 900 to 690 cm^{-1} showed the presence of aromatic hydrocarbons or arenes that are represented by C-H bending vibration. The presence of oxygen in the liquid was represented by the C=O stretching vibration between 1670 and 1820 cm^{-1} which indicated a carbonyl group. Then, the O-H stretching vibration that was observed at peaks in the range of 3600 to 3200 cm^{-1} and the C-O stretching vibration in the range of 1300 to 1000 cm^{-1} were identified as alcohols and esters. The aromatic compounds are represented by the C=C stretching was observed at peaks in the range of 1600 to 1400 cm^{-1}. The low intensity absorption peak at 508 cm^{-1} was caused by commercial antimony oxide, which is used as a flame retardant additive for polystyrene.

6.4 Conclusions

The results were showed that the high liquid yields was obtained in the range temperature of 400 to 600 °C, reaction times of 15 to 45 min and palm shell/polystyrene ratios of 40:60 to 60:40. The optimization study using response surface methods indicates that the ratio of feed was the most significant variable on liquid yield. The polynomial model obtained fits well to predict the response with a high determination coefficient of R^2 (0.972) and Q^2 (0.610). The characteristic results showed that the HHV and the composition of the pyrolytic liquid were very close to those of conventional fuel.

CHAPTER VII

OPTIMIZATION OF FUEL RECOVERY THROUGH THE STEPWISE CO-PYROLYSIS OF PALM SHELL AND SCRAP TYRE

7.1 Introduction

Lignocellulosic or wood-based biomass is a major renewable energy source available worldwide, which can be used to produce oil through pyrolysis. Oil from this process has potential use as fuel or feedstock for various commodity chemicals (Thangalazhy-Gopakumar et al., 2010). Numerous types of lignocellulosic biomass have been successfully pyrolyzed by researchers to obtain liquid fuel. However, the fuel characteristics of oil from lignocellulosic biomass remain lower than those of fossil fuel because the liquid product contains high levels of oxygenated compounds, which can lead to low calorific values, corrosion problems, and instability (Lu et al., 2009). A large amount of oxygen content is present usually around 40-50 wt% in the pyrolysis liquid (Oasmaa & Czernik, 1999). For quality improvement, the liquid needs to be upgraded by an additional upgrading process. Catalytic cracking and hydrodeoxygenation are the most commonly used upgrading processes (Mortensen et al., 2011). The upgrading process involves the addition of a catalyst, solvent, and large amount of hydrogen (Zhang et al., 2013), which potentially can cost more than the oil itself. Thus, a novel approach is necessary to overcome this issue and make the oil from lignocellulosic biomass more competitive and reliable as a renewable fuel.

Co-pyrolysis is a technique with design and operation simplicity, which is suitable for the production of high-grade pyrolysis oil. This method can be run without the presence of any catalysts or solvents and with free hydrogen pressure. This process involves two or more different materials as feedstock. The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. Basically, the process is performed in a reactor system with moderate operating temperatures and the absence of oxygen. Most of the studies were performed using a fixed-bed reactor for the purpose of liquid production. According to Fei et al., 2012, the extent of contact between the used feedstock is an important factor to achieve the synergistic effect; therefore, the synergistic effect is more favorable for the pyrolysis operation carried out on a fixed-bed reactor than on a fluidized-bed reactor. As a general rule, temperature in co-pyrolysis can be adjusted within the range of 400–600 °C to maximize liquid yield production. Moreover, it is important to highlight the salient features of co-pyrolysis process being regarded as a promising, economic and environmental friendly technology for both the energy production and waste remediation (Lin et al., 2014). The detailed features of co-pyrolysis are summarized in Table 7.1.

Table 7.1: Features of co-pyrolysis (Abnisa & Wan Daud, 2014)

Operation condition and reactor	Product yields	Product quality	Advantages
- Temperature range of 400–600 °C. - No need to add catalysts, solvents, and hydrogen pressure. - Short hot vapor residence times of less than 2 s. - Hot vapor should be maintained at >400 °C before it enters the condensation unit. - To achieve a synergistic effect, a fixed bed reactor and auger reactor are recommended for use. - No need for complicated equipment.	- Compared with normal pyrolysis, co-pyrolysis can produce extra liquid yield, typically between 1.42 and 22 wt%. - The yields of char and gas are lower than that of biomass pyrolysis alone.	- Liquid product has potentially decreased oxygen levels, reduced water content, and increased calorific value. - Potentially increased calorific value of char and gas as byproducts of co-pyrolysis.	- Feedstock is available worldwide. - The volume of waste can be significantly reduced as more waste is consumed as feedstock. - The cost of waste treatment is saved. - Environmental problems are solved. - No waste is produced by the process. - The process can be easily applied to existing plants for biomass pyrolysis.

The research on co-pyrolysis process is generally focused on the study of synergistic effects or the interactive effects between the feedstock used. All improvements in oil quality and quantity during co-pyrolysis occurred through synergistic effects. The positive or negative synergy depends on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors (Johannes et al., 2013). However, the type of blending feedstock has a significant influence among these factors; thus, synergistic effects on co-pyrolysis can be complicatedly varied based on the feedstock (Fei et al., 2012). Önal et al., 2014 argued that the synergistic effect in co-pyrolysis is a complex phenomena because of various chemical species. According to the authors, several reaction radicals can be induced during co-pyrolysis of high density polyethylene and biomass, including initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), and isomerization via vinyl groups], and termination by disproportionation or recombination of radicals.

Many researchers have studied co-pyrolysis for producing pyrolysis oil, and their results are encouraging. Most of them focused on the co-pyrolysis of lignocellulosic biomass mixed with plastic. The addition of plastic during the pyrolysis of lignocellulosic biomass can improve the quantity and quality of the oil product. Abnisa et al. 2014 studied the co-pyrolysis of palm shells and polystyrene (PS) to obtain high-grade pyrolysis oil. Their results showed that by adding the same weight ratio of PS during the pyrolysis of palm shell, the oil yield increased to approximately 61.63 wt%, whereas the pyrolysis of palm shell alone yielded oil at approximately 46.13 wt%. The high heating value (HHV) of the oil product was obtained (i.e., approximately 11.94 MJ/kg) for the pyrolysis of palm shells alone. However, the pyrolysis of palm shells mixed with PS raised the HHV of oil to 38.01 MJ/kg. Jeon et al. (2011) studied the co-pyrolysis of wood chips with block polypropylene (BP). Their study was conducted in a fixed-bed reactor, and the temperature was set at 500 °C for the pyrolysis of the wood chip and BP mixture. The results of their experiment showed that the liquid yield reached 39.30 and 63.10 wt% when the BP mass was 0% and 50% of the mixture, respectively. The authors also noted that the liquid produced from wood chips alone had an HHV of 19.90 MJ/kg, whereas this value increased to 45 MJ/kg when BP mass accounted for 50% of the mixture. In addition, Cornelissen et al., 2008b reported the reduction of water content in pyrolysis oil produced via the flash co-pyrolysis of biomass with polylactic acid. Berrueco et al., 2004 studied the co-pyrolysis of high density polyethylene mixed with sawdust in a fluidized bed reactor. The authors found a decrease in the concentration of oxygenated and aliphatic compounds in liquid fraction.

Tyres are another material with characteristics similar to those of plastics. This material can be added during the pyrolysis of lignocellulosic biomass to obtain high-grade pyrolysis oil. Pyrolysis of tyres alone can produce the liquid yield of up to 63 wt%, depending upon the operating conditions applied (Williams, 2013). A large majority of oils produced have energy values in the range of 28–46 MJ/kg (Quek & Balasubramanian, 2013). Oil containing very low levels of oxygen has a high H/C atomic ratio (approximately 1.5) and consists of aliphatic and aromatic compounds (Martínez et al., 2013). Consequently, the presence of tyres during the pyrolysis of lignocellulosic biomass can have a positive contribution to the heating value through synergy. However, studies that focus on the pyrolysis of lignocellulosic biomass/waste tyre blends are currently limited (Abnisa & Wan Daud, 2014). Therefore, some effort should be made to obtain a clear overview of synergistic effects during the co-pyrolysis of lignocellulosic biomass and waste tyres.

Limited examples of the co-pyrolysis study of biomass and waste tyres can be found in the literature. Martínez et al., 2014 studied the co-pyrolysis of pine wood chips with scrap tyres in a fixed bed reactor and a continuous auger reactor, while Uçar and Karagöz, 2014 performed the co-pyrolysis of pine nut shells with scrap tyres at different blend ratios. Both studies applied the same procedure of pyrolysis process, where the samples were placed into the reactor and the reactor was subsequently heated from ambient temperature to 500 °C. The studies were emphasized on the product distribution and characterization of all pyrolysis products at reaction temperature of 500 °C. However, no literature was reported about the possibility of fuel recovery after optimum temperature achieved. This issue is interesting to investigate since the co-pyrolysis process uses two materials as feedstock which have different characteristics of thermal properties. Hence, the use of stepwise temperature technique in the co-pyrolysis process seems reasonable to achieve this objective.

This study also tried to investigate the production of organic and aqueous phases during the co-pyrolysis. A study performed by Martínez et al., 2014 found that a single liquid phase was obtained for all the biomass/waste tyre blends. The authors assumed that radical interaction during the pyrolysis reaction leads to a new bio-oil that avoids phase separation. In another study, Cao et al., 2009 reported that the liquid produced from co-pyrolysis of biomass and tyre contained two layers: an aqueous layer and an oil layer, which is also observed in the present study. However, there was no detailed discussion provided in their report. In order to obtain a clear insight, the phenomenon on the phase separation of liquid product is covered in this paper. Furthermore, the byproducts produced during this process were quantified. To evaluate the fuel quality, all the products were characterized by several analytic approaches.

7.2 Materials and methods

7.2.1 Materials

Palm shells were selected as a representative source of lignocellulosic biomass, and they were obtained from the palm oil mill industry. The waste tyres used in this experiment were categorized as truck tyres. As previously reported (Abnisa et al., 2013), palm shell waste is a serious problem in Malaysia, and this waste is often managed with unsatisfactory practices that negatively affect the environment. Furthermore, incorrect handling often occurs for waste tyres. According to Thiruvangodan (2006), approximately 8.2 million waste tyres or 57,391 tons are generated in Malaysia annually. Approximately 60% of waste tyres are disposed via unknown routes. Preventive actions are required to protect the environment from hazardous consequences brought about by the increasing volume of waste. Therefore, the use of co-pyrolysis can be an optional solution to address this issue.

All the samples used in this experiment were treated by drying in the sun for a day and subsequent grinding to obtain the desired particle size of 1–2 mm. The drying process was again performed in an oven at 105 °C for 24 h to remove moisture. The samples were then stored in a desiccator to keep them free of moisture. The ratio of palm shells and scrap tyres varied at 100:0, 75:25, 50:50, 25:75, and 0:100.

7.2.2 Co-pyrolysis experiments

Co-pyrolysis was performed in a fixed-bed reactor under a nitrogen (N_2) atmosphere at the desired temperature. The fixed-bed reactor was found to be effective in achieving the synergistic effects of co-pyrolysis (Fei et al., 2012), and it was also relatively inexpensive, simple, and reliable (Bridgwater, 2003). Approximately 800 g of each sample was placed in a stainless steel reactor with an internal diameter of 7.57 cm and length of 85 cm. An external vertical furnace was used to heat the reactor. The temperature was monitored using a K-type thermocouple inside the reactor. A series of condensers was installed at the condensation unit to condense the vapors released from the process. The condenser was set at a temperature of ±0.5 °C. The detailed design of the co-pyrolysis setup is shown schematically in Figure 7.1.

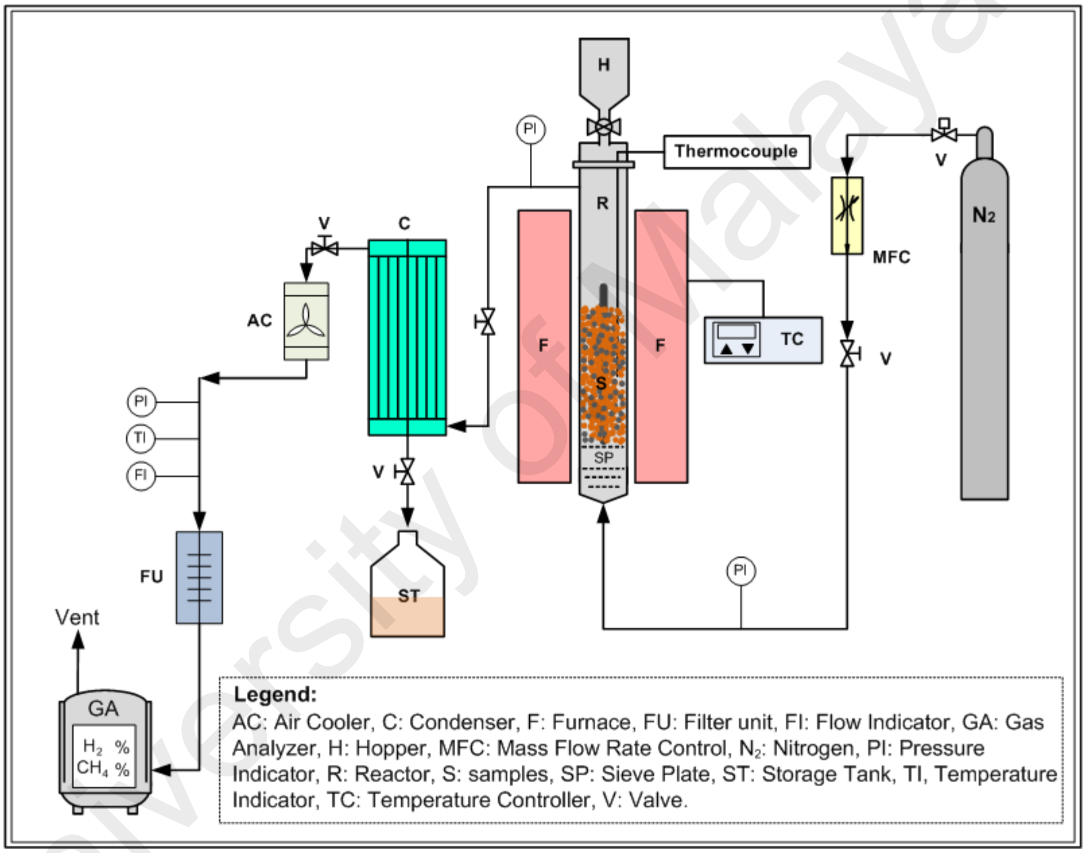


Figure 7.1: Flow diagram of the experimental set-up for the co-pyrolysis of palm shells mixed with scrap tyres

Initially, the reactor was heated to the desired temperature. Subsequently, N_2 was released for 2 min to remove the air from the reactor. After N_2 purging, materials were loaded onto the vertical reactor by opening the feed valve at the top of the reactor. The feed valve was then closed, and N_2 was again released to accelerate the sweeping of vapors from the hot zone (pyrolysis zone) to the cool zone (condenser). The N_2 flow rate was set at 1 L/min. It was controlled using mass flow controllers (Dawyer, USA) in the range of 0–2 L/min.

The experiments were divided into two scenarios. The first scenario aimed to observe the quantity and quality of fuels from co-pyrolysis at the optimum temperature condition (500 °C) with a reaction time of 60 min. The second scenario aimed to obtain an overview of the amount of remaining fuels that could be converted after the optimum conditions were achieved. The study was initially started by performing the experiment in the first scenario. After the first scenario was completed, the experiment continued by increasing the temperature to 800 °C. When the temperature reached 800 °C, the reaction was maintained for 45 min. The results of both scenarios were then compared. To validate the experimental data, each experiment was repeated with three replicates, and the average result was used as the final yield. The reactor, condenser, and piping system were sterilized between each set of experiments to avoid any sample contamination.

Three products were obtained during co-pyrolysis, namely, liquid, char, and gas. The liquid was collected from the condensation unit and subsequently weighed to obtain the mass of the liquid product. The char was collected from inside the reactor and then weighed. To obtain the final percentages of the products (liquid and char), all of the yields were calculated using the following equation:

$$Y_P = \frac{X_1}{X_2} \times 100\% \tag{7.1}$$

where Y_P is the product yield, X_1 is the mass of the desired product, and X_2 is the initial weight of the raw material. The gas yield was determined by subtraction: gas yield = 100 − (liquid yield + char yield).

7.2.3 Characterization

All feedstock used in this study were analyzed using proximate and ultimate analyses. The results from proximate analysis included the moisture, fixed carbon, volatile matter, and ash contents. Proximate analysis was performed according to the ASTM standards described in the literature. Ultimate analysis followed ASTM D-5291 using a Model 2400 Perkin Elmer Series CHNS/O Analyzer. The amounts of carbon, hydrogen, nitrogen, and sulfur were determined using this method. The oxygen content was determined by subtraction: $O = 100 - (C + H + N + S)$. Weight loss analysis of the sample was performed with a thermogravimetric analyzer (TGA 4000, Perkin Elmer) under a nitrogen flow rate of 25 mL/min and heating rate of 40 °C/min.

In this study, the liquid yield was considered the main product, whereas char and gas were considered byproducts. The liquid collected from the condensation unit was kept in a separating funnel for 2 d. Each layer that formed during the separation process was investigated. Several analyses, including the analysis of density, water content, pH, functional group composition by Fourier transform infrared (FTIR) spectroscopy, elemental analysis (C, H, N, S, and O), and HHV, were conducted to determine the quality of the liquid product. The analyses of the byproducts (char and gas) focused on the fuel characteristics. The analyses of the char product included elemental analysis and HHV. The analysis of the gas product focused on the production of H_2 and CH_4 gases.

A 25 mL pycnometer was used to determine the density of the pyrolysis oil. The pH was measured using a Mettler Toledo Delta 320 pH meter at 25 °C. The Karl Fischer titration method was used to measure the water content. This measurement was performed with a Karl Fischer 737 KF Coulometer from Metrohm. HYDRANAL

Coulomat AG (80 mL) and HYDRANAL Coulomat CG (5 mL) were used as the anolyte and catholyte reagents, respectively. FTIR analysis was conducted with a Perkin–Elmer Spectrum 400 spectrometer. The samples were scanned in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Elemental analysis was performed with a Model 2400 Perkin–Elmer Series II CHNS/O Analyzer to determine the C, H, N, and S contents. The oxygen content was determined by subtraction. A CHNS combustion tube and reduction tube were used for this determination. The elemental analysis results were also used to calculate the HHV. In this study, two equations were used to calculate the HHV of the liquid product. These equations were based on the obtained oxygen content. Equation 7.2 was used when the liquid product had an oxygen content lower than 15%, whereas Equation 7.3 was used if the oxygen content in the sample was greater than 15% (Buckley, 1991). The HHV of the char product was determined using the modified Dulong's formula, as shown in Equation 7.4 (Mohanty et al., 2013).

$$\text{HHV (MJ/kg)} = \frac{338.2\text{C} + 1442.8\left(\text{H} - \frac{\text{O}}{8}\right)}{1000} \tag{7.2}$$

$$\text{HHV (MJ/kg)} = 0.336\,\text{C} + 1.418\,\text{H} - (0.153 - 0.000720\ \text{O})\,\text{O} + 0.0941\,\text{S} \tag{7.3}$$

$$\text{HHV (MJ/kg)} = \frac{33.5\text{C}}{100} + \frac{142.3\text{H}}{100} - \frac{15.4\text{O}}{100} \tag{7.4}$$

An online gas analyzer was installed after the condensation process to measure the released hydrocarbon gases. Hydrogen and methane were measured by a calibrated online gas analyzer, namely, Rosemount Analytical X-STREAM$^{\text{TM}}$ (UK) apparatus.

