MODIFICATION OF BIO OIL FROM CHICKEN FAT PYROLYSIS USING SOLID BASED CATALYST

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CHAPTER 1: INTRODUCTION

1.1. Background of study

The increasing concerns of renewable energy encourage the searching for the new sources of liquid fuels. Selva and Partiban (2011) emphasized biofuel has gained worldwide popularity as an alternative energy source because it is a non-toxic, biodegradable, simple to use, significantly less harmful to environment and better lubricity resulting in longer life for diesel engines (Selva & Parthiban, 2011). Malaysia is one of the largest producers of palm oil in the world producing 85% of world's palm oil (Jayed et al., 2011). In the bio-oil production, rapeseed and sunflower are the most common feedstock in the EU followed by palm oil in Asian countries and animal fats in the U.S. region (Bajpai & Tyagi 2006). Biofuel production is expanding due to its various application and yield factor of palm. Waste edible oil and animal fats are untapped source of biofuel in this country that can be commercialized as similar as palm and vegetable oils. It is projected that the excessive animal fats waste from food industry has the huge potential to become feed stocks for biofuels production (Ruengwit & Somkiat, 2013).

The first challenge to convert biomass to automotive fuels is to find an inexpensive and abundant feedstock. There are several types of bio-oil feedstock around the world such as waste materials (agriculture wastes, crop residues, wood wastes, urban wastes), energy crops (starch crop for example corn, wheat, barley, vegetable oils and grasses), forest production (wood, logging residue and trees) and aquatic biomass (algae) (Huber et al., 2006). Rajat (2014) claimed most potential renewable fuels found from biomass resources can be categorized into several type which are, (i) edible vegetable oil (sunflower, soybean, rapeseed, palm and coconut); (ii) non-edible vegetable oil (microalgae, safflower oil and linseed oil); (iii) waste recycled oil (waste frying oil); and (iv) animal fats (chicken fat, duck tallow, feather meal, beef tallow and others). Mohammad (2012) defined biomass as living substance on earth with respect to the material derived either from growing plant or animal waste consisting of carbon, hydrogen, oxygen and smaller portions of inorganic species. Fats in animal waste have high water moisture content that can affect the stability, viscosity, pH, corrosiveness and bio-oil product produced from pyrolysis. Due to this moisture problem, it is necessary either to heat dry or freeze dry the feedstock but this drying step increase overall bio-oil production cost.

The second problem in bio-oil is to remove the abundant oxygen content efficiently from biomass-derived products and convert it into a hydrophobic molecule with the appropriate combustion or chemical properties. In order to achieve this purpose, many efforts have been devoted to the search of safe and green bio-fuel with less oxygen content. In this situation, suitable catalyst and mesoporous compounds may help researcher to develop new biofuel generation processes based on the special properties and characteristics of a material such as high concentration of active sites, high thermal/hydrothermal stability and enhanced shape selectivity. For example, zeolites are the excellent material acid/base catalyst that can be used in biofuel production. In a similar way, the development of new catalysts in the field of conversion of biomass to biofuel requires knowledge of the complex nature of the substrates to be converted.

Pyrolysis or thermal cracking of triglyceride materials is an alternative method of producing renewable bio-based products suitable for use in fuel and chemical applications. Pyrolysis is a thermal degradation method under to flow of inert gasses to produce bio-oil. There are significant advantages of pyrolysis process including lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility (Theodore & Juan, 2013). Mohammad et al., (2012) categorized pyrolysis into three categories which are slow, fast and flash pyrolysis. Different type of pyrolysis shows different heating rate, process temperature, residence time producing different quantity product of char, gases and liquid. It was reported liquid production (bio-oil) from biomass usually occurred at temperature between 350 °C to 550 ℃ (Mustafa et al., 2010 and Mohammad et al., 2012).

Crude bio-oil product from pyrolysis has a distinctive odor, dark brown with high organic compound concentration. Usually this crude bio-oil contains acid (acetic acid, propanoic acid), ester (methyl formate), alcohol (methanol, ethanol), ketones (acetone), aldehydes (acetaldehyde, formaldehyde), miscellaneous oxygenates (acetol, glycoladehyde), furan (furfural, furfurol), phenol (phenols, methyl phenol, dimethyl phenol), guaiacols (isoeugenol, eugenol) and syringols (propyl syringol, syringaldehyde) (Huber et al., 2006). This crude bio-oil has high oxygen content, high moisture content and low heating value. At the same time, the bio-oil is acidic with pH of about 2.5. To counter this limitation, crude bio-oil has to be upgraded before can be used in conventional diesel engines. It also can be upgraded several different routes such as hydrocracking, hydrotreating, supercritical fluid extraction, emulsification, solvent addition/esterification, steam reforming, and chemical extraction.

This research was focusing on solvent addition/esterification which offered a low energy route to oil stabilization. The main idea of upgrading by esterification was the addition of an alcohol compound can convert the unwanted acidic components into stable substances. At the same time, it is a simple pre-treatment to improve the stability of oil during storage and transportation. The addition of small concentration of ethanol or methanol was observed to improve bio-oil stability through the formation of ester and acetal through non catalytic reaction with carboxylic acids and aldehyde respectively.

This addition also can reduce the ageing rate of the bio-oil through homogeneous reaction originated by the organic acid itself (Xiu & Shahbazi 2012).

Catalyst addition during esterification may decrease the reaction time and increase reaction conversion in which ultimately reduce the reaction operation cost. Acidic catalyst can be either liquid acid or solid acid (S.Conrad et al., 2015; Ming Chai et al., 2014; Piyarat et al., 2012). For example, liquid acid such as sulfuric acid (H_2SO_4) is a strong mineral acid whereas para-toluene sulfonic acid (PTSA) is an example for a strong organic acid. For solid acid, zeolites or solid organic supports functionalized with sulfonic acid groups can be used. Zeolites are the most widely explored class of solid acid for bio-oil upgrading through esterification reaction.

Several reaction mechanism and modelling studies of zeolite modification reported from the literatures have been performed using simulated pyrolytic bio-oil (Gayubo et al., 2004, Panagiotis et al., 2006). Simulated pyrolytic bio-oil refers to the chemical spiking bio-oil and representing most of the species present in pyrolytic bio-oil. It was suggested that the removal of aldehydes and phenolics from the simulated pyrolytic bio-oil can reduce the amount of coke formation and increase the hydrocarbon yield (Gayubo et al., 2004, Panagiotis et al., 2006). Kamonlatth et al., (2017) reported ZSM-5 can significantly increase catalytic performances of the esterification in terms of increasing activity, desired product yield, and catalyst reusability for an esterification of carboxylic acids. In this research work, commercial ZSM-5 was used because this zeolite catalyst is an acidic hydrophobic material with medium pore dimensional network and high ratio of Si: Al at 15:1. The structure of ZSM-5 framework is shown in Figure 1.1

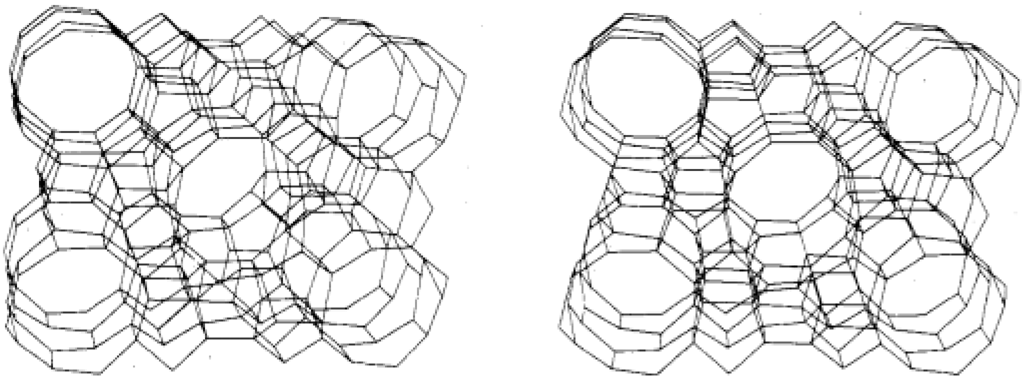

Figure 1.1: Stereo pair drawing of ZSM-5 framework (image with permission from ACS publication)

Thermal properties of the animal fat bio-oil are also critical for determining storage conditions, end use and overall material stability (Jayasinge & Hawboldt, 2012). Therefore, the studies of thermal and kinetic properties via thermogravimetric analyzer (TGA) analysis are important to understand the characteristic of bio-oil produced from animal biomass waste. The activation energy of the bio-oil can be obtained from model free-isoconversional method from TGA/DTG. Model-free isoconversional methods represent the most popular class of methods for determination of the kinetic parameters from thermoanalytical data. The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is performed. This kinetic study of TGA/DTA aims to present the determination of the activation energy through thermogravimetric analysis for the main region of the thermal decomposition for chicken skin fat by applying model free- isoconversional method.

1.2. Problem statement

The most significant problems of bio-oils are poor volatility, high viscosity, coking, corrosiveness, and cold flow problems. These problems have limited the potential of bio-oils. The main concerns for burning bio-oils in diesel engines are related to difficult ignition (due to low heating value and high water content), corrosiveness (high acids content), and coking (thermally unstable component). Compared with fossil fuel, these undesired properties present many obstacles for the bio-oil to be substitute as fossil based fuel. In our point of view, there is lack of understanding in the thermal degradation of feed used in the production of bio-oil that leads to feasibility problem of using bio-oil as substitutes for fossil fuel. In this research work, the pyrolysis of chicken fat waste was used to understand the thermal degradation of feed. Chicken fats waste was used in this study because chicken is one of the importance diets which are abundant and relatively cheap in Malaysia. Most chicken processing industries are operated at wet market and medium size stalls. Unfortunately, most of this medium scale chicken processing center is situated nearby the drainage that is ill equipped with waste treatment system upon their discharged. This untreated chicken processing waste water containing oil, grease, fat, blood and feather flow directly into drainage system and lead to environmental problem and causing high chemical oxygen demand (COD) in urban rivers. It is also known that animal fats with high biochemical oxygen demand (BOD5) in 5 days can reduce the dissolved oxygen in water (Bolan et al., 2010). At the same time, when the fats and oil forms on the surface of the water caused unsightly and reduces the natural re-aeration process. Consequently, this problem interrupts and kills the aquatic ecosystem. Open dumping and sanitary landfill is the main method in for domestic waste disposal in Malaysia including the waste disposal from chicken processing industry. These methods possibly lead to environmental degradation due to highly polluting leachate and methane gas. The methane emissions from landfills create about 30% of the global anthropogenic emissions of methane to the atmosphere (Saleh et al., 2011). Therefore, composting this waste to valuable bio-oil would be the best option in managing domestic solid waste. One of the cost effective and fast process to convert biomass to bio-oil is by using pyrolysis method. Since chicken skin is abundant and considered as waste, this research work focused on chicken fat skin (CFS) only. There have been many studies conducted on pyrolysis of vegetable oils but few goes into detailed about decomposition and characterization of the bio-oil properties related to animal waste. Zeolite ZSM-5 catalyst was used in bio purification to study the effect of the bio-oil after pyrolysis reaction.

1.3. Objectives

i. To study the kinetics of chicken skin fat (CSF) decomposition by using TGA/DTG analysis.

ii. To produce crude bio-oil from the pyrolysis of chicken skin fat (CSF).

iii. To perform bio-oil upgrading with and without zeolite ZSM-5 catalyst.

1.4. Scope and limitation of the study

To achieve the above objectives, studies are carried out within the scope and limitation. This research is focused on Chicken Skin Fat (CSF) as the feed since it has been a major waste from local wet market in Malaysia. The CSF waste containing major triglycerides and FFA has good potential hydrocarbon chain for bio-oils production. The research involved fixed bed pyrolysis reactor for bio-oil production. After pyrolysis completed, the bio-oil were upgraded via esterification using solid acids. GC-MS was used for bio-oil characterization whereas TGA was used for kinetic study. This research work was only focused on acid and ester composition (wt. %) products from the bio-oil. Jason et al (2009) reported the major composition of chicken skin fat consist of methyl ester of palmitic (C16:0), stearic (C18:0), linoleic (C18:2), and oleic (C18:0) acids. Biofuel containing compounds with carbon chain lengths of ≥ 15 produces high quality fuel. To achieve this target, effects of operating parameters in the product quality such as amount of catalyst and operating temperature had been studied. Only one zeolite catalyst which is ZSM-5 was used in this study because this catalyst is the most suitable catalyst in bio-oil upgrading due to its unique properties compared to other zeolite catalyst.

1.5. Significant of study

This research was focused on CSF as the feed for pyrolysis reaction and the upgrading of pyrolytic bio-oil via pyrolysis reaction. At the same time, kinetic processing of TGA/DTG data was performed via model free-isoconversional method to study the degradation and pyrolysis behavior of a CSF. This method was also important to determine the apparent activation energy of the CSF. Activation energy is a barrier that must be overcome for a chemical reaction to occur because reaction with high activation energy requires a high temperature. The optimum thermal process conditions obtained from TGA/DTG were used in the actual pyrolysis reaction. Then the crude bio-oil from pyrolysis reaction was upgraded in esterification process with and without zeolite ZSM-5 catalyst. In this reaction, the esterification reactions were optimized by varying several operating process conditions to produce bio-oil with high ester compositions.

CHAPTER 2: LITERITURE REVIEW

2.1. Introduction

The chapter covers literature review on the poultry waste in Malaysia, biodiesel as alternative for fuel, sources of biomass for bio fuel, biomass conversion technology, parameter of pyrolysis process, pyrolysis product, process optimization, catalytic upgrading of pyrolytic bio oil using esterification and effect of reaction condition on the catalytic esterification. Furthermore, this chapter also includes the critical part of thermal degradation kinetic analysis.

2.2. Biodiesel as alternative for bio-fuel sources

Conventional energy sources have proven to be effective ways in maintaining economics progress. Due to environmental issues, many related organization put great effort to get seriously involved in the research for more efficient and green power plants with advanced technology. From the time when environmental protection becomes a critical issue, both clean fuel technologies and new energies are intensively investigated. Therefore, shifting from fossil fuel to renewable energy can achieve the objective in reducing greenhouse emission and others issue that related to the environmental protection.

In technical terms (ASTM D 6751), biodiesel is a diesel engine fuel defined as monoalkyl ester of long chain fatty acids derived from vegetable oils or animal fats at which compatible with B100 and meeting requirements of ASTM D 6751(Ayhan, 2009). Table 2.1 shows the technical properties of biodiesel. In United States and Europe, soybean oil and rapeseed oil respectively are the major feedstock for biodiesel production. Meanwhile, in the East Asian countries, the production is mainly derived from palm oil. (Divya & Tyagi, 2006). Table 2.2 shows the production of biodiesel from different countries around the world. The increasing demand for petroleum and environmental concerns encouraged the search for new sources of liquid fuels. Selva and Partiban (2011) emphasized biofuel has been gaining worldwide popularity as an alternative energy source because it is nontoxic, biodegradable, easy to use, significantly less harmful to environment and better lubricity resulting in longer life for diesel engines (Selva & Parthiban, 2011). Therefore investing in renewable energy can have significant dividend to worldwide energy security.

Table 2.1: Technical properties of biodiesel. (Table with permission from author Ayhan, 2009).

Common name	**Biodiesel (bio-diesel)**
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14} – C_{24} methyls esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density range (kg/m^3, at 288K)	860 - 894
Boiling point range (K)	>475
Flash point range (K)	420 – 450
Distillation range (K)	470 – 600
Vapor pressure (mm Hg, at 295K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum

Reactivity	Stable but avoid strong oxidizing agents.

Table 2.2: Production of Biodiesel from different countries. (Table with permission from author Bajrai & Tyagi, 2006)

Country	**Source of biodiesel**
USA	Soyabean
Brazil	Soyabean
Europe	Rapeseed oil and sunflower oil
Spain	Linseed and olive oil
France	Sunflower oil
Italy	Sunflower oil
Ireland	Animals fat, beef tallow
Indonesia	Palm oil
Malaysia	Palm oil
Australia	Animal fats and rapeseed oil
China	Guang pi
Germany	Rapeseed oil
Canada	Vegetable oil/animal fats

2.3. Sources of Biomass for bio-fuel

Biomass is an organic material from plants, trees and corps, and essentially the collection and storage of the sun's energy though photosynthesis. Biomass energy is the conversion of biomass into useful forms of energy such as heat, electricity and fuels. In other way, it can also serve as a feedstock to be converted to various liquid or gas fuels (biofuels) (Omar et al., 2014).

Figure 2.1 below presents percentages of all scientific journals in the ISI database related to renewable energies during the period from 1979 to 2009. It is noted that in the last 30 years, more than half of the global research effort (56%) has been in related to the use of biomass as renewable energy, followed by solar energy, which was more than double (26%) of wind power (11%). These data draw attention to the relatively low (2%) focus on hydropower research, which, as seen, is the renewable energy that produces more energy (Manzano et al., 2013).