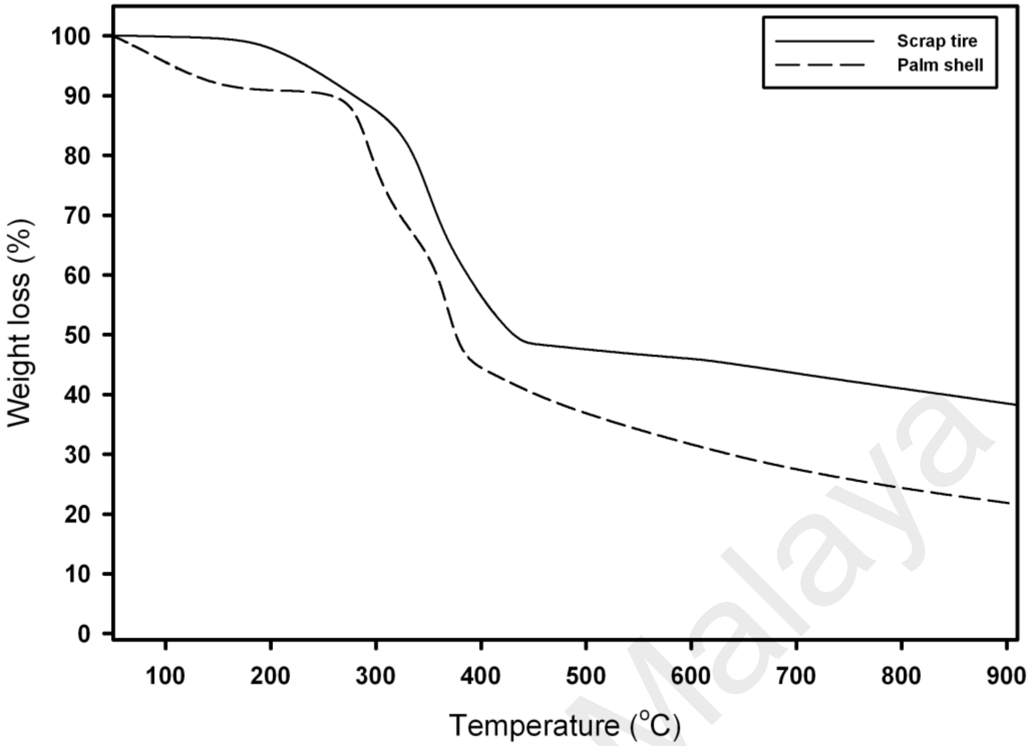


Figure 7.2: TGA thermographs of palm shell and scrap tyre

7.3 Results and discussion

7.3.1 Characteristics of the raw materials

The pyrolysis temperature plays an important role in liquid yield production. Generally, moderate operating temperatures are required to produce the liquid yield. However, this parameter is dependent on the feedstock characteristics. In this study, TGA analysis was used to obtain an overview of the thermal behavior of the materials. The use of TGA analysis also helped define the optimum temperature to produce the maximum liquid yield.

The TGA results of the palm shells and scrap tyres are shown in Figure 7.2. The figure shows that the increased temperature led to the decreased weight of both materials. Decomposition initially occurred for palm shells, and the scrap tyres started to decompose after the temperature reached approximately 180 °C. The decomposition of palm shells can be explained by lignocellulosic decomposition, which has been widely discussed in our previous studies (Abnisa et al., 2013a; Abnisa et al., 2013b). Unlike palm shells, scrap tyres need higher temperatures before they start to decompose, and the total weight loss of scrap tyres was lower than that of palm shells. The major decomposition of scrap tyre continuously occurred until the temperature reached approximately 500 °C. However, no further significant weight loss was observed after this temperature. Murillo et al. (2006) explained that the initial decomposition (approximately 150 °C) is associated with the decomposition of the tyre rubber additives (extender oils, plasticizers, and other additives). Further decomposition is attributed to the decomposition of natural rubber, as well as the decomposition of a mixture of styrene butadiene rubber and butadiene rubber. In addition, significant weight loss for both materials was observed at approximately 500 °C. At this temperature, approximately 63% of weight loss was identified for palm shells, whereas the amount of weight loss for scrap tyres was approximately 52%. The high percentage of weight loss observed from TGA analysis indicated that a high conversion rate of biomass occurred. Thus, 500 °C was found to be a suitable temperature for maximizing biomass conversion into other products.

Table 7.2: Proximate and ultimate analyses of palm shell and scrap tyre

Characteristics	Palm shell	Scrap tyre
Proximate analysis (wt%)		
Moisture	4.7	1.15
Fixed carbon	13.2	28.46
Volatile	73.5	66.10
Ash	8.6	3.65
Ultimate analysis (wt%)		
C	49.74	83.82
H	5.32	7.65
N	0.08	0.92
O (by difference)	44.86	6.03
S	0.16	1.58

The results of proximate and ultimate analyses are summarized in Table 7.2. From proximate analysis, the palm shells and scrap tyres were found to have high values of volatile matter. During the pyrolysis of biomass, this content is expected to be high because it has a positive contribution toward increasing liquid yield production. According to Omar et al. (2011), a high volatile content provides high volatility and reactivity, which favor liquid yield production. Compared with volatile matter, the presence of ash in the materials will lead to liquid yield reduction. This phenomenon has previously been recognized by several researchers. Fahmi et al., 2008 also described that the presence of ash leads to a decrease in the liquid yield, and tend to increase char and gas yields. Venderbosch and Prins, 2010b noted that the high ash content in the biomass can drastically drop the oil yield, sometimes below 50 wt%. In the present study, the measured ash content was approximately 8.6 and 3.65 wt% for palm shells and scrap tyres, respectively. Furthermore, the ultimate analysis results showed that scrap tyres were better materials for producing fuels because of their high carbon and hydrogen contents and low oxygen content. Therefore, the addition of scrap tyres in the pyrolysis of palm shells is expected to improve the calorific value of the liquid product.

7.3.2 Product yields

Three products were obtained from the co-pyrolysis of palm shells and scrap tyres: liquid, char, and gas. The details of the yield products derived from the first and second scenarios are presented in Table 7.3. Given that the process parameters in this study were adjusted to maximize liquid production, the obtained liquid yield was higher compared with the yields of other products. The lowest yield was observed for the gas product. The results from the first scenario showed that the addition of scrap tyres in the pyrolysis of palm shells significantly contributed to the increased liquid yield. The pyrolysis of palm shells alone produced approximately 43.82 wt% of the liquid yield.

Subsequently, the yield increased by 45.16, 46.22, and 48.06 wt% when the scrap tyre mass was 25%, 50%, and 75% of the reaction, respectively. The same trend was reported by Cao et al. (2009), who studied the co-pyrolysis of sawdust and waste tyres. The addition of scrap tyres could provide more hydrocarbons during co-pyrolysis. Thus, this approach can increase the liquid yield production. Moreover, the increased proportion of scrap tyres in the feedstock affected the enhancement of the char product. The pyrolysis of palm shells yielded approximately 34.20 wt% of char. The yield increased to 36.16 wt% with the maximum amount of scrap tyres in the feedstock (75%). According to Martínez et al. (2014), the increase in char product during the co-pyrolysis of biomass and scrap tyre can be attributed to the lower proportion of volatile matter and higher percentage of fixed carbon (by the carbon black added during tyre manufacturing) in the waste tyres compared with those in lignocellulosic biomass.

Table 7.3: Product yields of co-pyrolysis at different ratios and scenarios

Scrap tyre in feedstock (%)	Product yields (wt%)					
	Liquid		Char		Gas*	
	Scenario I	Scenario II	Scenario I	Scenario II	Scenario I	Scenario II
0%	43.82	47.36	34.20	29.10	21.98	23.54
25%	45.16	47.90	34.72	31.46	20.12	20.64
50%	46.22	47.86	36.36	34.14	17.42	18.00
75%	48.06	48.22	36.16	35.42	15.78	16.36
100%	48.12	48.34	37.11	36.11	14.77	15.55

*Calculated by difference

The results of the second scenario showed that the liquid yield increased for the pyrolysis of palm shells alone and co-pyrolysis of palm shells mixed with a low ratio of scrap tyres. This result indicated that the enhanced effect of temperatures beyond 500 °C was significantly influenced by the lignocellulosic biomass. The increased liquid yield in this scenario was mainly contributed by the decomposition of lignin. Lignin has thermal characteristics different from hemicellulose and cellulose. The decomposition of hemicellulose and cellulose is completed at 400 °C, whereas the complete decomposition of lignin requires a higher temperature. According to Yang et al. (2007), the decomposition of lignin slowly occurs during the pyrolysis of biomass; it starts at an ambient temperature and continues up to 900 °C. The effect of lignin on pyrolysis oil yield was previously studied by Fahmi et al. (2008), and their results showed that the total liquid yield increases with increasing amount of lignin. The liquid product from the pyrolysis of lignin typically consists of ~20% aqueous components and ~15% organic components (Mohan et al., 2006).

Furthermore, the effect of temperature enhancement in the second scenario plays an important role in reducing the yield of the char product. Table 7.3 shows that the decrease in char was followed by an increase in gas yield. This condition was observed with a higher ratio of biomass in the feedstock. These results showed that the yield of char obtained at 500 °C was again cracked, which led to higher gas yields when the temperature was increased to 800 °C. Bridgwater et al. (1993) noted that chars produced by rapid pyrolysis have a lower apparent density and are more reactive than those produced by slow pyrolysis. A fraction of this char can be further volatilized by pyrolysis at high temperatures.

7.3.3 Characterization of the liquid product

The results showed that the liquid consisted of organic and aqueous phases. This finding differed from those of Martinez et al. (2014), who reported the absence of phase separation in the liquid product produced from the co-pyrolysis of biomass and scrap tyres. Their experiment was performed in a fixed-bed reactor with different feedstock mixtures based on mass: 100% biomass (100/0); 90% biomass and 10% waste tyres (90/10); 80% biomass and 20% waste tyres (80/20); and 100% waste tyres (0/100). The findings of the present study confirmed that phase separation occurred in the liquid produced from the co-pyrolysis of biomass and scrap tyres. Phase separation seems unlikely when the ratio of scrap tyres is low in feedstock (≤25%) or when only biomass is used as feedstock. However, the use of spotlights (LED flood light, 30 W) can help define phase separation. Images of the liquid yields, which are lighted by spotlights, are shown in Figure 7.3. From this figure, the liquids produced by the pyrolysis of palm shells alone and pyrolysis of scrap tyres alone have two phases: organic and aqueous. By contrast, the liquids produced from the palm shell/waste tyre blends have three phases: a bottom organic phase, aqueous phase, and top organic phase. A similar phase separation trend in the liquid product was reported by another study (Samanya et al., 2012). As shown in Figure 7.3, no top organic phase was present in the liquid produced from the pyrolysis of palm shells alone. Moreover, no bottom organic phase was detected in the liquid obtained from scrap tyres alone. This finding denoted that the bottom organic phase was contributed by the lignocellulosic biomass, the top organic phase was contributed by scrap tyres, and the aqueous phase was contributed by both materials.

Figure 7.3: Comparison of liquid yields with different feedstock ratios of palm shells and scrap tyres

After the liquid products were stored in a separatory funnel for 2 d, the liquids were separated based on the layer that was formed. The quantities of each layer are presented in Table 7.4. Some interesting observations were noted among the scenarios. The yield of the bottom organic phase for both scenarios decreased when the palm shell ratio in the feedstock decreased. Furthermore, the yield of the bottom organic phase from scenario II was lower than that from the first scenario. By contrast, the increased temperature caused an increase in the aqueous phase. This phenomenon was clearly observed for the second scenario, although no significant enhancement in the aqueous phase yield was obtained. Moreover, the top organic phase for the second scenario increased in terms of the yield compared with that for the first scenario. In scenario II (Table 7.3), the increase in the liquid yield was caused by the top organic and aqueous phases.

Table 7.4: Distribution of liquid yields based on the type of phase

Scrap tyre in feedstock (%)	Yield of liquid type (wt%)					
	Bottom organic		Aqueous phase		Top organic	
	Scenario I	Scenario II	Scenario I	Scenario II	Scenario I	Scenario II
0%	29.08	28.48	70.92	71.52	NP	NP
25%	19.73	17.76	57.59	58.19	22.68	24.05
50%	9.09	6.58	35.87	36.14	56.04	57.28
75%	6.33	5.15	13.51	13.55	80.16	81.30
100%	NP	NP	2.58	2.25	97.42	97.75

NP: no product found

A high proportion of the organic phase in pyrolysis oil is generally preferred over the aqueous phase. The aqueous phase has a high water content, which can extremely reduce the energy content of pyrolysis oil. In the present study, the highest proportion of the aqueous phase was observed for the pyrolysis of palm shells alone at approximately 70.92 and 71.52 wt% for scenarios I and II, respectively. The aqueous phase was significantly reduced when the scrap tyre was added to the feedstock, thereby increasing the total accumulation of the organic phase. As shown in Figure 7.4, the total organic phase linearly increased with the decrease in the aqueous phase. This trend was observed for both scenarios. The co-pyrolysis of lignocellulosic biomass and scrap tyres was found to be an effective technique for increasing the organic phase of pyrolysis oil.

Table 7.5 shows that the addition of scrap tyres during the pyrolysis of palm shells decreased the water content in the bottom organic phase. This tendency was clearly observed for both scenarios. The highest water content for the bottom organic phase was approximately 14%, which was obtained from the liquid produced from the pyrolysis of palm shells alone. The water content decreased to 9.5% when the ratio of scrap tyres reached 75% in the feedstock. Furthermore, the water content in the top organic phase was very low (<1%). Compared with the organic phase, the water content in the aqueous phase gradually increased as the scrap tyre mass increased. The highest water content in the aqueous phase was observed for the liquid obtained from the pyrolysis of scrap tyres alone (approximately 82%).

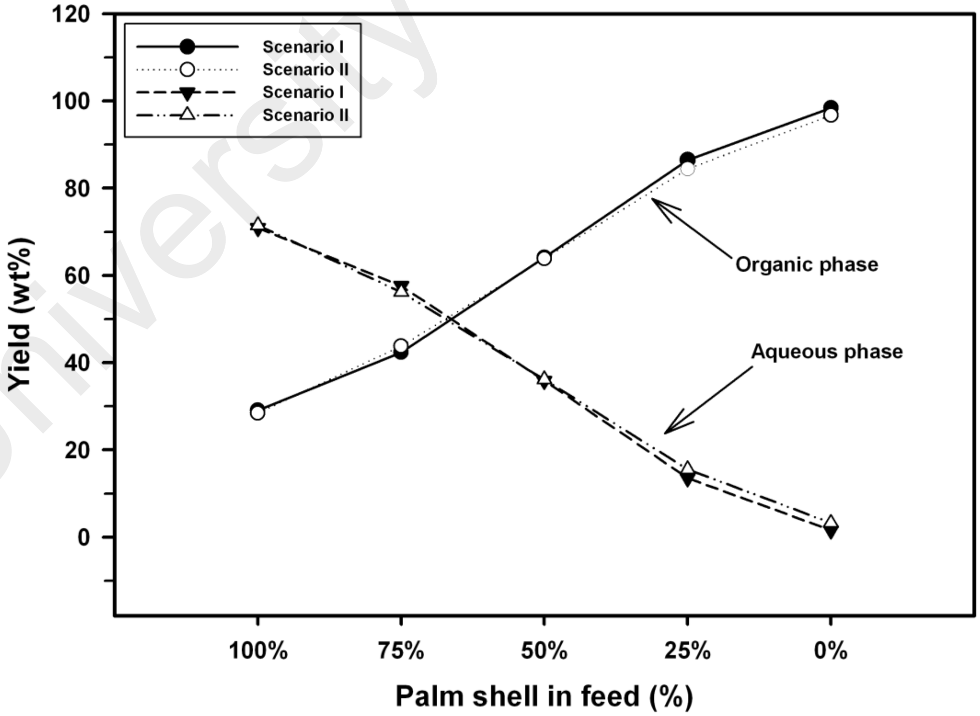


Figure 7.4: Distribution of the total organic phase versus the aqueous phase

Table 7.5: Results of water content analysis

Scrap tyre in feedstock (%)	Water content (%)					
	Bottom organic		Aqueous phase		Top organic	
	Scenario I	Scenario II	Scenario I	Scenario II	Scenario I	Scenario II
0%	13.96	14.16	69.48	69.64	NP	NP
25%	10.72	10.33	72.61	72.90	0.94	0.92
50%	10.85	10.08	73.82	73.00	0.53	0.54
75%	9.57	9.63	75.15	75.32	0.28	0.25
100%	NP	NP	82.66	82.36	0.13	0.12

NP: no product found

Table 7.6 presents the results of pH analysis of pyrolysis oils, which were grouped into the bottom organic, aqueous, and top organic phases. The results showed that all of the liquid types were considered acidic. Pyrolysis oil is highly unstable and corrosive when its acidity is high. However, the pH increases during co-pyrolysis, which exerts a positive effect by reducing the acidity of the liquid product. Table 7.6 shows that the phases of all the liquid types exhibited an increase in pH when scrap tyres were mixed during the pyrolysis of palm shells. The liquid produced from the pyrolysis of lignocellulosic biomass had a pH ranging from 2.0 to 3.0 (Mohan et al., 2006). This condition resulted from the high concentration of acidic compounds in the liquid, which mainly contributed to the degradation of hemicellulose and lignin during pyrolysis. Therefore, the reduction in lignocellulosic biomass and addition of scrap tyres as feedstock in pyrolysis enhanced the pH. Furthermore, the pH slightly increased for scenario II. The pH of liquid products increased with increasing temperature. This finding occurred for all conditions of samples used in this study. A similar trend was reported by He et al. (2009) and Thangalazhy-Gopakumar et al. (2010).

Table 7.6: Results of pH analysis

Scrap tyre in feedstock (%)	pH					
	Bottom organic		Aqueous phase		Top organic	
	Scenario I	Scenario II	Scenario I	Scenario II	Scenario I	Scenario II
0%	2.88	2.89	2.71	2.75	NP	NP
25%	2.94	3.06	3.82	3.83	2.81	3.09
50%	3.08	3.21	3.12	3.29	3.33	3.51
75%	3.45	3.72	3.31	3.58	3.71	3.75
100%	NP	NP	5.88	5.96	5.05	5.96

NP: no product found

Table 7.7: Results of elemental analysis from scenario I

Liquid types	Scrap tyre in feedstock (%)	Elemental analysis (wt%)				
		C	H	N	S	O
Top organic phase	0%	NP	NP	NP	NP	NP
	25%	83.63	11.07	0.38	1.69	3.23
	50%	85.23	11.17	0.43	1.69	1.48
	75%	85.56	11.64	0.52	1.85	0.43
	100%	85.74	11.79	0.54	1.88	0.05
Aqueous phase	0%	17.90	10.62	0.33	0.86	70.27
	25%	15.17	9.45	0.27	0.89	74.22
	50%	16.23	9.56	0.51	0.94	72.76
	75%	12.52	9.11	0.91	1.14	76.32
	100%	7.47	10.73	3.57	1.42	76.81
Bottom organic phase	0%	60.76	8.42	0.66	0.91	29.25
	25%	63.05	8.55	1.00	1.02	26.38
	50%	64.95	8.70	1.57	1.68	23.10
	75%	64.58	8.78	2.49	1.88	22.27
	100%	NP	NP	NP	NP	NP

NP: no product found

The complete results of elemental analysis for scenario I are shown in Table 7.7. The amount of oxygen, which was categorized as an undesirable component in liquid, decreased for both organic phases when scrap tyre in the feed blend increased. However, the oxygen content in the aqueous phase was different from that in the organic phase. This finding indicated that a synergistic effect occurred during co-pyrolysis. The highest oxygen content was detected for the aqueous phase (>70 wt%), whereas the oxygen contents in the bottom organic and top organic phases were <30 and 3.23 wt%, respectively. This study also found that the decrease in oxygen in the organic phases was followed by an increase in the carbon and hydrogen contents. All the trends that occurred in scenario I were also found in scenario II (Table 7.8).