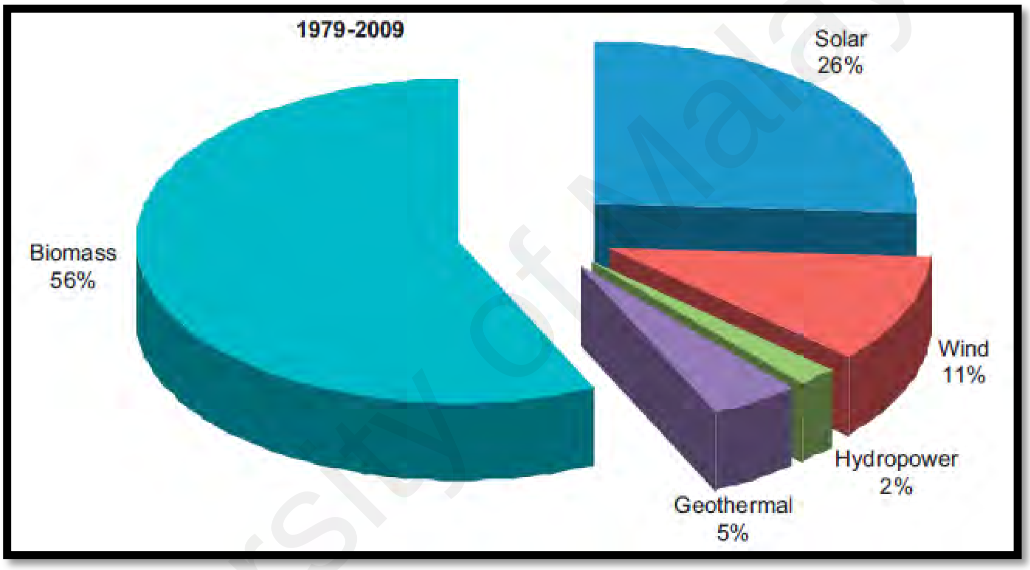

Figure 2.1: Distribution of scientific publications (1979–2009) per renewable energy (Figure with permission from author, Manzano, 2013).

Biomass from plants generally consists of cellulose, hemicelluloses, lignin, lipids, simple sugars, starches, hydrocarbon (aliphatics, sterols, steroid, carbocylics, furans, phenols and benzene) and other compounds such as plant nutrients, trace element, pesticide residue and pharmaceutical whereas biomass from animal waste consists of fats and oils (triglyceride) (Schnizter et al., 2007; Bolan, 2010; Carlos & Schnizter, 2011). Relevant lipid classes correlated to bio oils include triacyglycerols (TAG), hydrocarbons (HC), ketones, alcohols, cholesterol, sterols, wax esters, free fatty acid

(FFA), gycero-phopholipids, glycerol-glycolipids, etherlipids and sphingolipids. Anjana and Prasad (2000) reviewed thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Many researches have reported the pyrolysis of triglycerides to achieve products that suitable for diesel engines (Ben Hassen et al., 2014; Liew et al., 2013; Takuya et al., 2012). Triacyglycerols (TAG) are the key lipid fraction of bio oil which contained three fatty acids with a glycerol molecule. Fuel properties of bio oil depend on fatty acid carbon chain length, degree of saturation of carbon bonds and number of unsaturated carbon bond of fatty acids. Degree of saturation of carbon bonds include saturated fatty acid (single bonds), monounsaturated fatty acid (one double bond) and polyunsaturated fatty acid (multiple double bond) (Jayasinghe & Hawboldt , 2012).

Currently, many researchers have focused on feedstock that has high lipid and protein in animal fats (Ben Hassen et al,. 2014,; Wisniewski et al., 2010), poultry manure (Kim et al., 2009; Agblevor et al., 2010) and cooking oil (Takuya et al., 2012). Triglyceride based vegetable oils or animal fats have potential to be a suitable source of fuel under the right processing conditions.

2.4. Animal fat as a biomass

Currently, livestock farming has received growing interest from farmers due to growing demands for dairy product and meats. Metin and the team (2010) investigated on chicken fat methyl ester blended with diesel fuel as an alternative fuel in conventional diesel engines. It was found that chicken fat methyl ester–diesel fuel blending has low sulphur and aromatic contents. Magnesium based additives reduced the pour point, flash point and viscosity of biodiesel fuel. The engine tests results showed that the engine torque had not changed significantly with the addition of 10% chicken fat biodiesel, while the specific fuel consumption increased by 5.2% due to the lower heating value of biodiesel compared to typical fossil fuel. Nevertheless, the cylinder peak pressure slightly rose than normal and started of combustion prematurely. CO and smoke emissions decreased by 13% and 9%, although NOx emissions increased by 5% with the addition of biodiesel to diesel fuel. Optimum conditions recorded in this study could be applied to commercial scale biodiesel production process and the methyl ester blending with diesel can be considered as an alternative and environment friendly fuel (Metin et al., 2010).

2.5. Biomass conversion technology

A number of methods are presently available and have been implementing for the production of biodiesel fuel. Energy from biomass can be converted via three general categories which are (1) thermochemical; (2) physical or chemical processes; and (3) biological conversion. Thermochemical conversion processes include combustion, gasification and pyrolysis processes. Physical processes basically include pressing processes and extraction of vegetable oils, which can be used directly or indirectly as biofuels. Chemical processes generally involved chemical transformations of oil and other products extracted from plants in order to convert them into biofuels. Animal fat waste has high moisture content can affect the stability, viscosity, pH, corrosiveness in the pyrolysis product. Due to this problem, it is necessary to perform either thermal dry or freeze dry step to the biomass waste. After drying, the biomass is fed into the reactor and the pyrolysis takes place. Three main products obtained from pyrolysis process are char, gases and liquid (bio-oil). The bio oil produced from the condensation of vapour from the reaction. Bio oil can be upgraded or blended to be used in diesel engines. It can be upgraded via three different routes which are hydrodeoxygenation with typical hydrotreating catalyst, zeolite upgrading and emulsions formation with the diesel fuel. For biological processes, two processes, namely alcoholic fermentation and biomethanization from the biodegradable organic matter are used to produce biogas. Generally, biofuels are derived from agriculture biomass. Nevertheless, the conversion pathways: biological, physical, chemical, or a combination of processes is depending to their biomass type and characteristics. For example, biogas, ethanol, and biodiesel can be produced via microbial/enzymatic fermentations with or without using physical and chemical pretreatment steps (Carucci et al., 2005). Other than that, conversion of biomass into bio-oil, biochar, syn-gas, and others involves only thermochemical processes, such as torrefaction, carbonization, thermal liquefaction, pyrolysis, and gasification (Catoire et al., 2008 ;Demirbas, 2004).

2.5.1. Thermochemical process

The aim of pyrolysis is the optimization of high-value fuel products from biomass via thermal treatment (Balat et al., 2009). Conversion of vegetable oils and animal fats composed primarily of triglycerides using pyrolysis type reactions presents a promising option for the production of biodiesel (Maher et al., 2007).

However, the physiochemical characteristics of biomass contrast with their source. For example, the primary components of the biomass from plant/ crop origins are carbohydrates and lignin which can vary depending on the type of the plant. Some biomass includes plant/ crop roots, seeds, and seed residue are rich in starch and cellulose. Other than plant, many of the biomass waste sources are from agriculture crops, forest residue, municipal waste, cattle, and human manure. As mentioned above, the utilization of biomass waste to liquid biofuels is a necessary alternative to avoid harmful effects of direct combustion of biomass (as unprocessed/raw solid fuels) which can lead to poor air quality, secondary pollution, and undesired health impacts. (Baratieri et al., 2008).

Thermochemical processes have advantage over biological processes where lingocellulosic biomass requires several pretreatment steps, more process time and high investments. In the recent years many studies have suggested biomass pyrolysis process is more favorable in sustainable development aspect compared to combustion and gasification processes. Biomass pyrolysis generates syngas, bio-oil, and biochar which can have miscellaneous utilization such as energy, chemical feedstocks for industries, liquid fuels, carbon sequestration, bioremediation, and soil enhancement. Nevertheless, gasification and combustion have limited uses to heating and energy produced (Verma et al., 2012).

Table 2.3: Comparison of the advantages between thermochemical conversion processes versus biological/biochemical process**.**

Thermochemical	**Biological/Biochemical**
Effectively applied to almost any biomass feedstock	Involves the use of microbes, enzymes, and/or chemicals to utilize the limited range of biomass
Relatively higher productivity (production per unit time) due to completely chemical nature of reaction	Productivity is limited due to biological conversion. Increase would require higher capital investment such as bigger reactor
Multiple high-value products possible using fractional separation of products	Limited to one or few products and would require additional microbial culture, enzymes for more products
Independent of climate conditions, operates at much higher temperature range, therefore, effect of ambient temperature will be minimal	Mostly susceptible to ambient temperature, and so forth such as anaerobic digester, sunlight for algal ponds
Mostly complete utilization of the waste/biomass	Production of secondary wastes such as biomass sludge

2.5.2. Physical / Chemical process

Oil extraction is performed through a physical process involving homogenizing, heating, pressing and filtering. Mechanical separation methods using heat, filtration and centrifugation are used to remove some of the solid impurities and water from brown grease. Fats and oil from meat products are recovered through rendering which is crushing and/or grinding the animal fats followed by cooking at controlled temperatures and mechanical or solvent separation (Bozell et al., 2004 ; Nelson et al., 2006). Bozell et al, (2004) investigated the way to avoid hydrolyzing during cooking/heating at which water is typically removed; however this has resulted in increasing free fatty acid (FFA) content. Mechanical separation of oils from the cooked fat is carried out through pressing followed by centrifuging step. Supercritical CO_2 extraction was also employed for oil extraction in meat processing (Bozell et al., 2004).

Transesterification is the most frequently used method for conversion of waste and virgin bio-oils to biodiesel. In this process, TAG are converted to fatty acid alkyl esters by reacting the acetyl part of the TAG with the alkyl part of the alcohol, where the glyceride group is replaced with hydroxyls (from the alcohol) to form glycerol as a by-product (Sanli et al., 2008; Naik et al., 2006). The viscosity of bio-oils reduces, without affecting the cetane number and the heating value. A catalyst is used in this process (acid, base, or enzymes) to increase the TAG process during reaction (Sanli et al., 2008)

TAG reaction is depended to several factors such as: feedstock composition; FFA content in raw materials, water concentration; alcohol to TAG molar ratio; catalyst type and concentration; type of alcohol; temperature; pressure; and mixing intensity. Researches have been intensively conducted to calculate variables affecting ester yields and their respective interactions. Selva et al., (2011) suggested that the optimal reaction conditions for production of methyl esters from chicken and mutton fats should be performed at 90 min of reaction time (60°C), 6:1 molar ratio of methanol to oil and 0.38gm of KOH/gm. Narasimharao et al., (2009) investigated about the production of biodiesel of feather meal through transesterification using using KOH and methanol. It was concluded that catalyst loading at 1 wt. % and a molar ratio of oil to methanol at 1:9 were the optimum conditions for the transesterification reaction to obtain high composition methyl esters compounds of palmitic (C16:0), steric (C18:0), linoleic (C18:2), and oleic acids (C18:1).

2.5.3. Biological conversion

Fermentation and hydrolysis are biological conversion processes used for recovering oil from waste biomass. (Johnson et al., 1985; Ivar et al., 2005). Hydrolysis is carried out by decomposition of organic matter with the addition of water and enzymes. Fermentation uses bacterial culture and sugar or organic acids to digest organic matter (animal fats) and produce silage, where oil is recovered as a by-product (Johnson et al., 1985).

Anaerobic digestion is one of technology involving biological treatment of livestock waste that has been scaled-up to full-scale production of combustible biogas industry. Bujoczek et al., (2000) studied about high solid anaerobic digestion of chicken manure conducted in a batch screening assay. Salminen et al., (2002) studied anaerobic digestion of organic solid poultry slaughterhouse waste and found that the technology is practicable for the treatment of organic solid slaughterhouse waste with excellent material recovery and high potential in bio-energy production. At the same time, the operation conditions could be optimized and the process was made economically sustainable.

2.6. Pyrolysis from animal waste

Pyrolysis or thermal cracking of triglyceride materials is an alternative method in producing renewable bio-based products which is suitable for fuel and chemical applications. There are significant advantages of this type of technology including lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility (Theodore & Juan, 2013). Rajat (2014) claimed the renewable bio-fuels from plant are categorized in several type which are (i) edible vegetable oil (sunflower, soybean, rapeseed, palm and coconut), (ii) non-edible vegetable oil (microalgae, safflower oil and linseed oil), (iii) waste recycled oil (waste frying oil) and also (iv) animal fat waste (chicken fat, fish, duck tallow, feather meal, beef tallow and others).

Pyrolysis process has significant advantages over transesterification process because pyrolysis process can lower processing costs, compatibility with infrastructure, engine and fuel standards, and feedstock flexibility (Maher & Bressler, 2007). Bio-oil is composed from a large variety of condensable chemicals derived from cracking and sequential processes during the pyrolysis. In pyrolysis process, the biomass waste was heated above the boiling point temperature under continuous inert gas flow. As hot volatile compounds leaving the reactor, the volatile compounds that are carried by inert gas are immediately quenched by condenser. Depending on the operating condition, pyrolysis is classified into three main types: (i) slow; (ii) fast; and (iii) flash pyrolysis. These differences between this pyrolysis are described in Table 2.4.

Table 2.4: The differences of process conditions and products for pyrolysis processes (typical biomass) (Table with permission from author Mohammad, 2012).

Pyrolysis process	**Residence time (s)**	**Heating rate (K/s)**	**Particle size (mm)**	**Temperature (K)**	**Product yield (%)**		
					Oil	**Char**	**Gas**
Slow	450 -550	0.1 – 1	5 – 50	550 - 950	30	35	35
Fast	0.5 – 10	10 – 200	<1	850 - 1250	50	20	30
Flash	<0.5	>1000	<0.2	1050 - 1300	75	12	13

Slow pyrolysis is usually performed via slow heating rates, relatively long solid and vapor residence times (5 min to 30 min). This process yields huge amount of char at low temperatures and low heating rate. Due to high residence time and low temperature, it would affect bio oil yield and slow pyrolysis is suitable for char production process.

For fast pyrolysis, biomass is rapidly heated at a high temperature and this process produces higher yield of oily product (60% - 75%). The basic characteristic of this process are high heating rate, short residence time and rapid cooling of vapors. Fast pyrolysis relatively requires high energy efficiency compared to other processes, especially in a small scale reactor. Flash pyrolysis is defined as extremely high heating rate with higher reaction temperature (450 °C and 1000 ℃) and shorter gas residence time compared to fast pyrolysis. The main product is significantly higher than fast pyrolysis as the yield can reach up to 75% of bio oil.

The products obtained from fast pyrolysis process are char, gases and liquid (bio oil). The liquid (bio oil) will occur at usually around 350 ℃ – 550 ℃ due to biomass waste cracking during the pyrolysis (Mustafa et al., 2010; Mohammad et al., 2012). It is known that the yield produced from pyrolysis is depending to water content in the biomass since the presence of water moisture produces large quantities of condensate water in the product compositions.

Even though bio oil has ability as an alternate energy source, the application is limited due to its high viscosity, low heating value, chemical instability and high corrosiveness. On the other side, bio oil has some promising properties such as less toxicity, good lubricity and better biodegradation compared to fossil fuels. Upgrading is required for bio-oil from pyrolysis since crude bio-oil is not compatible with conventional engine. Several reaction processes have been developed for bio-oil upgrading such as catalytic cracking, hydrodeoxygenation (HDO), zeolite upgrading, steam reforming, esterification, emulsification and supercritical extraction (Anjani et al., 2016)

2.6.1. Physical and chemical properties determination

The fatty acid compositions for animal fats are depending to the type of animal waste. Fatty acid composition determination was carried out in three step analyses: extraction of the fat, derivatization to their alkyl ester form and gas chromatography mass spectroscopy (GCMS) analysis. In this research work, the derivative fatty acids and esters are analyzed using GCMS. The fatty acid composition of animal fats consist of saturated fatty acid (myristic, palmatic, stearic) and unsaturated fatty acid (oleic, linoleic).

The fatty acid composition of CSF is presented in Table 2.5. Divya (2006) also reported, fats and oil have varying length of carbon chain that usually ranging from 10 to 18 carbons which means C10 to C18. Jason et al., (2009) reported the major composition of chicken skin fat consist of methyl ester of palmitic (C16:0), stearic (C18:0), linoleic (C18:2), and oleic (C18:0) acids. Biofuel containing compounds with carbon chain lengths of ≥ 15 produces high quality fuel. Generally, higher cetane number will improve the bio oil emission. Major chemical composition of chicken skin bio oil such as aliphatics, followed by carboxylic acid, alcohol, ketone, ester, aromatic, anhydride, ether and aldehyde are expected to be observed (Liew et. al., 2013).

Table 2.5: GC-MS composition of CSF (Table with permission from author Selva, 2011)

Fatty acid	Chemical structure	CSF (%)
Myristic acid	C14:0	0.7
Myristoleic acid	C14:1	0.3
Palmitic acid	C16:0	22
Palmitoleic acid	C16:1	8.0
Stearic acid	C18:0	5.9
Oleic acid	C18:1	42.5
Linoleic acid	C18:2	15
Linolenic acid	C18:3	0.7

2.6.2. Thermal properties

Thermal properties of the CSF bio oil are critical for determining storage conditions, end use and overall stability of the biomass waste. Jayasinge and Hawboldt (2012) emphasized thermal properties includes melting/freezing, crystallization, enthalpy and specific heat capacity, and reactions such as thermal oxidation and decomposition impact fuel properties.