The addition of tyre in the pyrolysis of biomass could increase the sulfur content in liquid. This effect may be due to the thermal degradation of the accelerators used in tyres during vulcanization; these accelerators include sulfur- and/or nitrogen-based organic compounds, such as 2-mercaptobenzothiazole and benzothiazole disulfide (Frigo et al., 2014). The increase in sulfur in the liquid product was also observed in scenario II (see Table 7.8). The sulfur and nitrogen contents in Table 7.8 were higher than those in Table 7.7. The increase in sulfur was detected for the top organic phase, whereas the increase in nitrogen content was clearly observed for the bottom organic phase. These findings clarified that the increase in temperature played an important role in increasing the sulfur and nitrogen contents in liquid. The increase in the sulfur content was mainly caused by scrap tyre, as reported by other researchers. The research performed by Díez et al., 2004 reported that the sulfur content in the produced liquid was 1.3 wt% at 350 °C and it was subsequently increased to 1.4 wt% and 1.6 wt% as the temperature reached at 450 °C and 550 °C, respectively. de Marco Rodriguez et al., 2001 studied the pyrolysis of scrap tyres at temperatures between 300 °C and 700 °C with an interval of 100 °C. The authors reported that the increase in sulfur content was observed with the increase of temperature from 300 °C to 500 °C. Furthermore, the increase in the nitrogen content in the bottom organic phase (Table 7.8) was mainly caused by lignocellulosic biomass. Odetoye et al., 2014 reported this trend in the study of pyrolysis of *parinari polyandra* benth fruit shell for bio-oil production.

Table 7.8: Results of elemental analysis from scenario II

Liquid types	Scrap tyre in feedstock (%)	Elemental analysis (wt%)				
		C	H	N	S	O
Top organic phase	0%	NP	NP	NP	NP	NP
	25%	83.44	11.41	0.40	1.84	2.91
	50%	84.48	11.23	0.49	1.78	2.02
	75%	86.13	11.38	0.53	1.90	0.06
	100%	87.83	11.99	0.76	1.92	0.00
Aqueous phase	0%	15.90	10.89	0.38	0.70	72.13
	25%	13.26	11.07	0.50	0.78	74.39
	50%	14.75	8.58	0.61	0.70	75.36
	75%	11.73	11.92	1.02	1.00	74.33
	100%	10.95	9.43	1.25	1.31	77.06
Bottom organic phase	0%	62.33	7.55	1.08	0.75	28.29
	25%	64.22	7.15	1.12	0.96	26.55
	50%	68.57	7.98	2.03	1.37	20.05
	75%	65.59	7.88	3.00	1.57	21.96
	100%	NP	NP	NP	NP	NP

NP: no product found

In terms of liquid fuel, the presence of sulfur and nitrogen is undesirable because they can contribute to the formation of SO_2 and NOx during combustion (Williams et al., 1998). SO_2 and NOx are known as harmful pollutants that can negatively affect the environment, and specifically contribute to global warming. Therefore, liquid fuel should be free from sulfur and nitrogen or at least contain acceptable amounts in accordance with the ASTM standards. Raj et al. (2013) suggested the removal of sulfur from the pyrolysis oil of waste tyres. The authors explained that the pyrolysis oil with free moisture can be mixed with 6 wt% H_2SO_4, allowed to settle for 24 h, and further processed with Fuller’s earth to remove impurities and sulfur. Desulfurized oil is then fractionally distilled in vacuum to remove the sludge. In oil refining industry, the conventional method to remove sulfur from fuel/bio oils is by using a catalytic hydrotreatment.

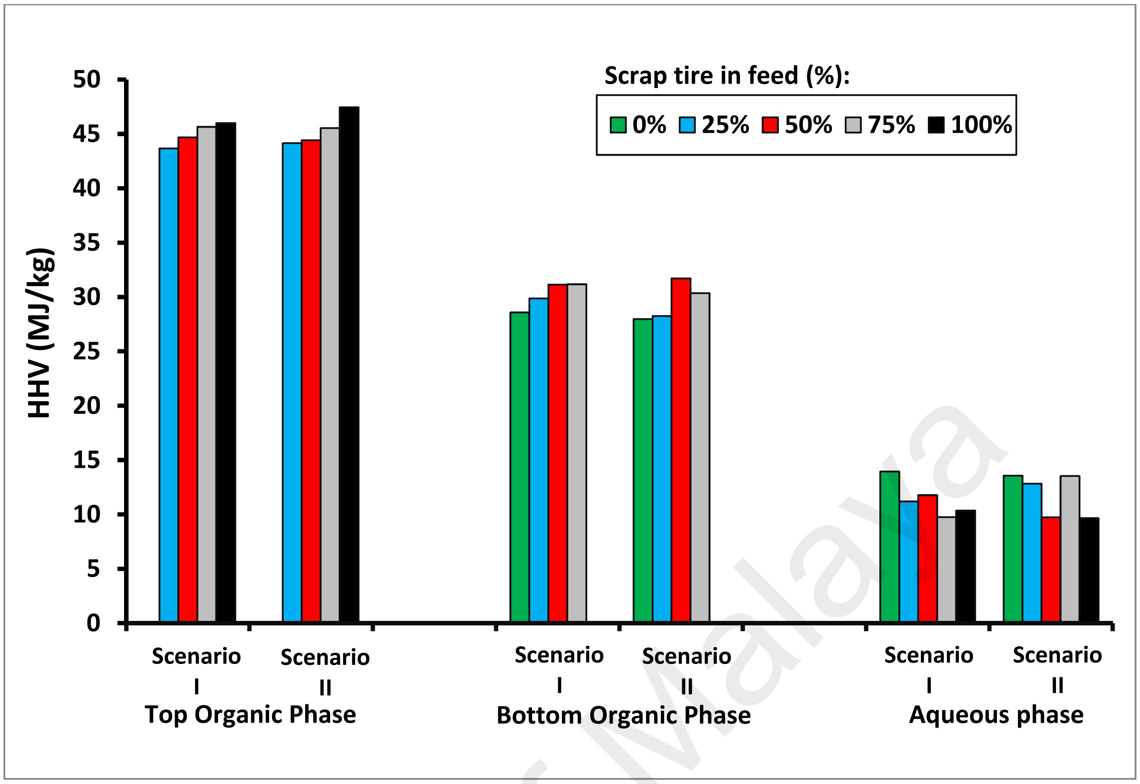


Figure 7.5: HHV of pyrolysis oils

HHV is one of the important parameters in determining the energy content of a fuel. The HHV results of pyrolysis oils obtained from scenarios I and II are illustrated in Figure 7.5. The HHV of each phase differed. The top organic phase had the highest HHV, and the bottom organic and aqueous phases were categorized into the medium and low levels, respectively. As shown in Figure 7.5, the addition of scrap tyre in biomass pyrolysis obviously contributed to the increase in HHV of the organic phases. However, based on the results from scenario II, no significant increment was found when the temperature increased. Furthermore, the HHV of the top organic phase was in the range of 43–46 and 44–47 MJ/kg for scenarios I and II, respectively. These results showed that the HHV of the top organic phase could be categorized similar to commercial diesel fuel. The HHV of the bottom organic phase from both scenarios varied in the range of 28–31 MJ/kg. This result was higher compared with typical HHV of biomass pyrolysis oil (16–19 MJ/kg) (Zhang et al., 2007). In addition, the HHV of the aqueous phases was found to be very low at a range of 9–14 MJ/kg.

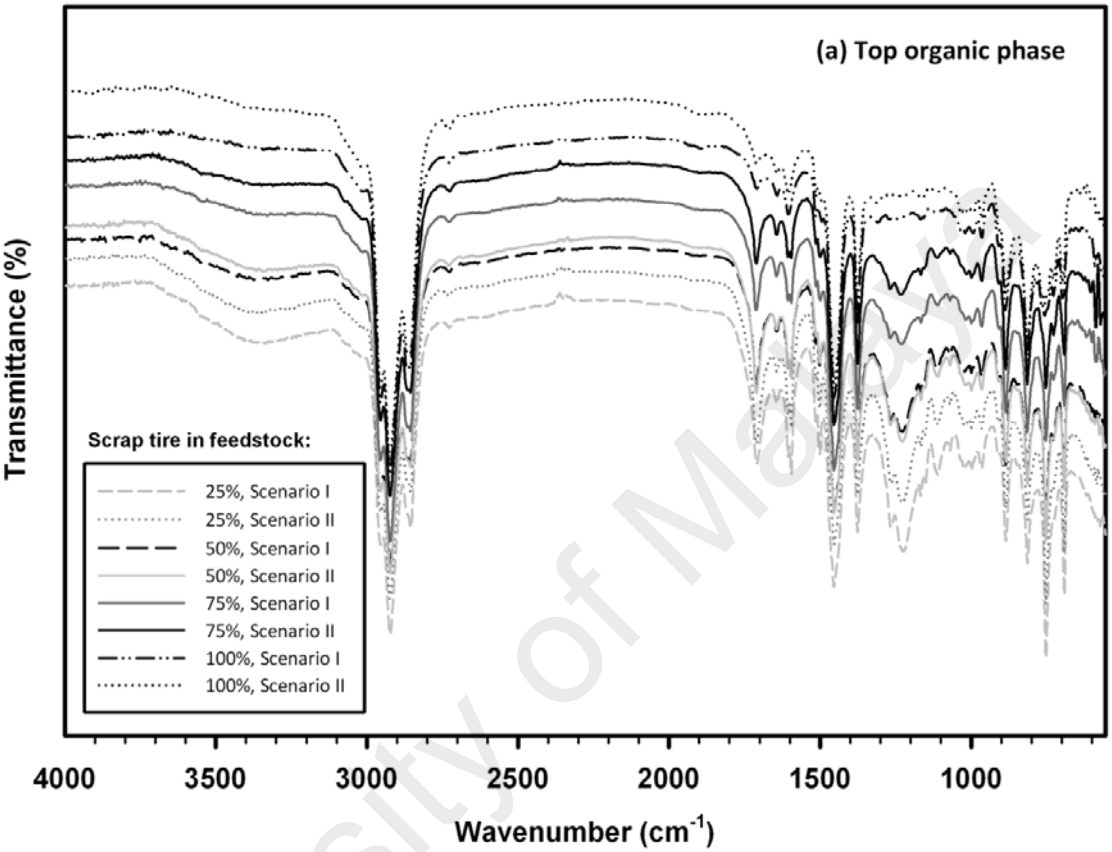


Figure 7.6: FTIR spectra of the top organic phase

The FTIR spectra of the top organic, aqueous, and bottom organic phases are shown in Figures 7.6, 7.7, and 7.8, respectively. Many researchers recognize that O-H, C-H, C-O, and C=O are the most abundant chemical bonds detected in liquids produced from the pyrolysis of biomass. The functional group of O-H was generally found at peaks between 3200 and 3400 cm^{-1}, which indicated the presence of phenols and alcohols. Such peaks were clearly observed for the aqueous phase (see Figure 7.7). Figure 7.7 shows that the intensity of peak areas between 3200 and 3400 cm^{-1} increased significantly when the scrap tyre ratio increased in the feedstock, thereby indicating an increase in concentration of the O-H group. This result was in agreement with the results from water content analysis and elemental analysis, in which the water and oxygen contents were also found to increase as tyre mass increased in the pyrolysis of palm shell. Furthermore, the O-H stretching vibrations between 3200 and 3400 cm^{-1} were observed for the bottom organic phase (see Figure 7.8). However, the intensity of this peak differed from that in the aqueous phase, where the intensity decreased with increasing scrap tyre ratio in the blend. Martínez et al. (2014) stated that phenolic compounds originate from the decomposition of lignin in the biomass wood, whereas the presence of phenols and carbonyls in tyre-based oil may be explained by the pyrolysis of oxygenated compounds, such as stearic acid and extender oil, of the tyre (Shah et al., 2009).

The C-H stretching vibrations between 2800 and 3000 cm^{-1}, as well as C-H deformation vibrations between 1350 and 1450 cm^{-1}, showed the presence of alkane groups. The peaks between 2800 and 3000 cm^{-1} were only observed for the top and bottom organic phases. The effect of scrap tyre addition increased the intensity of peak areas between 2800 and 3000 cm^{-1} (Figure 7.8). Moreover, the deformation vibrations between 1350 and 1450 cm^{-1} were observed for all liquid types. A strong intensity of peak areas between 1350 and 1450 cm^{-1} was observed for the top and bottom organic phases, whereas medium intensity was observed for the aqueous phase. This result showed that some hydrocarbon compounds still remained in the aqueous phase, and they could be recovered by catalytic conversion. Abnisa et al. (2014b) showed that the use of zeolite catalyst (HZSM-5/50) at 555 °C is effective in recovering liquid fuel from the aqueous phase with an oil yield of about 4 wt%; the obtained oil was dominated by aromatics and phenols, with an HHV of 38.44 MJ/kg.

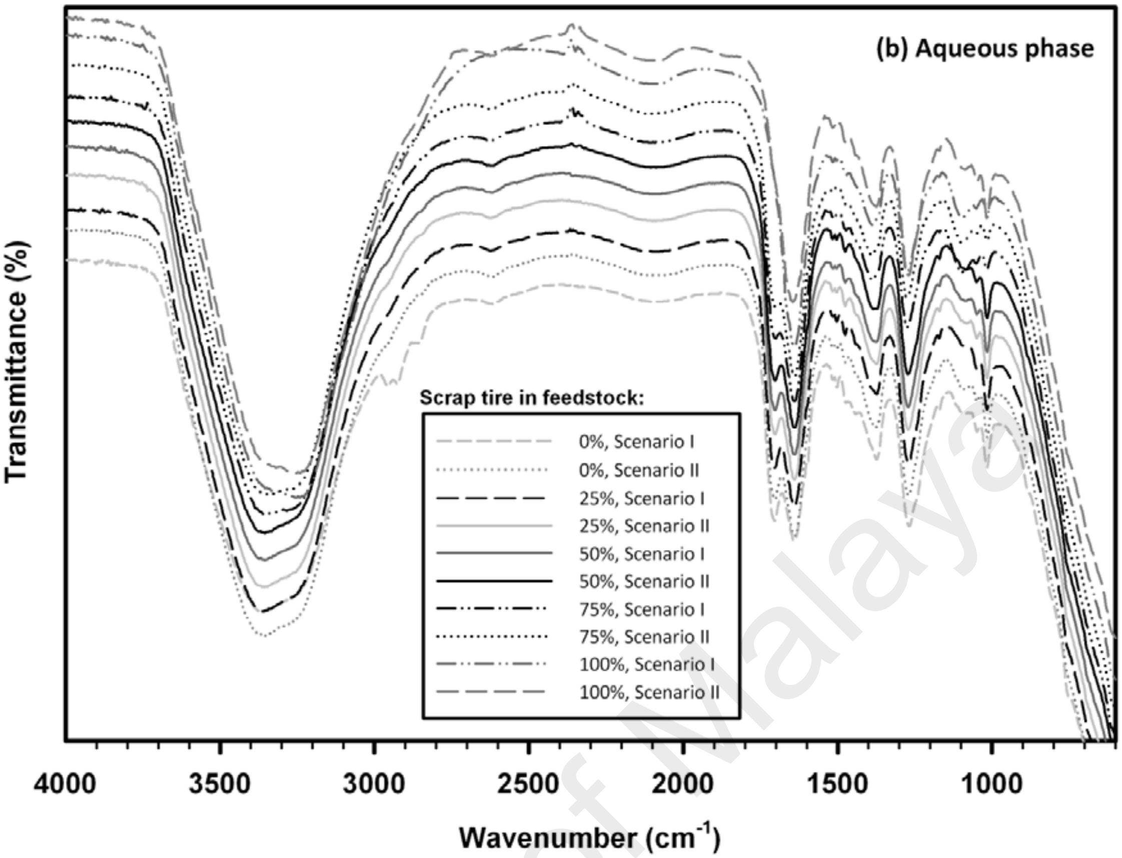


Figure 7.7: FTIR spectra of the aqueous phase

Moreover, the presence of oxygen was also observed for all liquid types in the range of 1650–1850 and 1000–1300 cm^{-1}. The peaks between 1650 and 1850 cm^{-1}, which were related to C=O stretching, indicated the presence of ketones, carboxylic acids, and aldehydes. The C-O stretching vibration in the range of 1000–1300 cm^{-1} was attributed to alcohols and esters. However, both peaks disappeared from the top organic phase when scrap tyres were involved in the pyrolysis of palm shell. By contrast, these peaks were still detected for the bottom organic phase, although the scrap tyre mass occupied 75% of the mixture. The results from elemental analysis (Tables 7.7 and 7.8) confirmed that the oxygen content was high for the bottom organic phase.

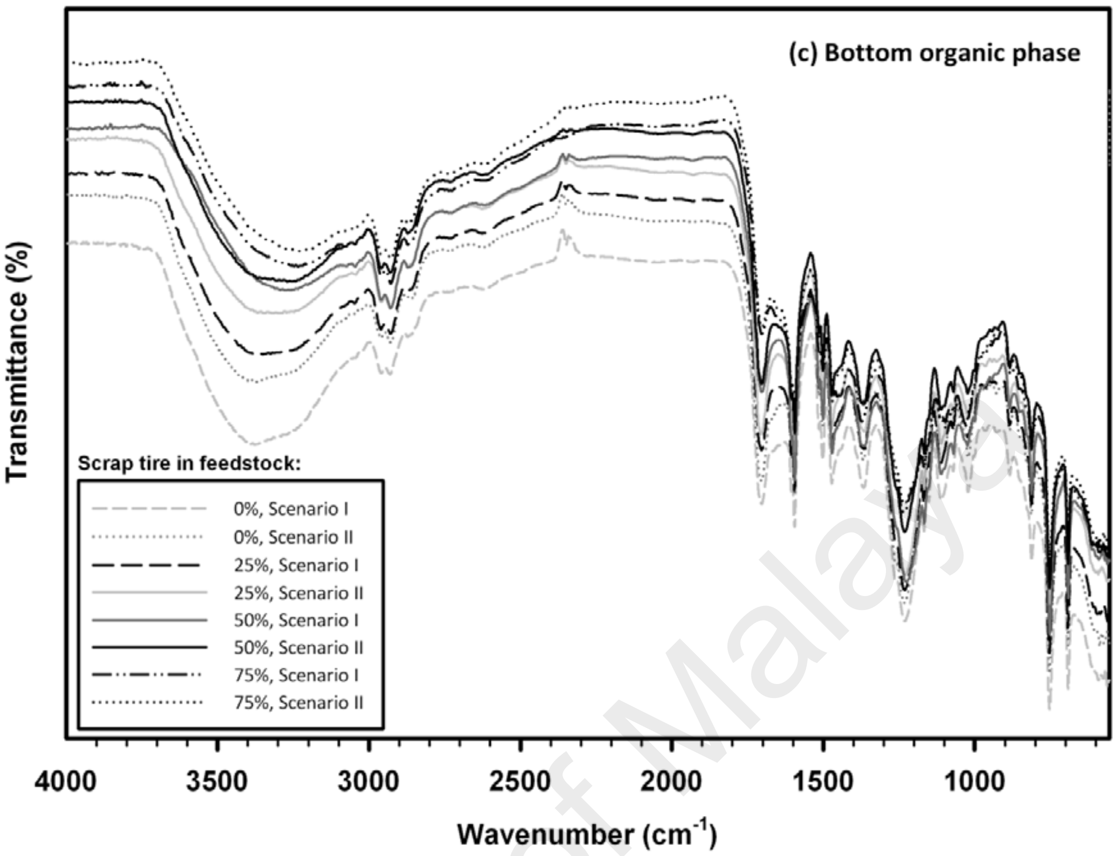


Figure 7.8: FTIR spectra of the bottom organic phase

7.3.4 Characterization of byproducts

7.3.4.1 Char product

In this study, the characteristics of char were investigated using elemental analysis and HHV to determine its fuel quality. The results of elemental analysis for char product are listed in Table 7.9. Carbon, the main element in all of the produced chars, was present in significantly great amounts (>75 wt%). In scenario I, the addition of scrap tyres did not significantly increase the carbon content. Hydrogen, an important content in fuel, decreased when the proportion of palm shell decreased in the feedstock. Both these trends showed that palm shell was the main contributor in producing carbon and hydrogen during the co-pyrolysis of biomass and scrap tyres. Similar to liquid product (Tables 7.7 and 7.8), the sulfur content also increased when scrap tyres in the feedstock increased. The results from scenario I also showed that oxygen and nitrogen both decreased after the addition of a certain proportion of scrap tyres.

The results from scenario II showed that the increase in temperature after optimum conditions eliminated all elements from the char. However, the analyses in this scenario demonstrated that the carbon contents increased in the char products. The increase in carbon content was observed in the experiment with palm shell:scrap tyre ratios of 100:0 and 75:25. This condition may be explained by the formation of carbon during the pyrolysis of lignocellulosic biomass. Imam and Capareda (2012) noted that losses in hydrogen and oxygen are due to the breaking of weaker bonds within the char structure, and char becomes highly carbonaceous at high pyrolysis temperatures. Devolatilization reactions are favored with increasing temperature; such reactions degrade all elements from char and increase gaseous product yields (Demiral & Kul, 2014). The yields of gas products listed in Table 7.3 supported this finding.

Figure 7.9 shows the HHV of chars obtained from different scenarios. The HHV of chars from scenario I was obtained in the range of 24–27 MJ/kg, whereas char produced from scenario II was in the range of 23–26 MJ/kg. The highest HHV in scenario I resulted from the pyrolysis of palm shell alone. However, the HHV of char gradually decreased when the percentage of scrap tyres in the feedstock increased. This result showed that the addition of scrap tyres in the pyrolysis of biomass resulted in the drop in the HHV of char product. Moreover, the increase in temperature also caused a decrease in the HHV of char. This condition was clearly observed in scenario II. The drop in HHV could be explained by the degradation of hydrogen and carbon from the char product. Although the HHV of char decreased during co-pyrolysis, the char samples exhibited HHVs comparable with those of some coals and are acceptable for use as alternative solid fuels. The HHV of some Indian coals are obtained in the range of 12.75–28.37 MJ/kg (Majumder et al., 2008), while the HHV of Turkish coals are reported in the range of 9.37–20.34 MJ/kg (Akkaya, 2009).

Table 7.9: Results of elemental analysis of char product

Scenario	Scrap tyre in feedstock (%)	Elemental analysis (wt%)				
		C	H	N	S	O
I	0%	78.00	3.09	0.81	0.15	17.95
	25%	78.05	2.04	0.71	1.38	17.82
	50%	78.09	1.52	0.60	2.13	17.66
	75%	78.13	1.06	0.58	3.40	16.83
	100%	78.31	0.58	0.51	3.61	16.99
II	0%	79.92	1.43	0.72	0.02	17.91
	25%	79.66	1.32	0.71	0.33	17.98
	50%	78.08	0.80	0.98	2.05	18.09
	75%	77.24	0.60	0.40	3.11	18.65
	100%	76.39	0.52	0.30	3.46	19.33

7.3.4.2 Gas product

The gas composition arising from pyrolysis is dependent on the composition of the feedstock used. The main gases from the pyrolysis of wood biomass generally comprise CO, CO_2, H_2, CH_4, C_2H_4, and C_3H_6, as well as minor amounts of other hydrocarbons; the main gas components detected from the pyrolysis of tyre are CO, CO_2, H_2S, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, and C_4H_{10} (Abnisa & Wan Daud, 2014). Among them, methane and hydrogen are considered important gaseous fuels because they are mainly responsible for the HHVs of gases. In scenario I, the generation of methane was clearly observed for all conditions of samples, whereas no hydrogen was detected in the obtained gases (see Figure 7.10). The percentage of methane in this scenario increased when the proportion of scrap tyres increased in the feedstock. The highest level of methane (27.5%) was observed for the pyrolysis of scrap tyre alone. This condition demonstrated that the contribution of methane mostly contributed to the presence of tyre in the feedstock.

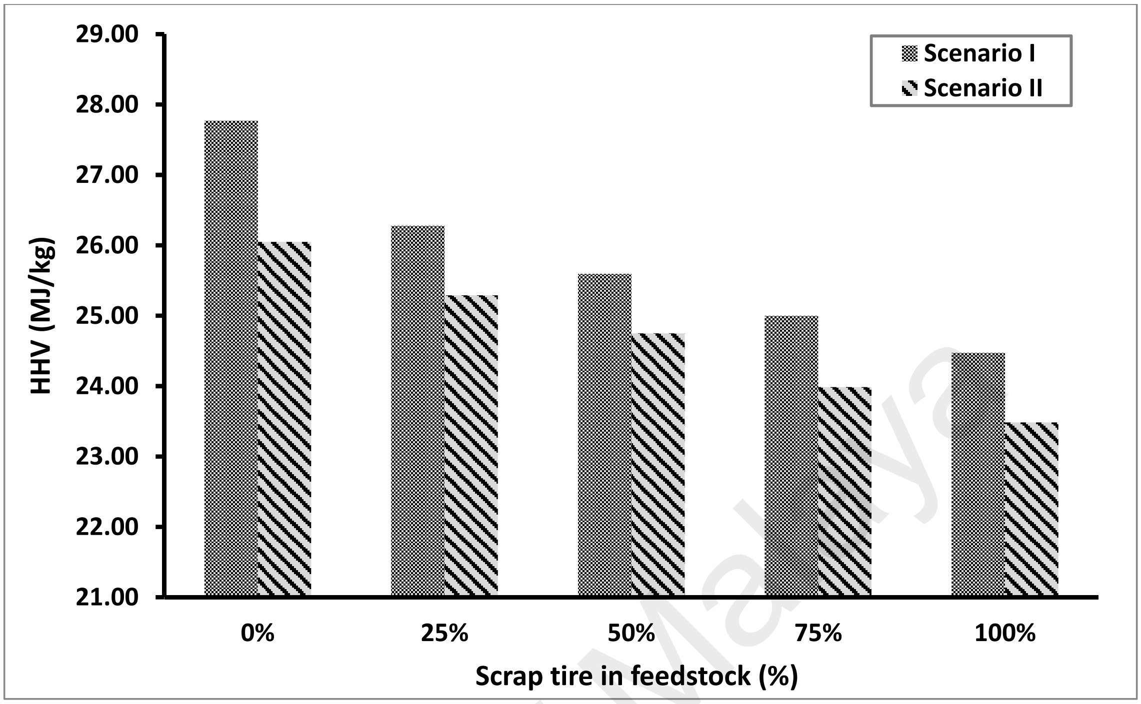


Figure 7.9: HHV of char product

As shown in Figure 7.10, the maximum methane production was obtained at a reaction time of 10–18 min. The addition of scrap tyres decreased the reaction time by maximizing methane production. The results from the pyrolysis of palm shell alone showed that the maximum percentage of methane was achieved at a reaction time of approximately 18 min, whereas the maximum methane production was recorded at 16 min with 50% of scrap tyre in the feedstock. However, methane production gradually decreased with increasing reaction time (of up to 60 min). The pyrolysis experiments showed that a methane percentage of around 3% was obtained at 60 min. It should be noted that no hydrogen was produced during the process of scenario I.

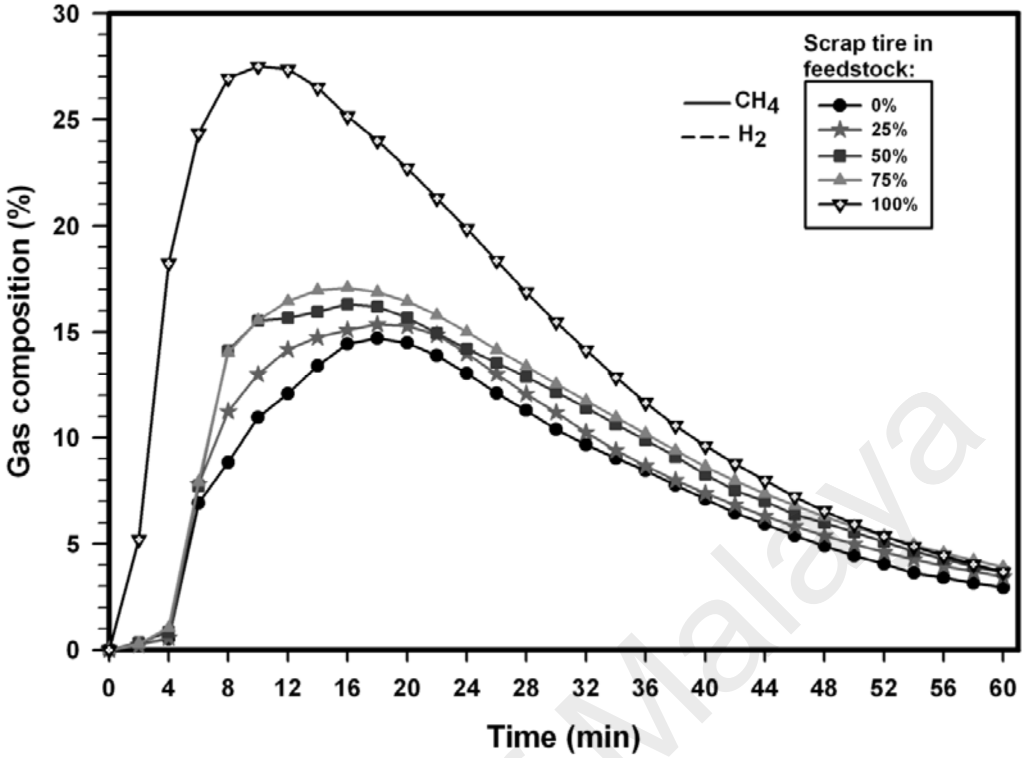


Figure 7.10: Percentage of methane and hydrogen as a function of time, and the different ratios of scrap tyre in the feedstock at 500 °C

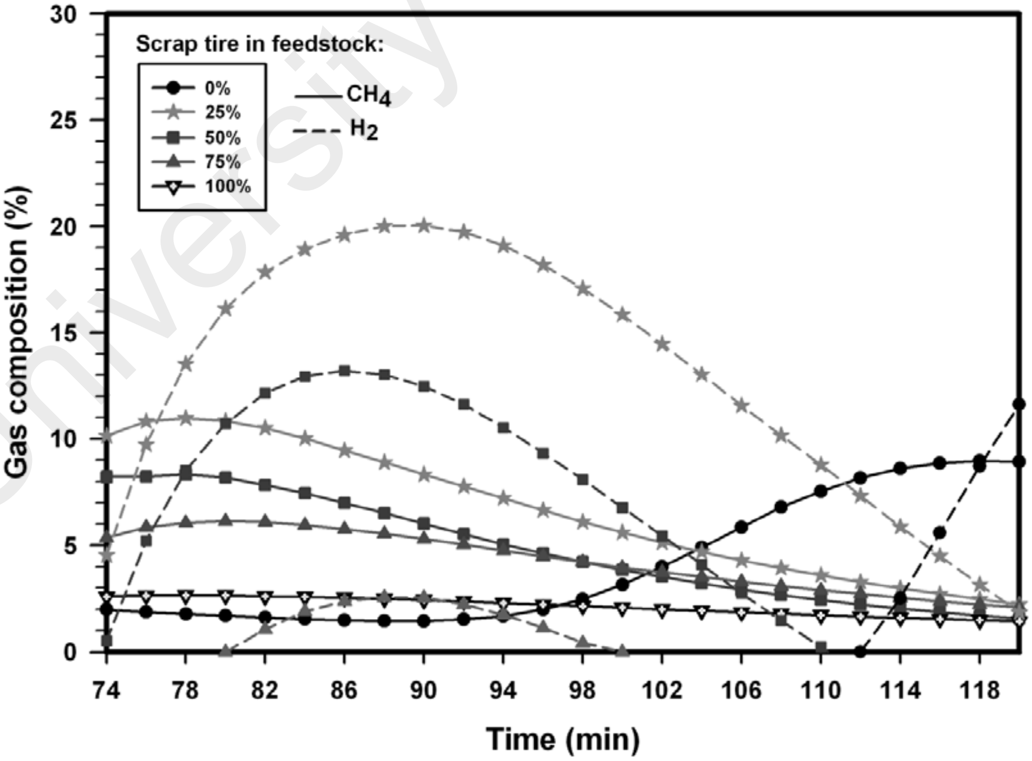


Figure 7.11: Percentage of methane and hydrogen as a function of time, and the different ratios of scrap tyre in the feedstock at 800 °C

Figure 7.11 shows the result of gas composition obtained from scenario II at 800 °C. To increase the temperature from 500 °C to 800 °C in this scenario, an average time of 14 min was needed; therefore, the data presented in Figure 7.11 were collected from the reaction time of 74 min. Data were collected continuously until a reaction time of 45 min was reached (119 min). A discussion on gas composition released at 500 °C in scenario II was not provided because all findings in this scenario were similar to all findings in scenario I. Similar to scenario I (see Figure 7.10), around 3% of methane was observed in scenario II at 500 °C and 60 min. However, the increase in temperature in scenario II increased the percentage of methane again. Methane increased when the temperature reached 800 °C. This finding was observed clearly for the pyrolysis of the mixture of palm shell and scrap tyre. However, no increase in methane was found for the pyrolysis of pure scrap tyre in this scenario. The highest amount of methane at 800 °C was approximately 10.96%, which was obtained from the co-pyrolysis of 75% palm shell and 25% scrap tyre.

As shown in Figure 7.11, the increase in temperature in scenario II obviously contributed to hydrogen production. The highest percentage of hydrogen (20%) was detected for the co-pyrolysis of 75% palm shell and 25% scrap tyre. The increase in scrap tyre proportion decreased the percentage of hydrogen in the gas yield. No hydrogen was found in the pyrolysis of scrap tyre alone. The absence of hydrogen production from the pyrolysis of scrap tyre was also reported by Kaminsky et al. (2009). The authors noted that the gas fraction from the pyrolysis of tyre mainly contains methane, ethane, ethene, and propene. Most of the hydrogen compositions from their experiment were found to be lower than 1%. Their study was performed at various temperatures within the range of 598–780 °C using tyre rubber from trucks as a feedstock.

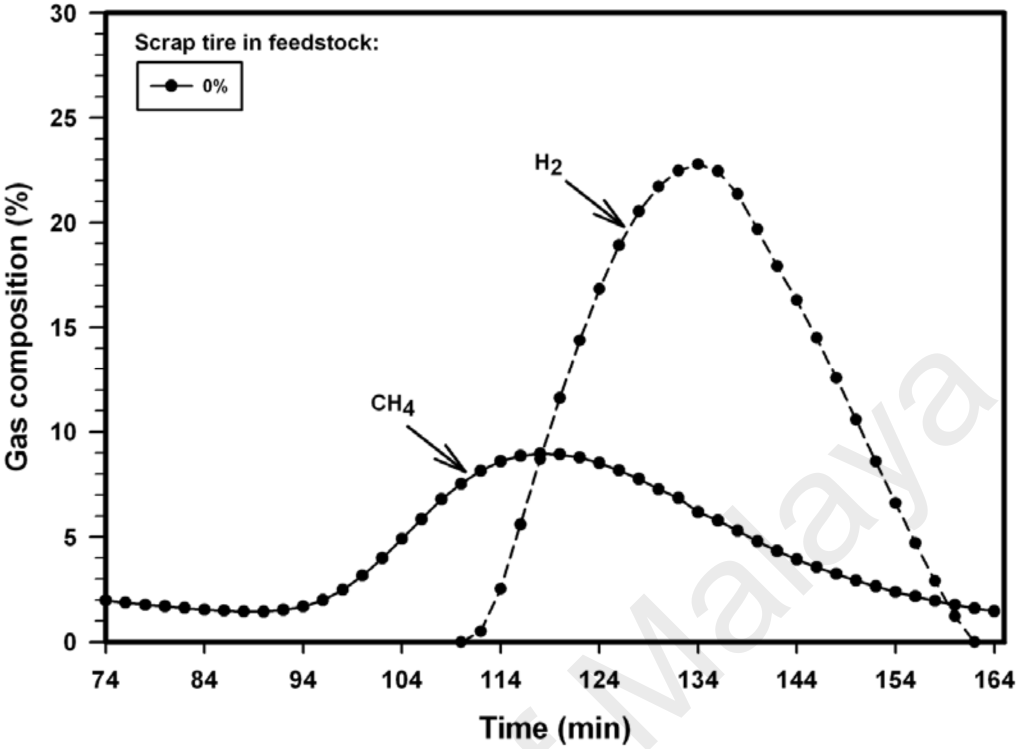


Figure 7. 12: Percentage of methane and hydrogen as a function of time at 800 °C for the pyrolysis of palm shell alone

The hydrogen obtained in the current study was mainly caused by palm shell, thereby indicating that the presence of biomass in co-pyrolysis played an important role in yielding hydrogen. However, hydrogen from the pyrolysis of palm shell alone was only 11.61% upon completion of the reaction time. To clarify this issue, an additional experiment was performed in which the reaction time was extended to 90 min. The results from additional analysis showed that hydrogen gas needed more time to initiate production. Figure 7.12 shows that hydrogen was produced at around 112 min, and the maximum hydrogen production (22.78%) was obtained at 134 min. The same trend was also observed for methane production. This finding showed that the presence of scrap tyre in the pyrolysis of biomass was significantly helpful in reducing the reaction time to maximize the production of methane and hydrogen.

7.4 Conclusions

The addition of scrap tyre in the pyrolysis of biomass successfully improved the quantity and quality of the liquid. The increase in temperature after optimum conditions of co-pyrolysis slightly increased the liquid and gas, and decreased char. All liquid products from this experiment confirmed the presence of the aqueous phase, and the liquid was divided into several layers. Although the aqueous phase was detected in the liquid, this phase sharply decreased when the proportion of scrap tyres increased in the feedstock. Moreover, the increase in tyre in the feedstock also decreased the oxygen content, pH, and water content in the organic phases. The decrease in these contents was more evident with scenario II. Elemental analysis demonstrated that the contents of carbon and hydrogen in the organic phase significantly improved with increasing scrap tyre in the feedstock. Notably, the sulfur content also increased when scrap tyres were involved. In addition, the HHV of the organic phase from both scenarios showed a tendency to increase. The FTIR results proved that the addition of scrap tyres in the pyrolysis of palm shell was effective in reducing the domination of the O-H group. Unlike the liquid product, the addition of scrap tyres was not favorable for increasing the fuel characteristics of char. No improvement in the carbon and hydrogen contents in char was observed during the co-pyrolysis of palm shell and scrap tyre. However, the char samples exhibited HHVs comparable with those of some coals, so they could still be considered for use as alternative solid fuels. For gas products, the results also showed that the addition of scrap tyres contributed to methane production, whereas wood biomass was favored to produce hydrogen. The addition of scrap tyres in the pyrolysis of wood biomass was significantly helpful in reducing the reaction time to maximize the production of methane and hydrogen.