Thermogravimetric analyzer (TGA) uses the initial temperature and amount of weight loses during heating. Weight loss is observed due to decomposition or interactions between compounds such as phospholipids, fatty acid and oxidation products present in oils. The constituent of bio oils such as lipids, fatty acid, and water and other impurities, aging and amount of heat treatment the oil was subjected to affect the freezing and melting point. CSF bio oil has high level of saturated fatty acid content which results in greater than 0 °C of melting and freezing points. Melting point below 0

°C would only occur when the saturated fatty acid is present and the number of double bonds is low. Physical properties of biodiesel produced from are presented in Table 2.6.

Table 2.6: Fuel properties of biodiesel produce from chicken fats. (Table with permission from Ivana, 2014).

Properties	**Unit**	**CSF**
Density at 15 °C	k/gm^3	867.0
Kinematic Viscosity	mm2/s	6.3
Cloud point	°C	-5.0
Acid Value	mg KOH /g	0.3

2.6.3. Pyrolysis process condition

Process optimization is the process in minimizing operation cost and maximizing throughput and/or efficiency. The process optimization for pyrolysis comprises of reaction temperature, heating rate and feedstock selection.

Reaction temperature

Ben Hassen-Trabelsi and co-worker (2014) investigated the effect of experimental parameter on the quality and the distribution of pyrolytic bio oil. As shown in Figure 2.2 the group indicated that the temperature of 500 °C and heating rate of 5 °C/min were the most suitable condition to achieve a high yield from 58% to 77.9% .

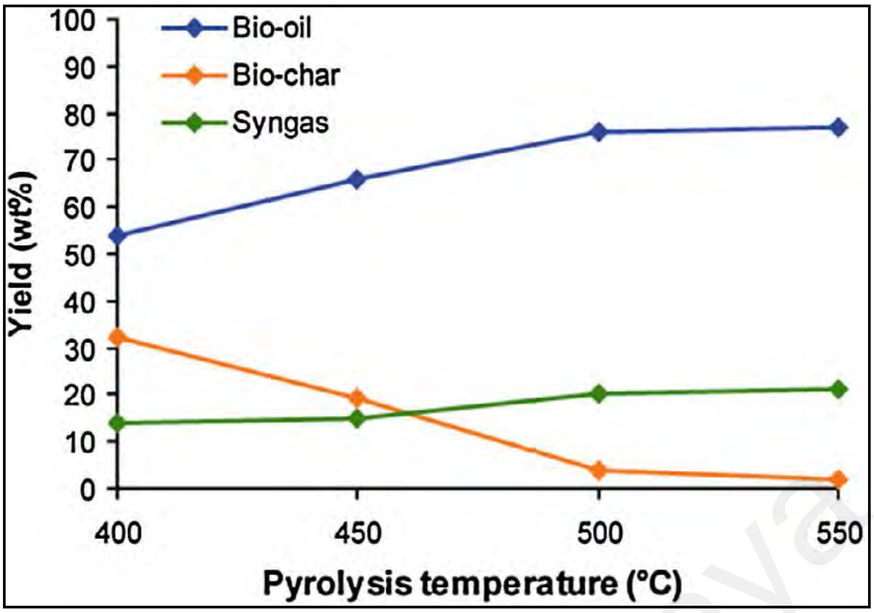

Figure 2.2: The effect of final temperature on pyrolysis product distribution. (Figure with permission from author A. Ben Hassen-Trabelsi, 2014)

Wisniewski et al., (2010) studied waste fish pyrolytic bio oil. The waste fish oil was converted via fast pyrolysis at 525 °C in continuous pilot plant reactor and found 72- 73 % bio-oil yield. Kim et al., (2009) investigated the pyrolysis characteristics in the pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. Poultry litter comprised relatively huge fractions of ash which are rich in potassium, phosphorus, calcium, and magnesium. The pyrolysis between 450 °C and 550 °C produced 15% to 30% viscous brown bio oil yield respectively.

Takuya et al., (2012) investigated efficient pyrolysis process conditions and pattern of from fats and oil derived from animal manure. It was found the addition of palladium supported by activated carbon (Pd/C) catalyst during pyrolysis process allowed the selective decarboxylation to obtain light oil. It was claimed that at pyrolysis temperature of 420 °C, hydrocarbons are formed by decarboxylation of ester compound groups.

Heating Rate

From the work performed by Ben Hassen and co-worker, Figure 2.3 shows the increasing of heating rate (5 °C/min, 10 °C/min, 15 °C/min) had decreased the bio-oil yield significantly while bio-char and syngas yield increased proportionally. These trends are observed due to the increasing of liquid phase cracking as the heating rate is increased. In fact, the long carbon chains contained in condensable vapors were broken into short cuts producing more gaseous products. Therefore, triglycerides materials heated at high heating rate producing more cracking hydrocarbons in the condensable vapors. Ben Hassen and co-worker concluded that the pyrolysis temperature of 500 °C and the rate of 5 °C/ min are the most optimum conditions to achieve high bio-oil yield. Li and team (2007) also reported that the increasing of heating rate from 5 °C/min to 20 °C/min lead to the increasing amount of bio-char residue. The residue was about 29% for 5 °C/min heating rate while more residue forms at higher heating rate (20 °C/min) which is 34%. At the same time, the maximum velocity of weight loss changes also increased with the increasing of heating temperature (1.8 %/min to 10.95 %/min)

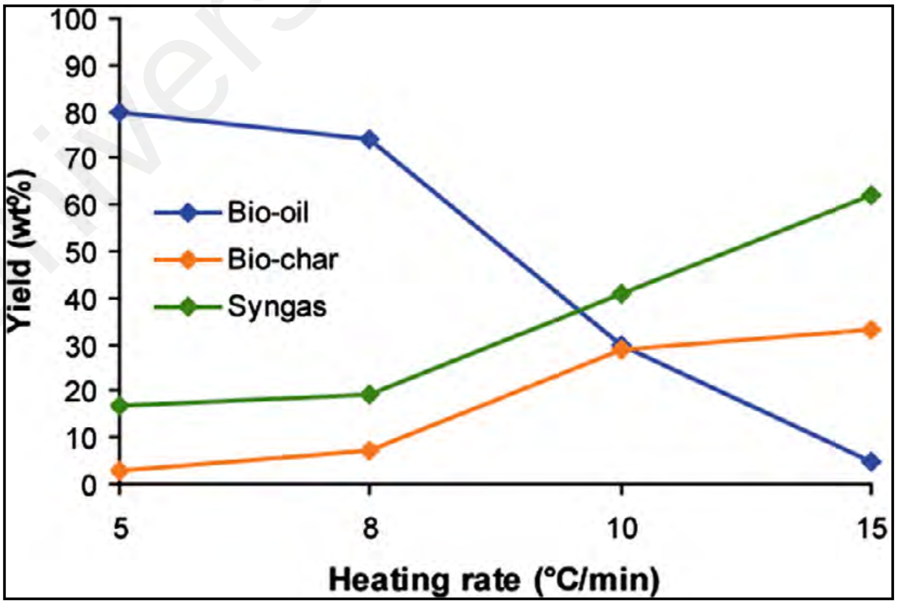

Figure 2.3: The effect of heating rate on pyrolysis product distribution. (Figure with permission from author A. Ben Hassen-Trabelsi, 2014)

Feedstock selection

The stimulus of the process parameters and the pyrolysis products properties have been widely discussed for many biomass resources. The effect of raw material types can be seen from the comparison of the bio oils yields. Ben Hassan et al., (2014) determined that pyrolysis of lamb fats produced the highest liquid fraction yield (77.9 wt. %) compared to poultry and swine waste that were around 67.6 and 58.0 wt. % respectively. Waste cooking oil also includes long-chain saturated compound and free fatty acids derived from animal fats. Takuya et al (2012) investigated pyrolytic using waste cooking oil and it was reported high yield of 85 wt. % bio-oil. Wisniewski et al., (2010) was studied pyrolysis of waste fish oil using fast pyrolysis process at 525 °C in a continuous pilot plant reactor and reported yield of bio-oil around 72-73 wt. %. Municipal solid waste (MSW) was also used in the production of for promoting biofuel. The MSW are mostly mixtures of organic food wastes, papers, broken glasses, metals and plastics. The organic food wastes, that are the cellulosic biomass, were the main raw materials in this pyrolysis work. It was found the yield of bio-oil was around 45 wt. %. (Muhammad et al., 2010).

2.6.4. Types of pyrolysis reactor

There are several types of pyrolysis reactors both at developmental and commercial scale (Bridgwater et al., 2002; Meier et al., 1999; Mohan et al., 2006; Scott et al., 1999; Peacocke et al., 1994). Different types of reactor were based from the requirements such as the high heat transfer rates, separation of solids and gas phase are described in Table 2.7.