Based on the results, this study recommends that co-pyrolysis is a potential technique to develop for the generation of fuels from biomass waste. Stepwise co-pyrolysis could be considered as an alternative for optimizing the production of fuels from biomass waste. The mixture of palm shell and scrap tyre was found to be suitable and effective in promoting synergistic effects during pyrolysis. Notably, palm shell was selected as a model from lignocellulosic biomass, so it could be replaced with other lignocellulosic biomass. Scrap tyre was added to improve the quantity and quality of liquid produced from the pyrolysis of lignocellulosic biomass. Therefore, scrap tyre could be regarded an additive material, and its proportion was designed to be less than that of the main feedstock (lignocellulosic biomass). The co-pyrolysis of 50% biomass and 50% scrap tyre is recommended because of the following considerations: (a) the amount of 50% of scrap tyre in the feedstock significantly improved liquid and byproducts; and (b) the generation of waste tyre was generally found to be lower than that of lignocellulosic biomass. Therefore, the limited source of additive material is expected to be sufficient for the amount of lignocellulosic biomass available. Some tyre wastes are necessary for recycling purposes.

CHAPTER VIII

RECOVERY OF LIQUID FUEL FROM THE AQUEOUS PHASE OF PYROLYSIS OIL BY USING CATALYTIC CONVERSION

8.1 Introduction

Currently, developments in the production of pyrolysis oil as a renewable liquid fuel from biomass are attracting increasing attention in the renewable energy research community. One important reason for this interest is the abundant amount of biomass that is now available around the world. As a renewable source, biomass is easy to obtain in various forms (Ertaş & Hakkı Alma, 2010) and can be regenerated in a short period of time (Abnisa et al., 2011). Besides, the oil produced from biomass pyrolysis has received positive comments as a more environment-friendly fuel because it contributes to reducing the amount of CO_2 in the atmosphere, which also has the effect of minimizing the emission of greenhouse gases (Li et al., 2009; Peng et al., 2009; Xu et al., 2010; Xu et al., 2009).

Basically, the oil from pyrolysis of biomass consists of two different layers which are defined as the aqueous phase and organic phase (viscous oil phase). The aqueous phase can be obtained at the top layer of the pyrolysis oil, while the bottom layer is referred to as the organic phase. In the case of co-pyrolysis of biomass, the oil can be obtained in three different layers, where the middle layer is determined as aqueous phase (Samanya et al., 2012). Yields of aqueous phase vary in the range of 15 – 75 wt% of the total pyrolysis oil (Melero et al., 2012; Yang et al., 2013). The physical form of the aqueous phase is light brown in color and has a lower viscosity than the organic phase. Some studies have shown that the aqueous phase from pyrolysis oil generally has a high water content, measured in the range of 36 – 70 wt% (Abnisa et al., 2013a; Mercader et al., 2010). Sugars, organic acids, hydroxyacetone, hydroxyacetaldehyde, furfural, and small amounts of guaiacols are chemical compounds contained in the aqueous phase (Teella et al., 2011).

Several methods have been developed to separate the aqueous and organic phases for various research purposes. Ertaş and Hakkı Alma developed a simple method using only a separatory funnel (Ertaş & Hakkı Alma, 2010). Bartero et al. performed the separation process by using a centrifuge maintained at 3200 rpm for 8 minutes (Bertero et al., 2012). A study by Uçar and Karagöz (2009) conducted the separation by extracting the organic layer. The oil was mixed with diethyl ether, then the ethereal solutions obtained were dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at 25 °C. Upon removal of the diethyl ether, this fraction was weighed and called organic oil. Xiu et al. separated the aqueous phase by filtration under vacuum through a glass fiber filter (Xiu et al., 2010).

Many studies have performed an upgrading process to obtain liquid fuel from the organic phase of pyrolysis oil (Adjaye & Bakhshi, 1995; Carlson et al., 2008; French & Czernik, 2010; Samolada et al., 1998; Sharma & Bakhshi, 1993; Vitasari et al., 2011). However, no literature was found on the direct utilization of the aqueous phase for liquid fuel production. The high water content may be a reason why this phase is not getting attention for further study of liquid fuel production. In 2011, some research work tried to use the aqueous phase of pyrolysis oil to produce acetic acid and hydrogen gas. Teella et al. studied the extraction of acetic acid from the aqueous phase of fast pyrolysis bio-oil by a separation process using nanofiltration and reverse osmosis membranes (Teella et al., 2011). A similar study was conducted by Resrendra et al. (2011), where the recovery of acetic acid was performed by reactive extraction using tri-n-octylamine. Meanwhile, the production of hydrogen has been studied by Medrano et al. (2011) and Zhang et al. (2011) through the process of catalytic steam reforming in a fluidized bed reactor.

However, it is important to conduct research to obtain an overview of how much liquid fuel can be produced from the aqueous phase. Catalytic cracking is a technique that can be selected for this purpose, and is known as a cheaper process since it is performed in low-pressure conditions (Vitolo et al., 2001) with no need for complicated equipment or reactor plugging in the proposed process. In application, there are two types of catalytic cracking: off-line catalytic cracking which uses pyrolytic oil as raw material, and on-line catalytic cracking which uses pyrolysis vapors as raw material (Hew et al., 2010). Zeolite or silica-alumina is an acidic catalyst that is frequently used to support this process. The positive performance of zeolites on upgrading the pyrolytic oil has been widely studied by many researchers (Adjaye & Bakhshi, 1995; Horne & Williams, 1996; Samolada et al., 2000; Williams & Brindle, 2002). Strong acidity, high activities and shape selectivity are the characteristics of this catalyst, which enables a high level of conversion of oxygenated compounds to hydrocarbons (Williams & Horne, 1995).

The objective of this study was to determine the yield of liquid fuel that can be produced from the aqueous phase of pyrolysis oil. Two different HZSM-5 catalysts were used to support the catalytic conversion with condition temperatures set at 405, 455, 505 and 555 °C. The oil product was then characterized using several laboratory instruments to obtain an overview of their chemical and physical properties.

8.2 Experimental

8.2.1 Raw material of pyrolysis oil

The pyrolysis oil used in this study was produced from pyrolysis of 200 g palm shell at a temperature of 500 °C, as described in previous work conducted by Abnisa et al. (2013a). The oil was then separated into two phases based on a procedure developed by Bartero et al. (2011a). The physical and chemical properties of the aqueous phase of the pyrolysis oil are listed in Table 8.1.

Table 8.1: Physical and chemical properties of aqueous phase of pyrolysis oil

Properties	Value	Unit
Viscosity at 50 °C	1.9	cP
pH	2.5	
Density at 24 °C	1051	kg/m^3
Elemental composition (wet basis)		
C	15.30	wt %
H	11.58	wt %
N	0.16	wt %
O[a]	72.90	wt %
S	0.06	wt %
High Heating Value (HHV)	14.24	MJ/kg
Water content	53	wt %
Elemental composition (dry basis)		
C	32.55	wt %
H	12.00	wt %
O	54.98	wt %

[a] By difference

8.2.2 Preparation and characterization of catalysts

In this study, two different commercial zeolites are used as catalysts to perform the cracking process. The first zeolite contains a silica-alumina ratio of 50 (HZSM-5/50). It was supplied by Zeolyst International, London, UK. The zeolite was received in NH_4-exchanged form. To remove the ammonia, the catalyst was heated for 60 min in a stream of nitrogen at 500 °C. The second catalyst used in this study is the zeolite HZSM-5/70. This catalyst was supplied by Acros Organics, New Jersey, USA.

Table 8.2: Properties of the catalysts after the pressing process

Product Zeolite	SiO_2/Al_2O_3 mole Ratio	Nominal cation form	Surface area (m^2/g)	Total pore volume (cm^{-3}/g)
HZSM 5/50	50	Ammonium	315	0.16
HZSM 5/70	70	Hydrogen	159	0.11

Prior to use, both of the catalysts were compacted using a press machine with a pressure of 20 tons. The catalyst was filled into a square-shaped mold which was made from stainless steel. For each catalyst, the pressing process was held for 15 min. Then, the compacted catalyst was crushed and sieved with 1-2 mm. These works were performed to prevent loss of the catalyst from the catalyst bed in the reactor during the process. The properties of the zeolite catalysts after the pressing process are shown in Table 8.2. The surface area of the catalyst was determined using the Brunauer-Emmett-Teller (BET) method with a Quantachrome Autosorb-1 instrument using nitrogen gas at -196 °C.

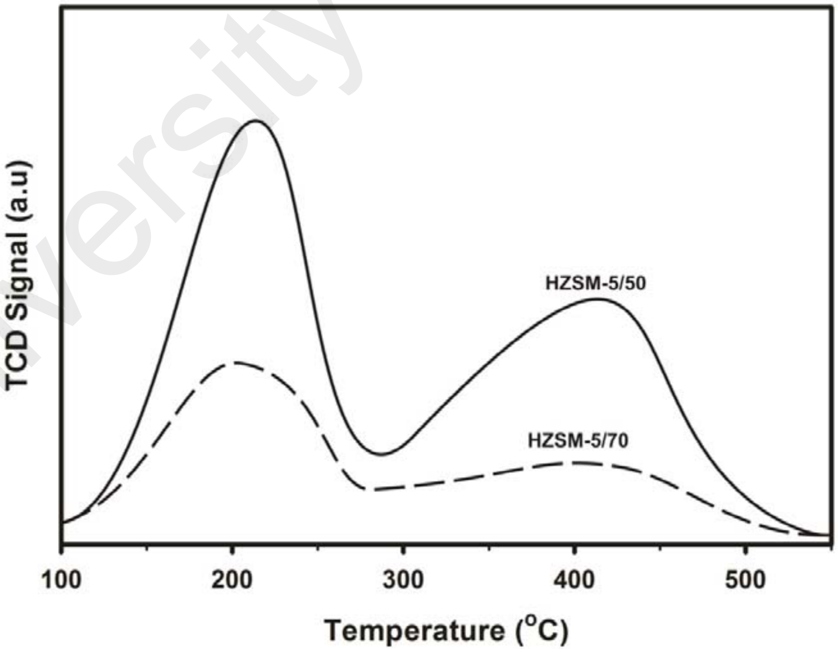


Figure 8.1: NH_3-TPD profiles of the zeolite catalysts

Furthermore, the acidic properties of catalysts were characterized by the temperature programmed desorption of ammonia (NH_3-TPD), using a ChemiSorb 2720 (Micromeritics). The result of NH_3-TPD profiles for both catalysts are shown in Figure 8.1. As can be seen from Figure 8.1, both of catalysts exhibit two NH_3-desorption peaks which were generally observed in two temperature regions referred to as low-temperature and high temperature region, respectively. One strong peak around 220 °C was assigned to the desorption of NH3 from the weak acid sites, while another peak of NH_3-TPD around 440 °C corresponded to the desorption of NH3 from the strong acid sites (Gong et al., 2011). Moreover, it clearly observed that the intensity of peak areas is reduced significantly with an increasing of Si/Al ratio from 50 to 70, indicating the reduced acid amount and strength with an increasing Si/Al ratio. This finding is in agreement with previous studies (Ali et al., 2003; Shirazi et al., 2008).

The use of HZSM-5 catalysts has gained interest in many studies of catalytic upgrading processes. The catalyst also has been used widely for fluid catalytic cracing in refining industry. However, the performance of this catalyst has been hindered by its rather low stability, in other words its tendency for deactivation. The catalyst deactivation is mainly caused by the carbon deposition on the catalyst during the conversion of pyrolysis oil. According to Bi et al. (2013), the regeneration of the deactivated catalyst can be achieved by the coke burn-off method. Nevertheless, to obtain the optimum performance, the regeneration of the deactivated catalyst cannot be performed repeatedly. Guo et al. noted that catalytic activity changes moderately during the first three times of regeneration, while catalysts are gradually deactivated by the repeated regenerations after three times (Xiaoya Guo et al., 2009). Similar observations were also reported by Vitolo et al. who studied the behavior of the HZSM-5 catalyst when used in repeated upgrading-regenerating cycles (Vitolo et al., 2001).

8.2.3 Experimental Set-up

The experiments were conducted using a fixed-bed reactor in a batch process at atmospheric pressure. The height and inside diameter of the reactor were 550 mm and 10 mm, respectively. Figure 8.2 shows the detailed description of the experimental set-up of the catalytic conversion. The reactor was loaded by placing 0.2 g quartz wool as a support for the catalytic bed, followed by filling 10 g of catalyst and finally closed by placing 0.2 g of quartz wool on top of the catalyst.

The experiment was started by heating the catalyst at 200 °C for 60 minutes to obtain an anhydrous condition. Then the temperature was set to the desired condition (405, 455, 505 and 555 °C) in a stream of nitrogen at a heating rate of 10 °C/min. When the temperature of the reactor was reached, the nitrogen flow stopped. The aqueous phase was injected into the vertical reactor with a flow rate of 1.051 g/min using a peristaltic pump. Each run lasted for about 30 min and was performed in triplicate.

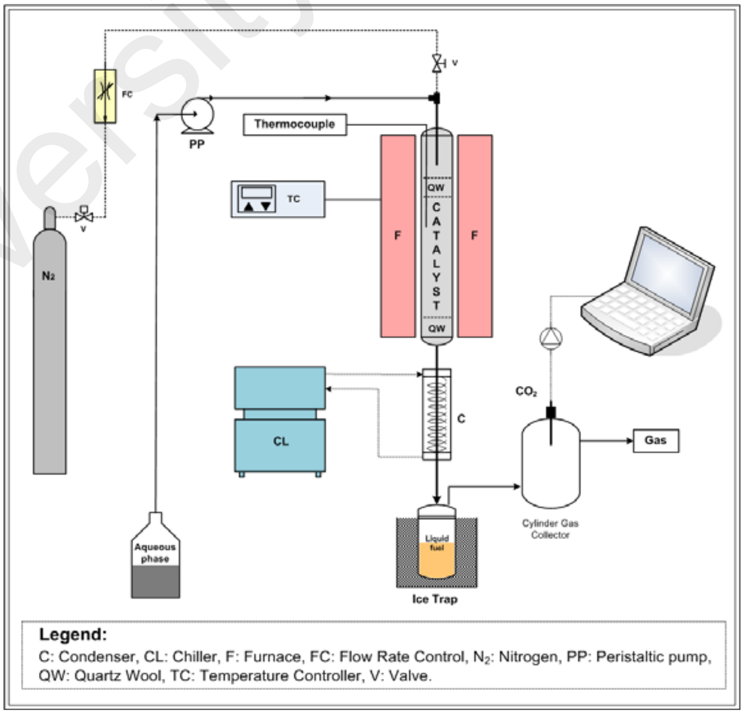


Figure 8.2: Flow diagram of experimental set-up for catalytic conversion of aqueous phase

During the process, the aqueous phase was evaporated due to the effect of the thermal conversion at reactor temperature. As the initial effect of the thermal reaction, a solid residue was formed on the top layer of quartz wool, derived from some of the ingredients of the aqueous phase. Furthermore, the vapors from the evaporation of aqueous phase flowed down and into contact with the catalyst, then passed through the cooler tube at 5 °C and finally flowed into an ice trap apparatus to condense as a liquid product. As a consequence, impurities were deposited on the surface of the catalyst and the presence of coke was indicated.

In this study, the amount of non-condensable gases was determined by the difference between the total weight of the aqueous phase (feed) and other products (oil, water, char, tar, and coke). Some preliminary studies have been conducted to measure the CO_2 released from the non-condensable gas and the results showed that more than 5000 ppm of CO_2 was produced in all the experiments. The CO_2 gas was recorded using a Vernier CO_2 Gas Sensor.

The liquid product was obtained in two immiscible layers which can be defined as oil and water fractions. The oil can be easily separated from the water fraction using a micropipette. After separation, both fractions were weighed separately and the obtained values were then calculated using Eq. 8.1.

After each run, the spent catalyst, and the top and bottom quartz wool plugs were removed from the reactor. The solid residue that was deposited on the top quartz wool was defined as char. The char was calculated by the weight difference of the top quartz wool before and after the experiment. Afterwards, the internal surface of the reactor, the spent catalyst and the bottom plugs of quartz wool were washed with acetone and then the acetone solution from the washing process was collected. After drying the acetone solution at 100 °C for 60 min, what remained of it was defined as tar. The catalyst that had been washed to define the tar was then used to obtain the coke. The catalysts were dried in an oven and heated in a furnace for 60 min at 100 °C and 60 min at 600 °C, respectively. The weight difference of the catalyst before and after heat treatment is termed as the amount of coke. To obtain the final percentage of products (oil, water, char, tar, and coke), all the yields that were obtained in this work were then calculated using equation (1):

$$\text{Yield}\,(\text{Wt}\,\%) = \frac{\text{Product}\,(\text{g})}{\text{Feed}\,(\text{g})} \times 100\,\% \tag{8.1}$$

In this work, each of experiments with different zeolites (HZSM-5/50 and HZSM-5/70) and different temperature conditions (405, 455, 505 and 555 °C) yielded oil, water, char, coke, tar and gas. The gas yield was assumed to be a CO_2 fraction. The formation of CO_2 is found to be dominant during the catalytic upgrading of pyrolysis oil (Park et al., 2012; Vitolo et al., 1999).

8.2.4 Products Analysis

The oil produced from catalytic cracking was analyzed by performing several tests. These included analysis of the water content, functional group composition analysis by Fourier transform infra-red (FTIR) spectroscopy, detailed chemical composition analysis of the oil using GCMS, elemental analysis (C, H, N, S and O) and thermogravimetric analysis.

The Karl Fischer titration method was used to measure the water content. The measurement was performed using a Karl-Fischer 737 KF Coulometer from Metrohm.

HYDRANAL Coulomat AG (80 mL) and HYDRANAL Coulomat CG (5 mL) were used as anolyte and catholyte reagents, respectively. Fourier transform infra-red (FTIR) spectroscopy was used to classify the chemical types in the oil. The analysis was conducted using a Perkin Elmer Spectrum 400 spectrometer. The oil samples were pressed into a disc with 1 g of KBr, and then scanned in the range of 550 – 4000 cm^{-1} with a resolution of 4 cm^{-1}. The chemical compositions were determined by gas chromatography/mass spectroscopy (GCMS). The analysis was performed with an Agilent Technologies 7890A gas chromatograph equipped with an Agilent 5975C mass-selective detector (mass spectrometer). High purity helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. An Agilent HP-5 50 m column with an inner diameter of 0.32 mm and a film thickness of 0.25 μm was used in the GCMS. The analysis was started by heating the column at 50 °C and it was then kept isothermal for 1 min and ramped to 270°C at a rate of 7 °C/min. This condition was held for 10 min. The volume of sample injected was about 1 μL.

The elemental analysis of the oils was determined with the Model 2400 Perkin-Elmer Series II CHNS/O Analyzer. CHNS combustion tube and reduction tube were used for this determination. Each of the elemental values was used for calculating the molar ratios of H/C and O/C in the upgraded oils using the following equations:

$$\mathrm{H/C} = \frac{\mathrm{H}/\mathrm{MW_H}}{\mathrm{C}/\mathrm{MW_C}} \tag{8.2}$$

$$\mathrm{O/C} = \frac{\mathrm{O}/\mathrm{MW_O}}{\mathrm{C}/\mathrm{MW_C}} \tag{8.3}$$

From the elemental analysis (wet basis), the dry elemental composition could be calculated by subtracting the contribution of H and O originating from the water (Mercader et al., 2010):

$$C_{dry} = \frac{C_{wet}}{(1-(H_2O/100))} \tag{8.4}$$

$$H_{dry} = \frac{H_{wet} - (H_2O\,.(2\,.MW_H/(2\,.MW_H + MW_O)))}{(1-(H_2O/100))} \tag{8.5}$$

$$O_{dry} = \frac{O_{wet} - (H_2O\,.\ (MW_O/(2\,.MW_H + MW_O)))}{(1-(H_2O/100))} \tag{8.6}$$

The results of elemental analysis are also used for calculating the high heating value (HHV). In this study, the HHV was calculated following equation (8.7) which is the Dulong-type formula modified by Mott and Spooner (Channiwala & Parikh, 2002). Generally, the formula is used for conditions in which the oxygen content is greater than 15%.

$$\mathrm{HHV\,(MJ/kg)} = 0.336C + 1.418H - (0.153 - 0.000720\,O)O + 0.0941\,S \tag{8.7}$$

The recovery rate of carbon ($C_{recovery}$) from the upgraded oils was determined as in equation (8.8):

$$C_{recovery} = \frac{\text{upgraded oil yield} \times \text{upgraded oil carbon content (dry basis)}}{\text{feed carbon content (dry basis)}} \times 100\% \tag{8.8}$$

Thermogravimetric analysis of the raw pyrolytic oil and upgraded oil was performed using a thermogravimetric analyzer (TGA 4000, Perkin Elmer). The analysis was done under a nitrogen flow rate of 25 ml/min and heating rate of 40 °C/min.

8.3 Results and Discussion

8.3.1 Product yields

The obtained products from the catalytic conversion are presented in Table 8.3. As can be seen, the oil yields from catalytic cracking of the aqueous phase ranged from 4 to

9.16 wt%, depending on the catalyst types and temperature conditions. The catalytic cracking using the HZSM-5/70 catalyst produced the highest yield of oil (about 9.16 wt%) at a low temperature of 405 °C. However, the yield of oil was significantly less when using the catalyst HZSM-5/50, followed by a raised water yield. It is noted that proper selection of the catalyst in the catalytic conversion will more effectively separate the water and oxygenated compounds from the oil. According to Iliopoulou et al. (2007), a catalyst with a large surface area, relatively large pores, and mild-to-moderate acidity can be considered as promising for the catalytic conversion. In this study, the larger surface area and pore volume was observed with the HZSM-5/50 catalyst (refer to Table 8.2). Furthermore, the effect of temperature also plays an important role in recovering the liquid fuel from the aqueous phase of pyrolysis oil. The increase in process temperature leads to decreased oil yield. This condition was observed for both of the catalysts used in this study. Williams and Nugranad (2000) studied the catalytic pyrolysis of rice husks and found a similar decrease in the oil production with increased pyrolysis temperatures.

Figure 8.3 shows a comparison of the physical appearance of oils after catalytic cracking using two different catalysts at a temperature of 555 °C. The oil obtained from HZSM-5/70 is shown in black and is present at the bottom layer, while the water obtained at the upper layer is light yellow in color. By contrast, the use of HZSM-5/50 catalyst resulted in oil obtained at the upper layer and the water is shown as colorless. In addition, a distinctive aromatic odor similar to gasoline was detected for the oil produced from HZSM-5/50.

Table 8.3: Product yields from the catalytic cracking of aqueous phase using HZSM-5/50 and HZSM-5/70

Catalyst	Temperature	Yield (wt %)					
		Oil	Water	Char	Tar	Coke	Gas[a]
HZSM 5/50	405	7.46	51.88	5.43	3.63	9.48	22.12
	455	6.19	53.14	3.77	3.81	8.27	24.82
	505	4.67	56.02	2.74	2.78	7.90	25.89
	555	4.00	55.82	2.38	2.57	7.75	27.48
HZSM 5/70	405	9.16	43.72	5.01	4.69	7.19	30.23
	455	9.01	44.83	4.34	4.66	6.51	30.65
	505	8.18	46.38	3.97	3.79	7.05	30.63
	555	7.31	46.85	3.99	3.62	7.24	30.99

[a] By difference

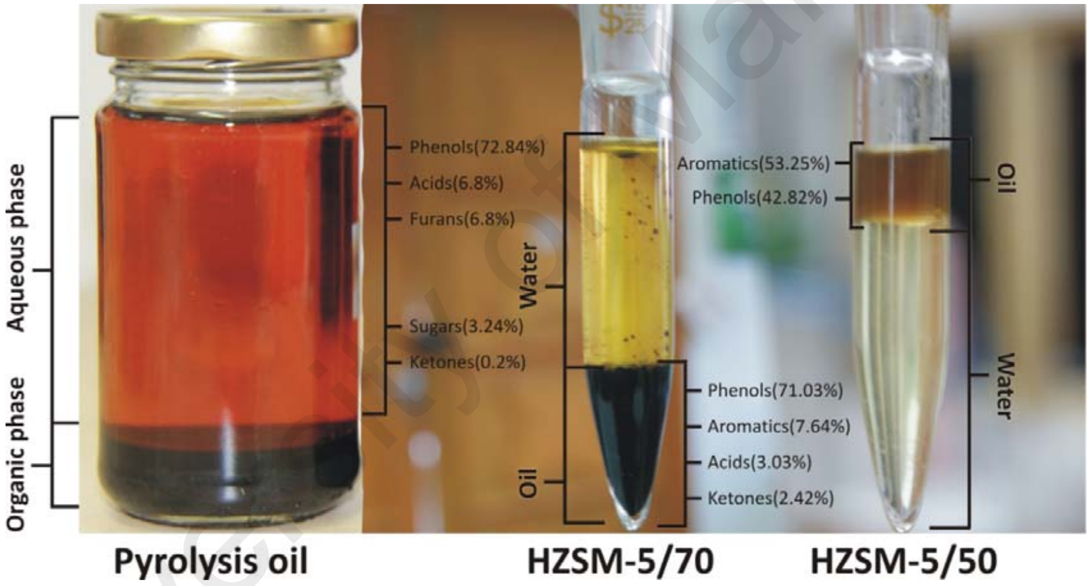


Figure 8.3: Comparison of oil yields after catalytic conversion with different catalysts at a temperature of 550 °C

As can be seen in Table 8.3, the water was observed to be the highest percentage of products obtained from the catalytic conversion. The result is in good agreement with our previous work (Abnisa et al., 2013a), where we observed that the aqueous phase produced from palm shell was dominated by the water content (about 53 wt%). Furthermore, the elevation in the temperature also plays an important role in increasing the yield of water. The experiment which used the HZSM-5/50 catalyst showed that the formation of water increased from 51.88 to 55.82 wt % when the temperature was increased from 405 to 555 °C. Sharma and Bakhshi (1993) studied the catalytic upgrading of pyrolysis oil at atmospheric pressure using HZSM-5 as catalyst. The upgrading was done in the temperature range of 340 – 410 °C in a fixed bed micro-reactor. Their results showed that the increase in temperature caused an increase in water yield.

During the process, the solid carbonaceous material that was identified as a char was formed above the catalyst bed (the top quartz wool). For the HZSM-5/50 catalyst, the results showed that the char was reduced from 5.43 wt % at 405 °C to 2.38 wt% at 555 °C, as the pyrolysis temperature increased. In this study, the highest char yield was observed at low reaction temperature. Pütün et al. (2006) noted that increasing the temperature in the catalytic upgrading process will have the effect of increasing the yield of conversion while decreasing the yield of char.

As undesirable byproducts, the yield of tar obtained was in the range of 2.57 – 4.69 wt%, while the yield of coke was in the range of 6.51 – 9.48 wt%. As can be seen from Table 8.3, both of these products were influenced by the operating temperature, with increasing temperature leading to a decrease in the tar and coke yields. These observations are in agreement with the study reported by Vitolo et al. (Vitolo et al., 2001). According to Phuphuakrat et al. (2010), the decrease in tar caused by the high temperature of the process had the benefit of increasing the gas production. Their conclusion is in good agreement with the yield of gas that is evident in Table 8.3, where the yield of gas was increased as the tar decreased. Furthermore, the proportion of coke was observed to be higher than the byproducts of char and tar. As described in the literature, the coke may result from the polymerization of some of the primary organic vapors which occurred during the catalytic reactions (Zhang et al., 2009). On the other hand, some of the aromatic compounds, particularly furans, might also undergo polymerization to form coke (Carlson et al., 2011). However, the presence of coke deposited on the catalyst surface is undesirable since it can lead to deactivation of the catalyst. In this study, the decrease of coke with respect to an increase of temperature was clearly shown for both catalysts. A similar tendency of coke decreasing has also been reported in another study (Williams & Nugranad, 2000).

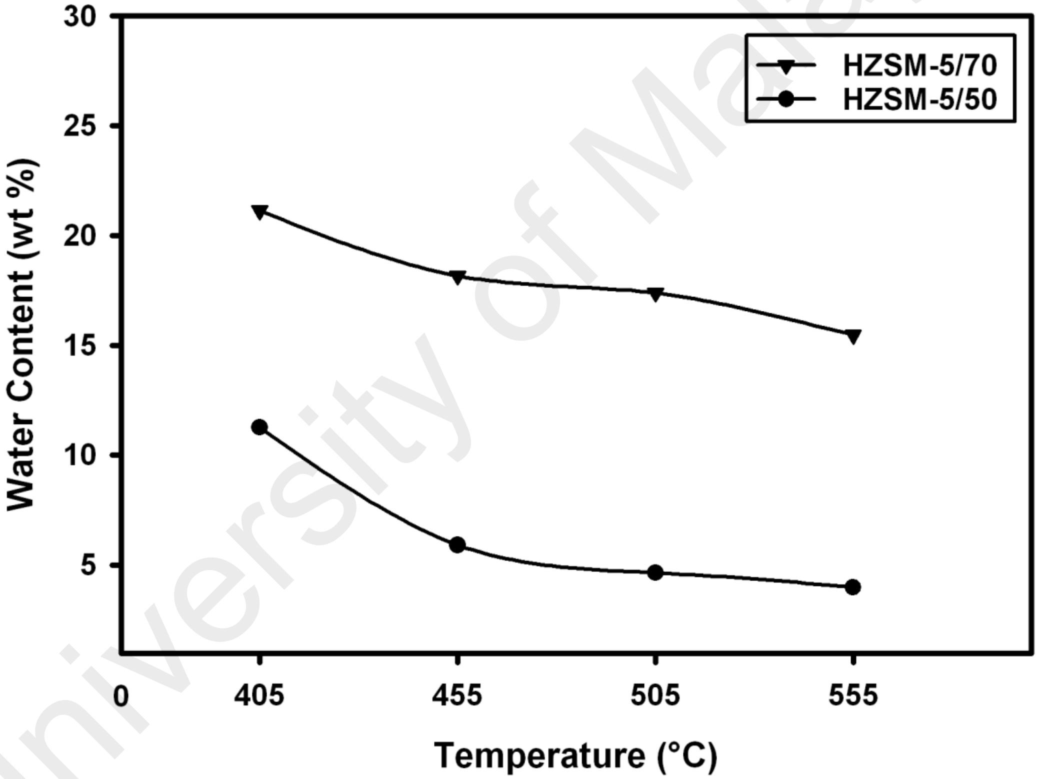


Figure 8.4: Effect of temperature on water content in the oils after catalytic conversion

8.3.2 Characteristics of the produced oil

8.3.2.1 Water content in the produced oil

The results of water content analysis of the oils produced under different zeolite catalysts are shown in Figure 8.4. During the process, a decrease in water content caused by an increase in temperature was clearly observed for all experiments. However, significant reduction of water content in the oil obtained was only observed when using the catalyst HZSM-5/50 at a temperature of 555 °C, where its value was about 3.97 wt%. Hilten et al. (2010) noted that the reduction of water content in catalytic cracking was due to the formation of hydrocarbons. As reported by Sharma and Bakhshi (1993), a small amount of water content will still remain in the oil after catalytic cracking, which is approximately 2 – 5 wt%.

8.3.2.2 Functional group compositional analysis

Comparison of the FTIR spectra results of the aqueous phase of pyrolysis oil and oils after cracking obtained at a temperature of 555 °C by using HZSM-5 catalysts are shown in Figure 8.5a. In this study, different wavelengths of the absorbed light were observed, which indicates that they have dissimilar characterization of the chemical bonds. Figure 8.5a clearly shows that some of the oxygenated groups are still present in the oils after cracking. The presence of oxygen in the oil was represented by the O-H stretching vibrations between 3200 and 3400 cm^{-1}, which indicated phenols and alcohols. However, some of the peaks indicated as oxygenated groups disappeared from the upgraded oil that was produced using the HZSM-5/50 catalyst. These are detected in the range of 1650 – 1850 cm^{-1} and 1000 – 1300 cm^{-1}. The peaks between 1650 and 1850 cm^{-1}, which are related to C=O stretching, indicate the presence of ketones, carboxylic acids, and aldehydes. The C-O stretching vibration in the range of 1000 – 1300 cm^{-1} was identified as alcohols and esters. The two low intensity peaks at 2350 cm^{-1} that are shown by the aqueous phase of the pyrolysis oil are due to the CO_2 presence in the air during the analysis. In addition, the spectrum of the oil yielded from HZSM-5/50 showed the emersion peaks between 2850 and 3100 cm^{-1}. Several distinct peaks in the range of 2850 – 3000 cm^{-1} were identified as alkanes that are represented by the C-H stretching vibration. The single medium peak due to =C-H stretching vibration that is shown in the range of 3010 – 3100 cm^{-1} was indicated as alkenes.

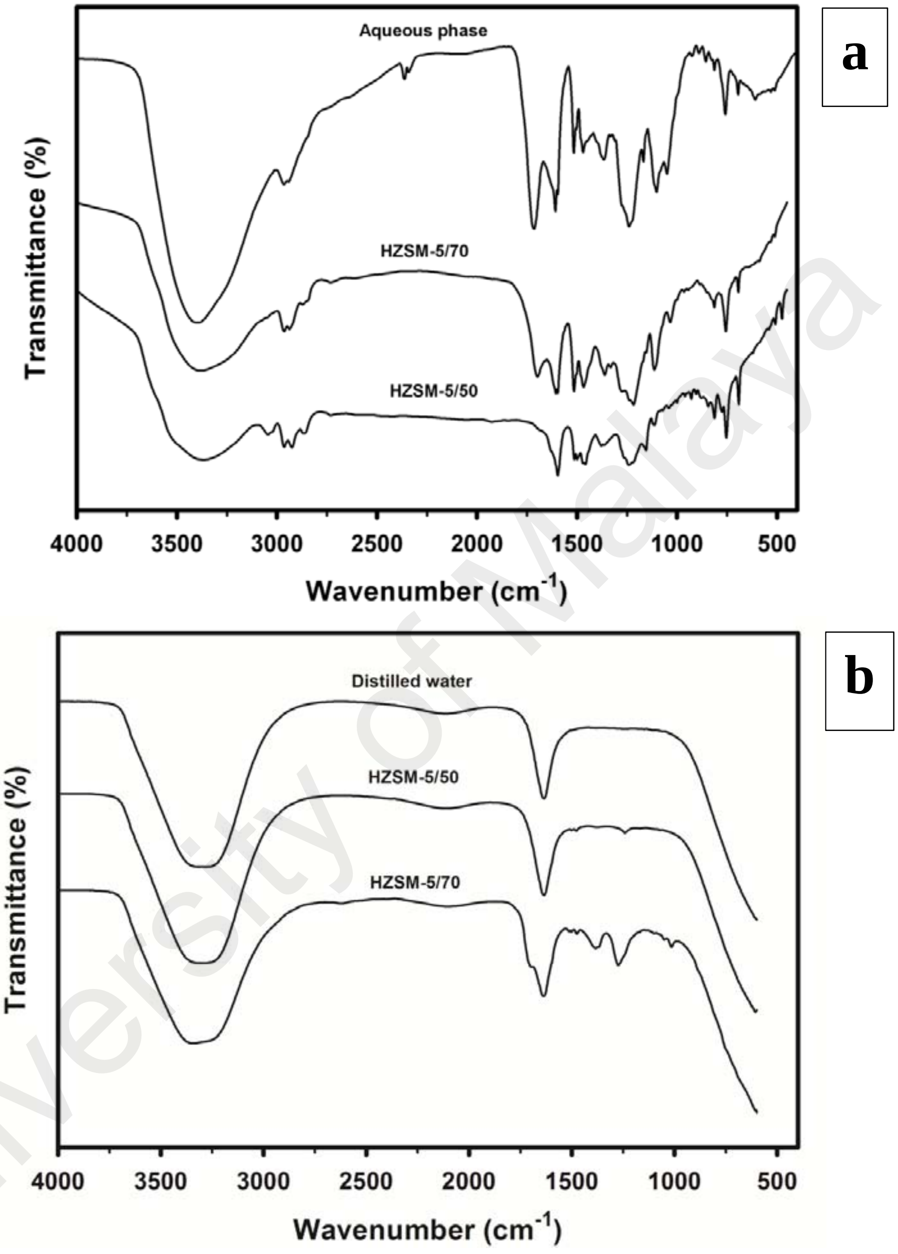


Figure 8.5: (a) FTIR spectra of aqueous phase and the oils after catalytic conversion at a temperature of 555 °C. (b) FTIR spectra of distilled water and the produced water after catalytic conversion at a temperature of 555 °C

In addition, the FTIR analysis was also used to identify the remaining chemicals in the produced water after the cracking process, which was obtained at a temperature of 555 °C. The IR spectrum of distilled water was used as a reference to compare the purity of the produced water after the process of catalytic cracking. From Figure 8.5b it can be seen that the produced water from the HZSM-5/50 catalyst has similar spectrum with distilled water, while the produced water from the HZSM-5/70 still clearly showed the presence of alcohols, acids, and esters which represented by the C-O stretching vibration in the range of 1000 – 1320 cm^{-1}. It is explained that the catalyst which has good performance in catalytic conversion will produce more pure water.

8.3.2.3 GCMS Analysis

In this study, GCMS analysis was carried out to get an idea of the nature and type of compounds that are in the obtained oils. The detected compounds were identified by search in MS library database and the results are listed in Table 8.4. However, since more than 100 peaks were detected, only the peaks with a high degree of probability (≥ 80%) and peak areas around or greater than 0.2% are included in the list. During the analysis, several compounds that could be grouped into aromatics, ketones, acids, furans, and phenols were detected in the oils obtained from the catalytic conversion.