Table 2.7: Comparison of various biomass pyrolysis reactors based on overall performance and efficiency. (Table with permission from author Bridgwater, 2002)

Pyrolysis type of reactor	**Unit operation**	**Bio-oil yield (wt. %)**	**Particle size**
Fixed bed	Pilot (single),lab (multiple)	75	Large
Fluidized bed	Demo(multiple),lab (multiple)	75	Small
Recirculating bed	Pilot(multiple),lab (multiple)	75	Medium
Rotating Cone	Demo (single)	70	Medium
Ablative	Pilot(single),lab (multiple)	75	Large

2.7. Bio-oil upgrading

There have been several researches in bio oil upgrading and many technologies have been developed for bio oil upgrading. Table 2.8 below describes current techniques used for bio oil upgrading (Xiu & Shahbazi 2012; Ming Chai et al.,2014; Aziz et al.,2017). The application of bio-oil as petroleum fuels is restricted by the issues of high viscosity, high oxygen substance, highly corrosive, high moisture content, and their thermal instability. Therefore, it is very crucial for bio-oil to be upgraded utilizing legitimate strategies before they can be utilized as a part of diesel or gasoline engines.

Table 2.8: Current techniques used for bio oil upgrading.

Method	**Reaction mechanism/ process description**
Hydrotreating/hydrofining - Mild conditions : (500 °C/low pressure), chemical needed: H_2/CO, catalyst (e.g, CoMo, HDS, NiMo, HZM-5)	Hydrogenation without simultaneous cracking (eliminating N, O and S as NH_3, H_2O and H_2S)
Hydrocracking/hydrogenolysis/catalyst cracking - Severe conditions (> 359 °C, 100-2000 Psi), chemical needed : H_2/CO or H_2 donor solvents, catalyst (e.g, Ni/AL_2O_3-TiO_2)	Hydrogenation with simultananeous cracking Destructive (resulting in low molecular product)
Sub- / super-critical fluid - Mild condition, organic solvents needed such as alcohol, acetone, ethyl acetate, glycerol	Promotes the reaction by its unique transport properties: gas-like diffusivity and liquid-like density, thus dissolved materials not soluble in either liquid or gaseous phase of solvent
Solvent addition (direct add solvent or esterification of the oil with alcohol ad acid catalyst) - Mild condition, polar solvents needed such as water, methanol, ethanol, and furfural	Reduces oil viscosity by three mechanism: 1. Physical dilution 2. Molecular dilution or by changing the oil microstructure 3. Chemical reactions like esterification and aceralization.
Emulsification/emulsions - Mild condition, need surfactant (e.g, CANMET)	Combines with diesel directly. Bio oil is miscible with diesel fuels with the aid of surfactants

2.8. Catalytic upgrading of pyrolytic bio-oil using esterification

Biomass pyrolysis routes to transportation fuels are therefore only feasible and viable if the bio-oil is subjected to upgrading treatments in order to improve their physicochemical properties. There are several promising catalytic processes for bio-oil upgrading/pre-treatment, including ketonisation, condensation and hydro-deoxygenation. This research work focused on catalytic upgrading by esterification which offers a low energy route to oil stabilization. The main idea of upgrading by esterification is the addition of an alcohol to convert the unwanted acidic components into stable substances. At the same time, it is a simple pre-treatment to improve the stability of oil during storage and transportation. The addition of small concentration of ethanol or methanol (<10%) has been observed can improve bio oil stability through the formation of ester and acetal via non catalytic reaction with carboxylic acids and aldehyde respectively. This addition also can reduce the ageing rate of the bio oil through homogeneous reaction originated by the organic acid itself (Xiu & Shahbazi 2012). Figure 2.4 below shows the principle reaction scheme. Carboxylic acids react with the alcohols in an equimolar mixture to the respective ester, following the lower reaction scheme. Furthermore, aldehydes and ketones react analogously to acetals according to upper reaction scheme, consuming 2 molecules of alcohol per molecule of aldehyde or ketone. Both reactions are catalyzed by acids, so initially the amount of acetic acid (for example) is high enough to initiate the reactions. With proceeding degree of reaction, the acidity in the liquid is reduced due to removal of free acetic acid, and therefore the reaction rate decreases and the full conversion of acids and ketones/aldehydes might not be reached.

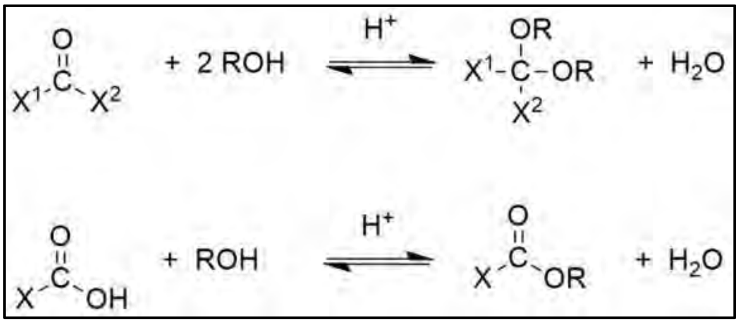

Figure 2.4: Reaction scheme for esterification (Figure with permission from author Xiu,2012)

The addition of acidic catalyst can increase the esterification reaction rate. Acidic catalyst is available either in liquid acid or solid acid (Conrad et al., 2015; Chai et al., 2014; Piyarat et al, 2012). Sulfuric acid (H_2SO_4) is a strong mineral acid whereas para-toluene sulfonic acid (PTSA) is an example for a strong organic acid. Meanwhile, solid acid such as zeolites or solid organic supports usually have functionalized with sulfonic acid groups. Homogenous liquid acid catalysts typically produced high reaction rate in esterification reaction but it is difficult to separate the catalyst from product after reaction. Solid acid catalysts can easily separate from the product after reaction and ultimately the catalyst can be recycled for further batches (Conrad et al., 2015). In this research work, commercial ZSM-5 was used because ZSM-5 is an acidic hydrophobic material with medium pore dimensional network and high ratio of Si: Al at 15:1

Generally, high characteristic of acetic acid (1-10%) and in low pH value (2-3) in pyrolytic bio oil product, lead to vessel corrosion and fuel instability. Esterification can occur with either alcohol component integral to bio oil (phenolic or oxygenates) or via external sources (methanol, ethanol or butanol). As the boiling points are lower than their parent acids, upgrading by esterification deals the possibility for reactive distillation to remove water, unreacted alcohol and volatile esters. These methods lower the acidity with good chemical stability and viscosity (Piyarat et al., 2012).

Sulphated zirconias have received an attention due to its exclusive balance between acid and base sites. The effect of the S=O bond in sulphate species on the surface of SZ improve the Lewis acid strength of the Zr^{4+}. Water presence is converted Lewis acid site to Brönsted acid site through proton donation from adsorbed water molecule. However, sulphated zirconias has low surface area and pore volumes thus a great deal of effort has been focused on development of structured zirconia materials employing surfactant templating methods to introduce mesoporosity (Deng et al., 2008; Larsen et al., 1996).

Zeolite has been used as a catalyst for over half a century with many types of synthetics zeolite available. Zeolites are proficient in possessing both Brönsted and Lewis acid sites. Moreover, the acid character of the zeolites is maintained with addition of active metal phases through ion-exchange which allowing for a good flexibility and bifunctional behavior. Figure 2.5 shows a schematic of the pore structure of four common zeolite classes.

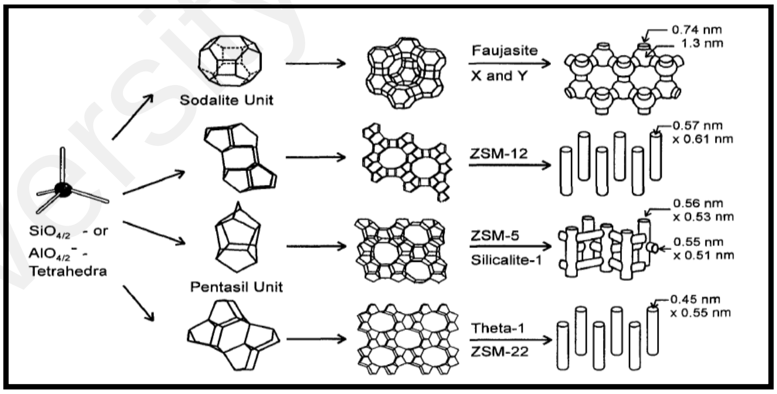

Figure 2.5: Structures of select zeolites highlighting their micropore network (Figure with permission from author Deng, 2008)

Normally, zeolites are highly microporous which are the most widely explored class of solid acid for bio-oil upgrading by esterification, with considerable efforts focused on the reaction pathways and relationships between zeolite structure, acidity and corresponding catalytic performance. Kamonlatth et al., (2017) reported ZSM-5 can significantly increase catalytic performances of the esterification in terms of increasing activity, desired product yield, and catalyst reusability for an esterification of carboxylic acids. Omar et al., (2018) investigated the potential of ZSM-5 catalysts in converting low value and short chain oleic free fatty acid (OFFA) to oleic acid methyl ester (OAME) biodiesel. It was found ZSM-5 was capable and promising catalyst for the esterification of oleic acid with methanol.