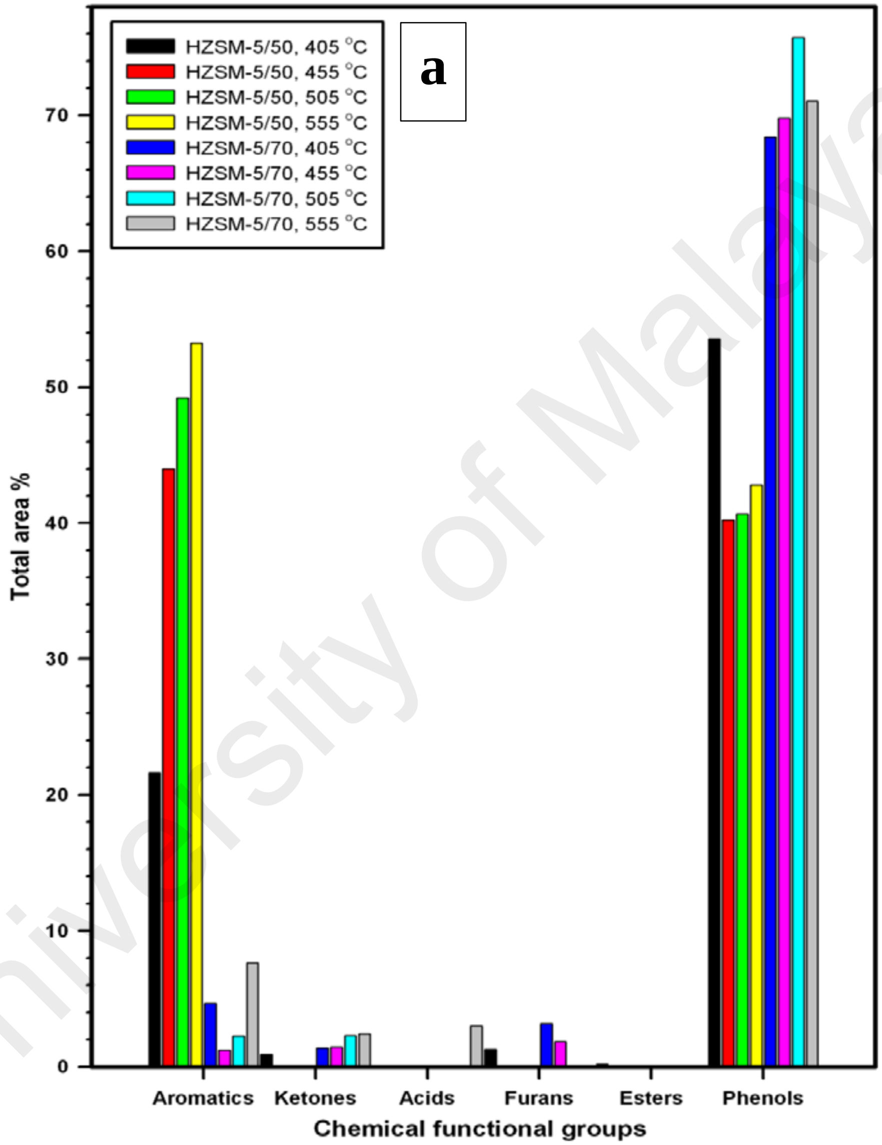
Table 8.4: Compounds in the produced oils as identified by GCMS analysis

Group	Compounds	Identified compounds (%)								
		Feed	HZSM-5/50				HZSM-5/70			
			405	455	505	555	405	455	505	555
Aromatics	Indane		0.68	1.48	1.65	1.52				
	Indan, 1-methyl-		1.81	2.38	2.55	2.48				
	Indene					1.94				
	1H-Inden-5-ol, 2,3-dihydro-		0.53							
	1H-Indene, 1,3-dimethyl-		2.83							1.21
	1H-Indene, 2,3-dihydro-4,7-dimethyl-		1.56							
	1H-Indene, 2,3-dihydro-4-methyl-		0.52	1.16		2.24				
	1H-Indene, 2,3-dihydro-1,3-dimethyl-			1.37						
	Benzene, 1,2,3-trimethyl-		2.89	7.39	6.04	4.03			0.61	
	Benzene, 1,3-dimethyl-		0.83	0.2		4.07				0.21
	Benzene, 1-ethyl-2-methyl-		2.48	5.94	4.55	3.49				0.42
	Benzene, 4-ethyl-1,2-dimethyl-			0.25						
	Benzene, 1-methyl-2-(1-methylethyl)-				0.27					
	Benzenemethanol, 4-(1-methylethyl)-				1.21					

	Benzene, (1-methylethyl)-					0.20				
	Benzene, methoxy-		0.73					0.21	0.36	0.56
	Benzene, cyclopropyl-									0.23
	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-						0.67	0.58	0.75	0.54
	Ethylbenzene				0.35					
	1,1':3',1''-Terphenyl, 5'-phenyl-		0.25							
	Naphthalene				2.51	3.98				
	Naphthalene, 1,4,5-trimethyl-		0.93							
	Naphthalene, 1,4,6-trimethyl-		1.05	0.61	0.33					
	Naphthalene, 1,4-dimethyl-			0.49	0.25	1.11				
	Naphthalene, 2,6-dimethyl-							0.43		
	Naphthalene, 2,7-dimethyl-		2.43	2.57	2.27	2.12			0.55	1.52
	Naphthalene, 1-methyl-									0.52
	Naphthalene, 2-methyl-		1.32	2.35	3.52	7.17				0.43
	Naphthalene, 1-ethyl-			0.55	0.94	1.30				
	Naphthalene, 2-(1-methylethyl)-			1.22	1.09					
	Naphthalene, 2-methyl-1-propyl-			0.27						
	Naphthalene, 2,3,6-trimethyl-					0.91				
	o-Xylene		0.78	5.53	3.66	1.43				
	2-Naphthalenol			0.99	1.58	2.22				
	p-Xylene			9.23	14.4	10.76				
	Anthracene				0.73	0.68				0.46
	Phenanthrene, 1-methyl-				0.47					
	Phenanthrene, 2-methyl-					0.71				
	.alpha.,.beta.,.beta.-Trimethylstyrene				0.85					
	1,1'-Biphenyl, 2-ethyl-					0.20				
	4-Hydroxy-3-methylacetophenone					0.36				
	9H-Fluorene, 2-methyl-					0.33				
	5-tert-butylpyrogallol						4.02			
	4-Methoxy-2-methyl-1-(methylthio)benzene									1.54
Ketones	2-Cyclopenten-1-one		0.45						1.68	1.53
	2-Cyclopenten-1-one, 2-methyl-		0.44				0.24	0.33	0.39	0.38
	2-Cyclopenten-1-one, 3-methyl-							0.22		
	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-						1.16	0.90	0.24	0.51
	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.20								
Acids	Benzoic acid, 4-hydroxy-	2.59								
	Benzoic acid, 4-hydroxy-3-methoxy-	3.96								3.03
	Hexadecanoic acid, methyl ester	0.25								
Furans	Furfural	3.61	1.31				2.51	1.86		
	2-Furancarboxaldehyde, 5-methyl-						0.66			
Phenols	Phenol	47.53	21.79	7.81	10.72	11.18	33.5	33.71	35.23	29.42

	Phenol, 2,3,5-trimethyl-		1.79							
	Phenol, 3,4,5-trimethyl-			0.82						
	Phenol, 2,6-dimethoxy-	11.24	4.57				9.99	10.68	9.55	6.68
	Phenol, 2,5-dimethyl-			7.90						
	Phenol, 2-methoxy-	5.24	10.45				9.05	9.33	10.61	3.18
	Phenol, 2-methoxy-4-methyl-	5.45	8.10				6.3	6.30	7.63	7.59
	Phenol, 3-methoxy-2-methyl-							0.32	0.54	
	Phenol, 3,4-dimethyl-					1.59		0.72		0.69
	Phenol, 3,5-dimethyl-		0.46			3.17				
	Phenol, 2-ethyl-5-methyl-					0.68				
	Phenol, 3-ethyl-		0.47	2.19	4.77	6.4	0.39		0.38	0.89
	Phenol, 3-ethyl-5-methyl-			3.94	2.72	1.96				
	Phenol, 2-methyl-			7.82	6.47	6.37			0.51	7.67
	Phenol, 3-methyl-		5.93	9.78	9.78	11.47	1.78			
	Phenol, 2-(1-methylethyl)-, methylcarbamate				1.37					
	Phenol, 3,5-dimethyl-, methylcarbamate				4.83					
	Phenol, 4-ethyl-2-methoxy-	3.18					4.3	4.17	4.62	3.05
	Phenol, 4-methyl-						1.62	3.89	5.03	8.83
	Eugenol						0.50			
	Vanillin	0.20					0.22	0.46	0.36	
	1,2-Benzenediol						0.77	0.23	1.25	2.20
	1,2-Benzenediol, 3-methyl-									0.83
Esters	Acetic acid, phenyl ester		0.20							
Sugars	D-Allose	2.51								
	.beta.-D-Glucopyranose, 1,6-anhydro-	0.73								
Total (%)		**86.69**	**77.59**	**84.24**	**89.88**	**96.07**	**77.68**	**74.34**	**80.29**	**84.12**

Many of the compounds identified in the oils are phenols and aromatics. The results from Figure 8.6a shows that the oil obtained from HZSM-5/70 at a temperature of 505 °C yielded the highest area of phenols (more than 70%), of which most were phenol (29.42%). For HZSM-5/50 catalyst, the highest area of phenols was observed for a condition temperature of 405 °C, and the main contribution, 21.79%, was the phenol area (refer Table 8.4). According to literature, the levels of phenols were found to be higher in pyrolysis oil of biomass. Lim and Andrésen (2011) performed a study on the composition of chemical compounds in pyrolysis oil produced from empty fruit bunches using GCMS, and the results showed that the most abundant compound detected was phenols. Duman et al. (2013) also support this finding in their study of two-step pyrolysis of safflower oil cake.



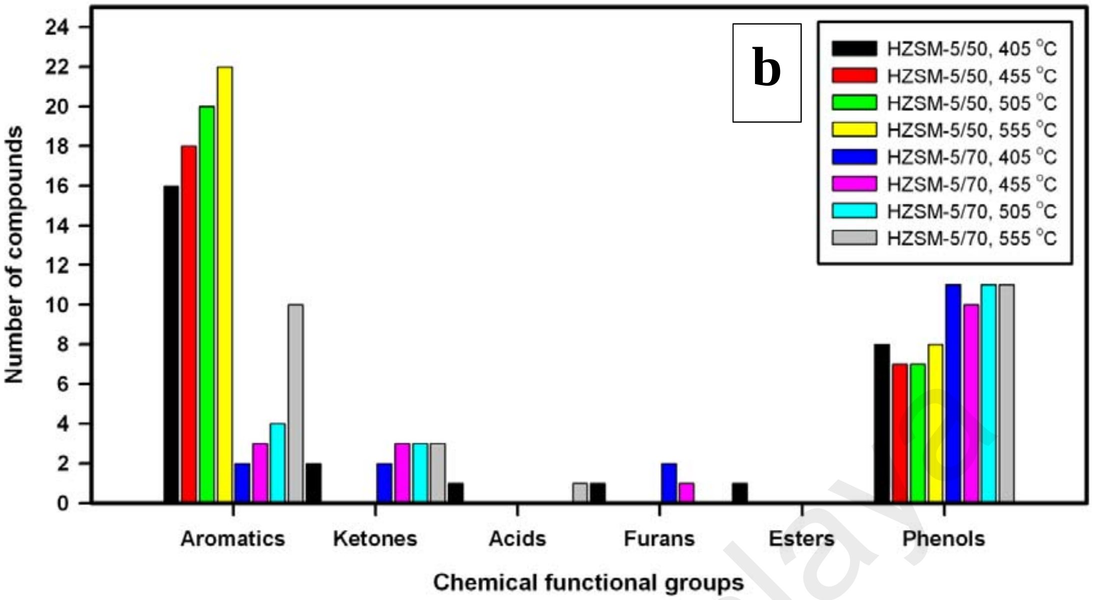


Figure 8.6: Distribution of chemical classes for the produced oils after catalytic conversion according to their area percentage (a) and number of compounds identified (b)

As seen from Figure 8.6a, aromatics were found to be the second most dominant species in all the obtained oils. However, a high percentage area of aromatics was only observed for the HZSM-5/50 catalyst, ranging from 21.62% to 53.25%. The greatest proportion of aromatics in the oils was mostly derived from indene, benzene, and naphthalene (refer to Table 8.4). The formation of these compounds was also observed in the study of catalyst evaluation for catalytic biomass pyrolysis that was conducted by Samolada et al. (2000). Moreover, it was clearly observed that the increase in process temperature causes the increment of aromatic compounds, particularly for naphthalene. Mathews et al. (1985) concluded that the use of HZSM-5 catalyst in the pyrolysis of biomass yielded an abundance of naphthalene and it occurred most effectively when the temperature was increased from 450 to 650 °C.

In this study, phenols and aromatics were confirmed as the compounds with the highest concentration in the oils, whilst the concentrations of ketones, acids, furans, and esters were found to be low. Amongst these, ketones have a slightly higher concentration in the oil obtained from catalytic cracking with the HZSM-5/70 catalyst. As can be seen in Table 8.4, the highest concentration of ketones obtained was around 2.42% for a temperature of 555 °C, while no ketones were found in the oil obtained from the HZSM-5/50 catalyst at the same temperature. This result is in agreement with the result from FTIR analysis, where no peaks were found between 1650 and 1850 cm^{-1} for the oil obtained from the HZSM-5/50 catalyst at a temperature of 555 °C (see Figure 8.5a). Ketones come from pyrolysis of hemicellulose (Rui et al., 2010) and their presence makes the oil hydrophilic and highly hydrated, which also creates difficulties in eliminating water from the bio-oil (Imam & Capareda, 2012). Clearly, Figure 8.3 has confirmed this finding, where the oil obtained from the HZSM-5/70 catalyst is still at the bottom layer and the color of the water is still yellowish.

Figure 8.6b presents an overview of the proportion of each group of compounds by referring to the number of compounds. The use of HZSM-5/50 catalyst resulted in high numbers of aromatic compounds. Increasing the temperature from 405 °C up to 555 °C also had a significant effect in increasing the number of aromatic compounds. Sixteen compounds of aromatics were obtained at 405 °C, while 22 compounds were detected at temperature of 555 °C. Furthermore, the oils obtained from catalytic cracking using HZSM-5/70 yielded more phenol compounds. Temperatures of 405 °C, 505 °C, and 555 °C yielded 11 compounds, while temperatures of 455 °C yielded 10 different compounds of phenols. Aromatics were found to vary depending on temperature: 2 compounds at a temperature of 405 °C, 3 compounds at a temperature of 455 °C, 4 compounds at a temperature of 505 °C, and 10 compounds at a temperature of 555 °C.

Table 8.5: Elemental analysis of the produced oils

Catalyst	Temperature	Elemental analysis (wt%)				
		Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen[a]
HZSM 5/50	405	62.18	9.35	0.64	0.27	27.56
	455	66.20	9.57	1.08	0.26	22.89
	505	74.77	9.96	0.66	0.35	14.26
	555	76.87	10.05	1.12	0.36	11.60
HZSM 5/70	405	47.47	8.94	0.91	0.18	42.50
	455	49.91	9.26	0.80	0.18	39.85
	505	52.02	9.32	0.77	0.16	37.73
	555	55.84	9.30	0.61	0.20	34.05

[a] By difference

8.3.2.4 Elemental analysis

Table 8.5 shows the elemental analysis results of the catalytic cracking of the aqueous phase of pyrolysis oil using the HZSM-5/50 and HZSM-5/70 catalysts. The main purpose of the catalytic cracking is to remove the oxygenated compounds in the aqueous phase which has the effect of an increase in hydrocarbon products. From Table 8.5 it can be seen that more than 48.12 wt% of oxygen content in the aqueous phase was eliminated by the cracking process using the HZSM-5/50 catalyst. The oxygen content was continuously decreased till about 11.60 wt% with the highest pyrolysis temperature (555 °C). A similar tendency was also seen in catalytic cracking using the HZSM-5/70 catalyst. However, the lowest oxygen content obtained was about 34.05 wt % at a temperature of 555 °C. Thus, the HZSM-5/50 catalyst was found to be more effective in removing the oxygen from the aqueous phase of pyrolysis oil than the HZSM-5/70 catalyst.

The carbon content of the oil obtained using the HZSM-5/50 or HZSM-5/70 catalysts was much higher (above 47 wt%) than that of the aqueous phase of the pyrolysis oil, as shown in Table 8.1. The hydrogen content in the oils produced from HZSM-5/50 was about 9.35 – 10.05 wt% over a temperature range of 405 – 555 °C, while in the oils produced from HZSM -5/70 it was about 8.49 – 9.30 wt%. In addition, the nitrogen and sulfur contents were found to be low for all the oils obtained.

Evaluation of the atomic ratios of H/C and O/C is important if the oil is to be used as a fuel. Generally, an increase in H/C results in higher value products like gasoline (de Miguel Mercader et al., 2010), and vice versa with an increase in O/C. Duman et al. noted that the effect of deoxygenation activity in catalytic cracking is favorable, leading to an increase in the H/C ratio (Duman et al., 2013). Figure 8.7 shows the atomic ratios of H/C and O/C of the produced oils presented through a Van Krevelen diagram. However, as can be seen from Figure 8.7, an uncommon trend was observed, where a high value of H/C resulted from the oil produced from the HZSM-5/70 catalyst, which has a low performance of deoxygenation activity. In contrast to the HZSM-5/70, the increase in the temperature of the catalytic cracking using the HZSM-5/50 catalyst caused the values of H/C and O/C to trend downward to 1.56 and 0.11, respectively. This low H/C ratio is caused by the occurrence of water formation reactions. It suggests that the catalyst that has good cracking performance will produce greater water yield, which will be followed by a decrease in the H/C ratio. Mullen et al. (2013) noted that the major path of oxygen rejection from catalytic pyrolysis is through the formation of water, which leads to hydrogen loss and products with low H/C ratios. In addition, some researches have recognized that reduction of the H/C ratio indicates an enhancement of aromatic compounds in the oil product (Jae et al., 2011; Li et al., 2004; Meng et al., 2011). This phenomenon is in agreement with the GCMS results presented in this paper (see Figure 8.6a).

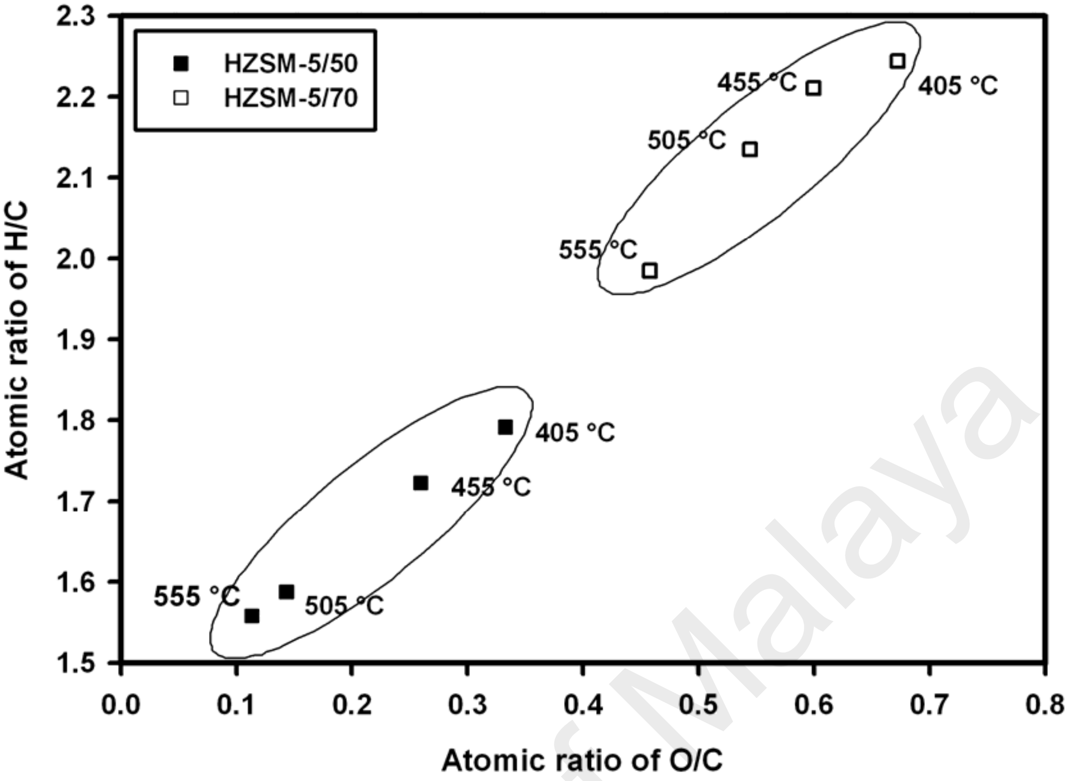
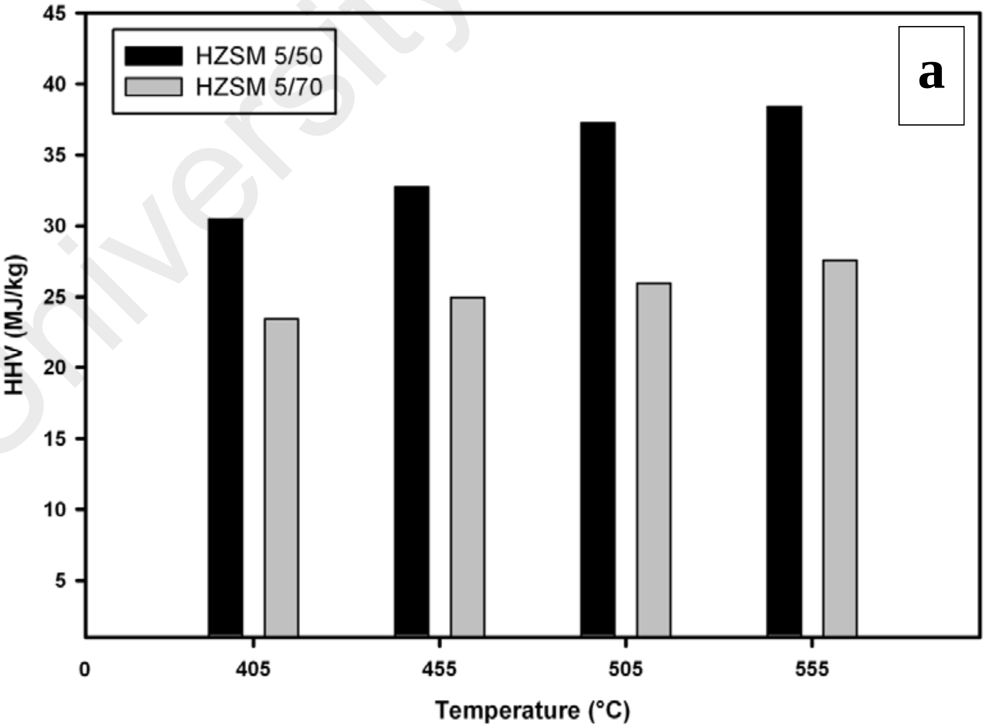


Figure 8.7: Van Krevelen diagram of the oils after catalytic conversion at different temperatures



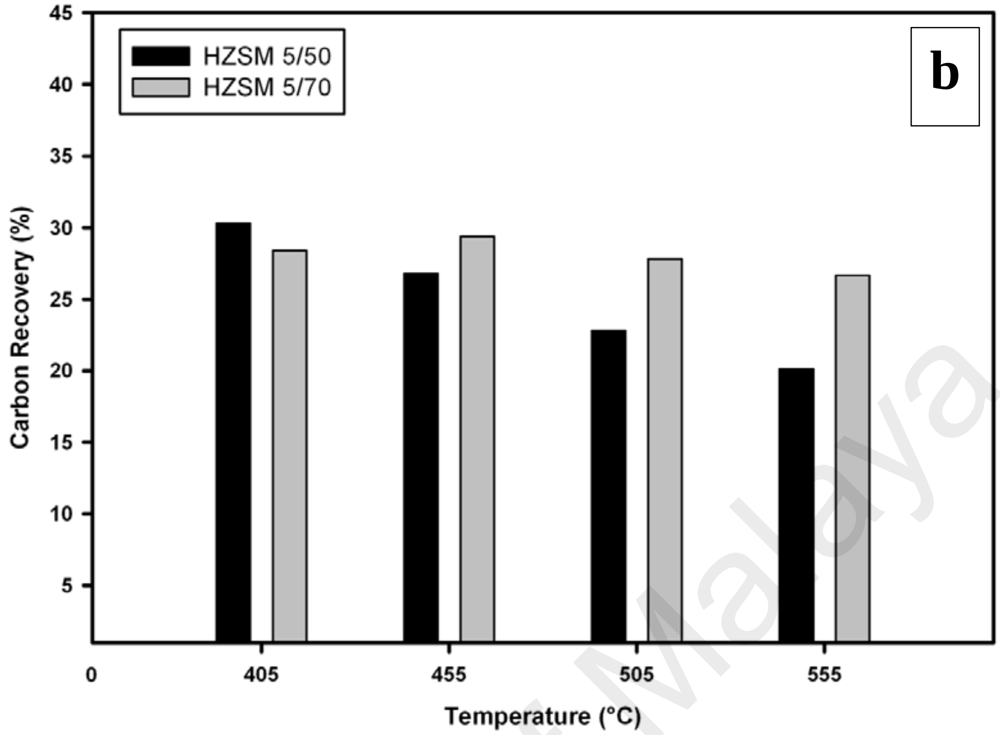


Figure 8.8: (a) High heating values of the oils after catalytic conversion. (b) Carbon recovery of the oils after catalytic conversion

The HHV is an important parameter to determine the energy content of the fuel. Estimating the HHV as a function of reaction temperature was concluded in Figure 8.8a by using the elemental composition of the oil. From this figure it can be seen that the HHV of the oils produced from HZSM 5/50 ranged from 30.51 to 38.44 MJ/kg, which was considerably higher than those for the oils produced from the HZSM 5/70 catalyst (23.44 – 27.59 MJ/kg). Furthermore, it is obvious that the HHV of the oils increases with the increment in reaction temperature. This result is in line with the work published by de Miguel Mercader et al. (2010).

The results of carbon recovery illustrated in Figure 8.8b indicate that catalytic conversion with HZSM-5 catalysts decreases the carbon conversion of upgraded oils. For HZSM-5/50 catalyst, the carbon recovery of upgraded oil obviously decreases from

30.32% (405 °C) to 20.10% (555 °C). This finding is consistent with the findings of Gan and Yuan (2013) who studied the effect of the reaction temperature on carbon recovery of concorb hydrothermal conversion. They noted that the oil carbon recovery rate will be decreased as reaction temperature increased. Further, it also clearly seen that the decrease of carbon recovery of upgraded oil was also followed by the decrease of the upgraded oil yields (see Table 8.3). The decrease in percent of carbon as temperature increases can be explained by the decomposition of the oil to other products (char, tar, coke, and gas).

8.3.2.5 Thermogravimetry analysis

The TG analysis results of the raw aqueous phase and oils obtained after catalytic cracking at a temperature of 555 °C are shown in Figure 8.9. Increasing the temperature in the TG analysis resulted in reducing the weight of the aqueous phase by up to 74 wt% at temperatures around 50-150 °C. However, at the same temperature, the weight loss of oils after catalytic cracking was around 36 wt% and 31 wt% for HZSM-5/50 and HZSM-5/70, respectively. This phenomenon represents the volatilization of water and compounds with lower boiling points such as: phenanthrene, 2-methyl-; p-xylene; benzene, 1,3-dimethyl-; o-xylene; 1-buten-3-yne, 2-methyl-; and 2-cyclopenten-1-one. Hence, the aqueous phase, which has the highest content of water, shows the most significant weight loss.

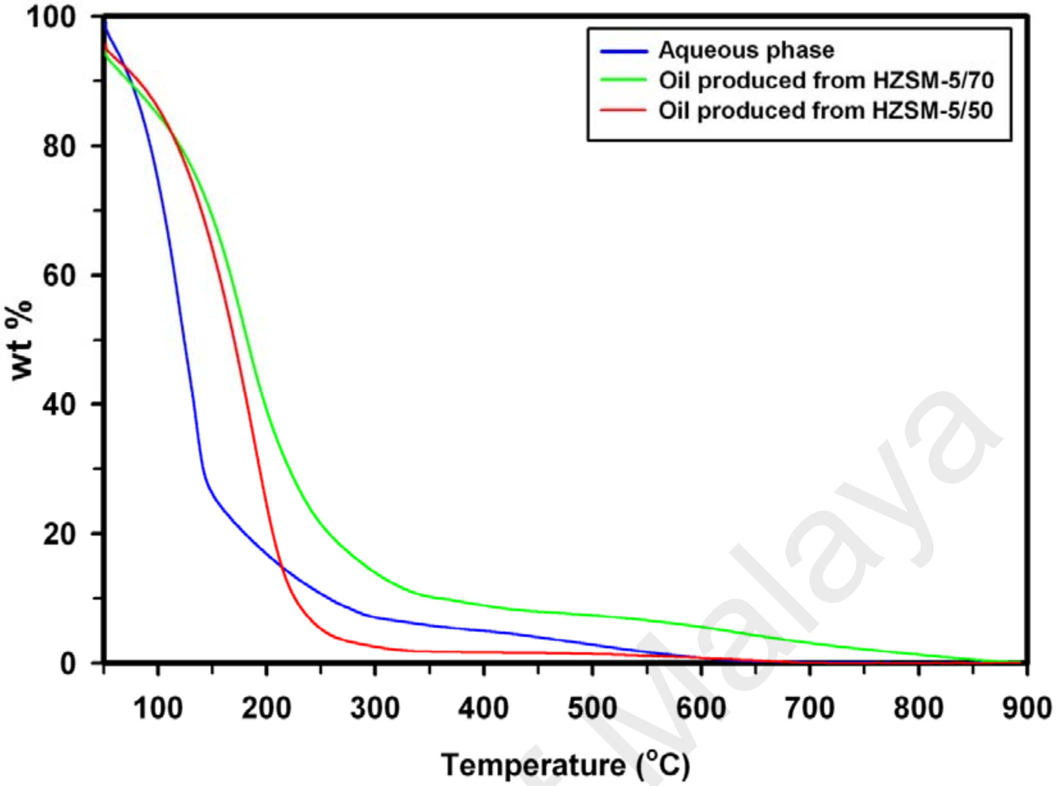


Figure 8.9: TGA profile of aqueous phase and the oils after catalytic conversion at a temperature of 555 °C

Furthermore, it can be observed that the major weight loss of obtained oils happens in the temperature range between 150 to 300 °C, where about 61 wt% of weight loss was obtained with HZSM-5/50 catalyst and 54 wt% of weight loss was obtained with HZSM-5/70 catalyst. The different in weight loss results are because the oil produced from HZSM-5/50 contained a lot of aromatics and phenols which have lower boiling points. Some of the compounds in the oil obtained with the HZSM-5/70 catalyst which have high boiling points are ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (334.7 °C); anthracene (340 °C), phenol, 2-methoxy-4-methyl- (408.6 °C); benzoic acid, 4-hydroxy-3-methoxy- (409 °C). In addition, a small part of the weight loss that occurred at temperatures between 500-800 °C was due to combustion of the carbonaceous residue (Vitolo et al., 1999).

8.4 Conclusion

This study showed that the recovery of liquid fuel from the aqueous phase of pyrolysis oil was successfully performed using a catalytic conversion. The study also proved that the temperature has a significant effect on the product yields distribution during the catalytic conversion. A high temperature condition around 555 °C was found to be most suitable for catalysts to perform the deoxygenation activity, which caused an increase in the production of water and gas. However, the use of HZSM-5/50 at 555 °C was found to be the optimum condition to produce high quality liquid yield with the lowest water content (3.97 wt %) and the highest level of HHV (38.44 MJ/kg). The oil was also observed to have an abundant amount of aromatic compounds. Finally, it can be concluded that the characteristics of the oil produced using the HZSM-5/50 catalyst at 555 °C are very close to heavy fuel oil and that it has the potential to be used as transport fuel.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

In this chapter, we tried to come up with several conclusions and recommendations based on the obtained results of this study. The results from the first objective showed that all of oil palm solid wastes can produce oil, char, and gas via the pyrolysis process. The pyrolysis of palm oil wastes yielded more bio-oil than bio-char or non-condensable gases. The variations in the yields were influenced by the differences in the relative amounts of cellulose, hemicellulose, lignin, volatiles, fixed carbon, and ash in the samples. Cellulose and hemicellulose have been found as significant compounds that affect oil yield production. The samples with higher lignin content might have relatively higher bio-char yield. Furthermore, the volatiles contents of all the oil palm solid wastes were high, which is favorable in producing more oil. More than 40 wt% of oil palm solid wastes can be converted into oil via the pyrolysis process at the following conditions: a temperature of 500 °C, a nitrogen flow rate of 2 L/min, and reaction time of 60 min. This research concluded that the yields of oils from the residues of palm oil mill activities are more attractive than those of residues from plantation activities. However, the oils were found acidic and contained high levels of oxygen.

The results of the co-pyrolysis study concluded that the addition of plastic in the pyrolysis of lignocellulosic biomass successfully improved the quantity and quality of pyrolysis oil. In the co-pyrolysis technique, the oxygenated compound was clearly reduced in the oil, whereas the HHV of oil increased. All plastic types have high characteristics of volatile matter, which means that all types of plastic have the potential to produce a high liquid yield via pyrolysis. The oil yield of palm shell pyrolysis was about 46.13 wt%. By mixing the palm shell with polystyrene, the yield of oil increased to about 61.63%. The oxygen content of oil was significantly changed from 71.40 wt% to 7.82 wt% when polystyrene was added in the pyrolysis of palm shell. The heating value was as high as 38.01 MJ/kg for oil from the pyrolysis of material mixtures. The hydrocarbon groups in the oil were mostly found in the form of aromatics and benzene, with percent areas of 39.59% and 32.99%, respectively. It should be noted that the use of palm shell waste as a source of biomass energy by producing pyrolysis oil has the potential to contribute 3.08 PJ/year to Malaysia's energy supply. This number significantly increases to 13.12 PJ/year when polystyrene waste is added in the palm shell pyrolysis.

In addition, the results of optimization study concluded that parameters such as temperature, feed ratio, and reaction time have important functions in the co-pyrolysis process. Among them, the ratio of feed was found to be the most significant variable in increasing oil yield. In this study, RSM was used to determine the optimum parameter and experimental design matrix according to the central composite design method. The polynomial model fits well to predict the response with high determination coefficient of R^2 (0.972) and Q^2 (0.610).

Aside from plastic, scrap tyre is also a potential source to use as a co-feed in co-pyrolysis to produce liquid fuel. The study of the co-pyrolysis of palm shell and scrap tyre showed that the addition of scrap tyre in the pyrolysis of biomass also successfully improved the quantity and quality of oil. The increase in temperature after the optimum conditions of co-pyrolysis slightly increased the amounts of oil and gas and decreased the content of char. Unlike the liquid product, the addition of scrap tyre was unfavorable in increasing the fuel characteristics of char. For gas products, the results showed that the addition of scrap tyre contributed to methane production, whereas wood biomass was favorable to produce hydrogen.

In addition, all liquid products from the pyrolysis of biomass alone and the co-pyrolysis experiment confirmed the presence of the aqueous phase, which makes the liquid divided into several layers. The aqueous phase contain many valuable compounds, which can be extracted for more beneficial purposes. In this study, the recovery of liquid fuel from the aqueous phase of pyrolysis oil was successfully performed using catalytic conversion. The oil yields obtained from the catalytic cracking of the aqueous phase ranged from 4 wt% to 9.16 wt%. The optimum performance of deoxygenation activity was obtained using the HZSM-5/50 catalyst at a temperature of 555 °C. The oil produced at the optimum conditions was dominated by aromatics and phenols and had an HHV of 38.44 MJ/kg.

9.2 Recommendations

Based on the results of this study, we recommend the use of the pyrolysis process in increasing the value of oil palm solid wastes in Malaysia. The oil from this process contained many valuable compounds that can potentially be used as a fuel or chemical feedstocks. Char can be used further for any application that uses coal, and the gas can be used to offset the total energy requirements of the pyrolysis process plant.

Technically, to obtain a high liquid yield, the process can be set at moderated operating temperatures (~500 °C), high heating rate, and short vapor residence times. Hot vapor should be maintained at >400 °C before it enters the condensation unit. To obtain high-grade pyrolysis oil, the co-pyrolysis technique can be used as an option. The fixed-bed reactor was found to be effective in achieving the synergistic effect during the co-pyrolysis process and was also relatively inexpensive, simple, and reliable. The suitable combination of feedstock in co-pyrolysis can include wood-based biomass with waste plastic or wood-based biomass with waste tyre. However, it should be noted that not all plastic types can be used in the process. PVC is not recommended as a feedstock material because it contains about 57% chlorine by weight, which will affect the diesel quality and can produce chlorinated hydrocarbons. Moreover, PVC thermally decomposes to hydrochloric acid, which is very corrosive and toxic. Furthermore, the addition of tyre in the pyrolysis of biomass could increase the sulfur content in oil. If the sulfur content in the oil is higher than the allowed standard, it needs to be desulfurized before it can be used for combustion. In addition, plastic or tyre waste can be called the additive material in the process. In this regard, the proportion of additive material was preferred to be less than that of the main feedstock (wood-based biomass).

Although fuels from biomass, especially wood-based biomass, typically have a lower energy content than fossil fuels, the use of the co-pyrolysis technology can improve this condition. It can also be noted that the improvement was achieved without any change in parameter settings, without any catalysts or solvents, and free of hydrogen pressure. When the co-pyrolysis method is used, the volume biomass solid wastes becomes easy to control. It also contributes to reducing the landfill needed, decreasing the cost for waste treatment, and solving several environmental problems.

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APPENDIX A: LIST OF PUBLICATIONS

Academic Journal (Published)

Faisal Abnisa, Arash Arami-Niya, W. M. A. Wan Daud, J. N. Sahu, Characterization of Bio-oil and Bio-char from Pyrolysis of Palm Oil Wastes, BioEnergy Research, **2013**, Vol 6, pp 830-840, Springer Link. ***(ISI-cited publication)***

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Faisal Abnisa, W.M.A. Wan Daud, Sujahta Ramalingam, Muhamad Naqiuddin Bin M. Azemi, J.N. Sahu, Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel, Fuel, **2013**, Vol 108, pp 311-318, Elsevier. ***(ISI-cited publication)***

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Faisal Abnisa, W. M. A. Wan Daud, J. N. Sahu, in Proceedings of Fourth International Symposium on Energy from Biomass and Waste-Venice 2012, 12-15 November in San Servolo, Venice, Italy. (Oral presentation by Mr. Faisal Abnisa)

Faisal Abnisa, W. M. A. Wan Daud, J. N. Sahu, in Proceedings of Management of Raw Materials for Metallurgical and Power Industries 2013, 9 - 11 January, 2013, Bhubaneswar, India. (Oral presentation by Dr. J.N. Sahu)