2.9. Thermal decomposition kinetic analysis

The studies of thermal and kinetic properties of biomass via thermogravimetric analyzer (TGA) analysis are important to understand the characteristic of bio-oil produced from biomass waste. TGA uses the initial temperature and amount of weight loses during heating in which the weight is lost due to decomposition or devolutions of compounds such as phospholipids, fatty acid and oxidation products present in oils.

The activation energy of the bio-oil can be obtained from model free-isoconversional method from TGA. Model-free isoconversional methods represent the most popular class of methods for determination of the kinetic parameters from thermoanalytical data. The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is performed. This type of kinetic method has several advantages because it is possible to calculate activation energy for the main degradation process without any knowledge of the form of the kinetic equation. It also suitable for deriving a rate law as it is also a simple method that can use TGA experiment to carry out one rate of heating under normal conditions (Friedman, 1964).

The activation energy of a fuel can effectively be obtained by an experimental setup, particularly by a thermal analysis. This method have gained wide acceptance in the study of the combustion and pyrolysis behavior of a potential fuel, as the method requires small quantity of sample, low operation cost and fast method analysis (Diego Galvan et al 2013). The relationship between temperature and the rate constant for a reaction obeyed the following equation.

$$k = Ae^{-Ea/RT} \tag{2.1}$$

In this equation, k is the rate constant for the reaction (h^{-1}), A is Arrhenius constant or pre exponential factor (h^{-1}), E_a is the activation energy (kJ/mol) for the reaction, R is the ideal gas constant (8.31447 J.K/mol), and T is the absolute temperature (K).

The Arrhenius equation can be used to determine the activation energy for a reaction and taking the natural logarithm of both sides of the equation.

$$\ln k = \ln A - \frac{Ea}{RT} \tag{2.2}$$

Activation energy is important as a barrier that must be overcome for a chemical reaction to occur. Christopher et al., (2010) investigated the activation energies between animal fat and glycerol by applying model free kinetic. It was found the animal fat and glycerol show the apparent activation energy of 108.87 ± 52.28 kJ/mol and 65.37± 13.17 kJ/mol respectively. As animal fat is a more complex substance than glycerol, its activation energy higher than the activation energy of glycerol. It was reported a kinetic test on rice husk indicated the apparent activation energy of 140± 60 kJ/mol. The activation energy is higher than animal fat and glycerol because main constituents of rice husk are cellulose, hemicellulose and lignin (Liou et al., 1997).

CHAPTER 3: METHODOLOGY

3.1. Material and Chemicals

3.1.1. Feedstock

Chicken skin fat (CSF) used in this study for pyrolysis feed was obtained from Wet Market, Section 6, and Shah Alam Selangor. In order to preserve the sample in chicken skin, freeze drying process is more preferable compare to normal heat drying for water removal. Therefore, the chicken sample used in this project was freeze dried at -40 °C for 2 week prior, grinded and conserved inside the refrigerator. For bio oil analysis using GCMS, analytical grade methanol was used as a solvent.

3.1.2. Chemical and gases list

A list of the chemicals, catalyst and solvent for gas chromatography (GC) are listed in Table 3.1 to 3.3:

Table 3.1: List of catalyst used (ZSM-5 was calcite at 800 °C for 5 hours).

Type	Si/Al ratio	Surface area (m^2/g)	Supplier
Zeolite (ZSM-5)	15	425	Zeolyst

Table 3.2: List of gases used.

Gas	Formula	Purity (%)	Brand
Nitrogen	N_2	99.9	Lindle

Table 3.3: List of GC solvent used.

Chemical	Formula	Purity (%)	Brand
Methanol	CH_3OH	GC ≥ 99.8	Merck

3.2. Methodology of Proximate and ultimate analysis of feedstock.

3.2.1. Determination of moisture and ash content

The percentage moisture (MC) of the CSF sample was determined by weighing 100 g of the sample into a pan which its weight was known prior the test. The sample was then dried at the temperature of 100 °C and according to ASTM (American Society for Testing and Materials) D3173 standards. The percentage moisture content was calculated according to the equation 3.1:

$$\% \text{ Moisture Content} = \frac{(\text{Wet weight} - \text{Dry weight})}{\text{Wet weigth}} \times 100 \tag{3.1}$$

The same sample was then used to determine the volatile matter (VM) content. This method was performed by burning the sample at 950 °C. The samples were weighed and placed in a furnace for about 6 min at a temperature of 950 °C according to ASTM D3175. After combustion, the samples were weighed to determine the ash dry weight. At this stage, the volatile matters were calculated according to the equation 3.2:

$$\% \text{ Volatile matter} = \frac{(\text{Weight of dry sample} - \text{Ash weight})}{\text{Dry sample weigth}} \times 100 \tag{3.2}$$

Ash content (AC) of the wastes is the non-combustible residue left after the sample is burnt. Fixed carbon (FC) is the residue or char remaining after evolves of volatile matters. The sample was dried at a temperature of 700 °C. In this test, fixed carbon was determined by removing the mass of volatiles from the original mass of the sample according to the equation 3.3:

$$\text{Fix Carbon (wt\% wet basis)} = 100 - (\text{ wt\% Moisture Content} + \text{wt\% Ash Content} + \text{wt\% Volatile Matter}) \tag{3.3}$$

3.2.2. The elemental composition (CHNO) of feedstock

CSF samples were determined at Chemistry Department University of Malaya using CHN/O 2400 Series II. The CHS mode is based on the classical Pregl-Dumas method where the samples were combusted in oxygen up to 950 °C which converting elemental carbon, and nitrogen into CO_2, NOx and N_2. A sample with a mass between 1.5 – 2.0 mg was weighed into a tin capsule is folded and re-weighed. The sample was then placed into an auto sampler and the instrument was set according to the following parameters:

He pressure	: 250 kPa
O_2 pressure	: 250 kPa
Furnace temperature	: 950 °C
Column oven temperature	: 65 °C
Sample holder	: tin capsules

3.3. Chicken skin decomposition kinetic study

The thermal decomposition characteristic of CSF without catalyst (ZSM-5) was determined using thermogravimetric (TGA) model TGA400 Perkin Elmer instrument. In each case the temperature increased from 50 °C to 900 °C at five different heating rates: 5.0 °C, 10.0 °C, 15.0 °C and 20.0 °C/min. All experiments were run once for each sample to calculate the activation energy. After that, CSF with catalyst (ZSM-5) samples were determined using same equipment in different catalyst loading (10%, 20%, 30% and 40%) at 5 °C/min. The samples were placed in a crucible and a mass of 10.0 mg with an allowance of ± 0.5 mg was used.

3.4. Procedure for bio oil production

Figure 3.1 shows the schematic diagram of fixed bed reactor for pyrolysis reaction. For this pyrolysis process, 200 g of CSF biomass was charged inside a pyrolysis reactor and the experiment was performed at different heating temperature (450 °C, 500 °C and 550 °C) at constant heating rate of 5 °C/min. At first, the reactor was heated under inert atmosphere and nitrogen was purged into the reactor for 10 minutes to create inert conditions. The reactor was heated at 5 °C/min from room temperature to 500 °C for 1 hour. The nitrogen was purged at a flow rate of 2 liters per minute to maintain an inert atmosphere and to ensure the quick removal of volatiles. The pyrolysis vapors were discharged from the reactor and cooled two condensers connected in series with temperature at 4 °C. The remaining uncondensed gases were released to the atmosphere. After pyrolysis reaction completed, the furnace was shut down and the reactor was allowed to cool under a nitrogen atmosphere until reaching room temperature. After the pyrolysis process, the reaction mixture was kept in dark bottle and kept in the fridge. The yield of liquid bio oil was calculated using the following equations (Selva & Parthiban 2011):

$$\%Y_b = \frac{W_b}{W_{CSF}} \text{ x } 100 \qquad (3.4)$$

Where $\%Y_b$ is the yield of bio oil and W_b and W_{CSF} are the weight of bio oil and weight of CSF fed during the experiment, respectively and

$$\%Y_c = \frac{W_{rae} - W_{rbe}}{W_{CSF}} \text{ x } 100 \qquad (3.9)$$

Where $\%Y_c$ is yield of the bio char, W_{rae} and W_{rbe} are the weight of reactor with char after experiment, weight of reactor before the experiment respectively.

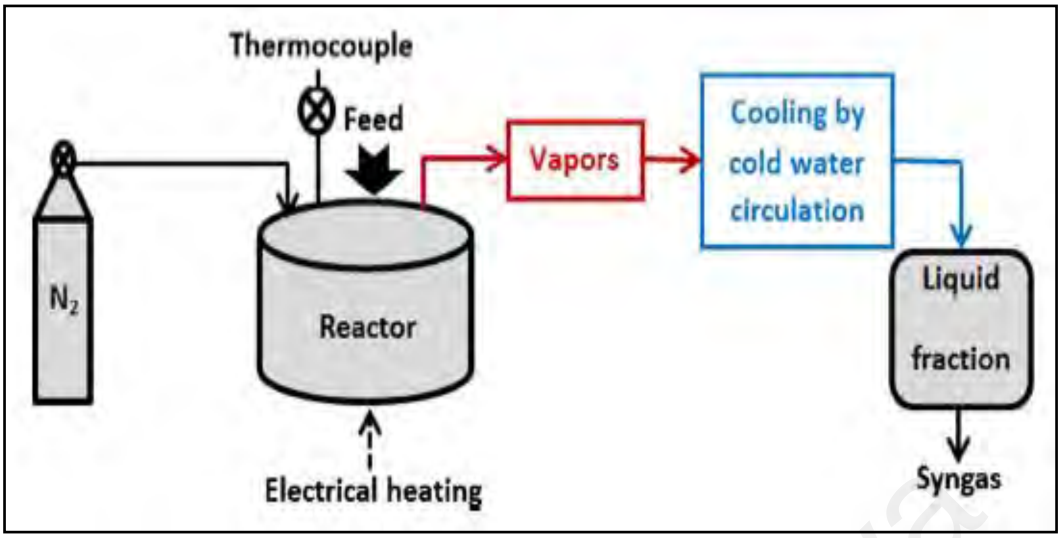

Figure 3.1: Schematic diagram of fixed bed reactor.

3.5. Catalyst characterization

ZSM-5 powder form (Zeolyst CBV 8014, Si/Al = 15) was used as catalyst in this study. ZSM-5 was calcined in an oven at 800 °C for 5 hours.

3.5.1. X-ray powder diffraction (XRD)

The XRD analysis was performed using a PANanalytical Empyrean. Data analysis is performed using HighScore Plus provided by PANalytical using PDF 4+ Database from ICDD. The sample was placed in the sample holder, with the powder slightly pressed into place using microscopic slide. The surface of the sample was smoothed and placed in the diffractometer stage for analysis. A continuous 2ϴ scan mode from 5° to 80° was used for high degree scanning at step time of 15s and step size of 0.05° 2ϴ. A divergence slit was inserted to ensure that the x-rays focused only on sample. The diffractograms achieved were matched against the International Centre of Diffraction Data (ICDD) PDF 4+ database.

3.5.2. Fourier Transform Infrared (FTIR) transmission

The FTIR analysis was performed using a Spectrum 400 FT-IR Spectrometer by Perkin Elmer. Data analysis is performed using Spectrum 10™ software. The sample was mixed with KBr and molded before mounting onto a sample holder. The sample was scanned from 400 ~ 4,000 cm^{-1} with infra-red source.

3.5.3. Nitrogen Physisorption Measurement

The surface area of the catalysts was determined using a Micromeritics ASAP 2010. The BET sample tube was initially degassed in one of the sample preparation ports and the weight of the tube recorded. Approximately 0.2 g of catalyst was then placed in the BET sample tube and the tube degassed once again prior to heating to 150 °C for 3 hours. The "dry" weight of the sample was then recorded. The sample tube was then backfilled with nitrogen to atmospheric pressure. This decreased the chance of the seal plug leaking during transfer to the sample analysis port. An isothermal jacket was placed over the sample tube to try to ensure homogeneous cooling on submergence in liquid nitrogen. The sample tube in the analysis port was again degassed before the dewar containing liquid nitrogen was automatically elevated upwards to submerge it. A known amount of nitrogen gas was introduced into the cooled tube. After equilibration, the pressure was measured and the sequence repeated with successive pulses of nitrogen. Knowing the volume of the system, the temperature and the amount of nitrogen gas added, the expected pressure in the absence of any adsorption can be calculated. From the difference between the calculated pressure and the observed pressure at each point the amount of nitrogen adsorbed was determined. Repeating this led to the generation of an isotherm from which the surface area of the sample was then calculated using the BET equation and N_2 cross-sectional area of 0.162.

3.5.4. TGA/DTG analysis

The thermal decomposition characteristic of Zeolite ZSM-5 was determined using thermogravimetric (TGA) model TGA400 Perkin Elmer instrument. The samples were placed in a crucible and a mass of 10.0 mg with an allowance of ± 0.5 mg was used. In this research work, the temperature increased from 50 °C to 900 °C at different heating rates 5 °C/min,10 °C/min and 15 °C/min under nitrogen flow.

3.6. Bio oil upgrading via esterification

Esterification experiments were carried out in a 250 ml 2-neck flask equipped with a Dean-Stark apparatus. The flask was heated in a water bath on a hotplate magnetic stirrer with thermometer dipped in the water bath and a water cooler condenser was connected to another neck on top of the flask to reduce evaporative loss of methanol. The set-up was flowed with N_2 gas throughout the reaction. The esterification experimental set-up is shown in Figure 3.2. All experiments were performed with methanol as alcohol. The ratio of methanol to bio oil was 2:1 (6 g of methanol to 3 g of bio oil) in 2.0 wt. % of solid catalyst which is zeolite (ZSM-5). The mixture was refluxed for 3 hours at 80 °C (Piyarat et al., 2012). The product was tested by using gas chromatography to determine the chemical composition. Table 3.4 shows the parameter for the experiment.

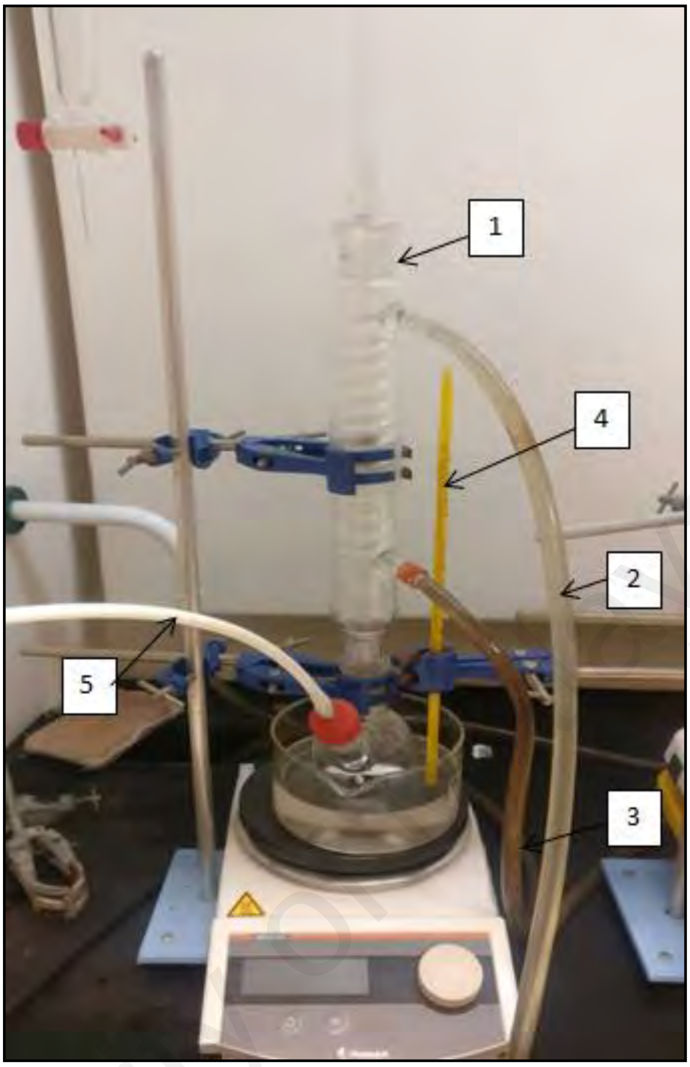

Figure 3.2: Apparatus setup for esterification reaction: (1) condenser, (2) water inlet/outlet, (3) water outlet, (4) thermometer, (5) N_2 inlet.

Table 3.4: Parameter for esterification.

Sample	Methanol : oil (wt% of oil)	Reaction temperature (°C)	Reaction time (hour)	Catalyst (wt% of oil)
CSF01	2: 1	80	1	0
CSF02	2: 1	80	2	0
CSF03	2: 1	80	3	0
CSF04	2: 1	70	3	0
CSF05	2: 1	60	3	0
CSF06	2: 1	70	3	2
CSF07	2: 1	70	3	4

3.7. Product analysis

The products from pyrolysis and esterification reactions were analyzed using Gas Chromatography/Mass Spectrometry (GCMS).

GCMS analysis

The bio oil was dissolved in analytical grade methanol and was injected into the column. A capillary HP5-MS (30 mm x 0.25 mm x 0.25 µm) was used. The initial oven was pressurize at 100 Kpa with a flow of 1.3 mL/min. The oven was initially heated at 150 °C, and increased up to 220 °C with heating rate at 5 °C /min and holding for 15 minute. Total run time was 29 minutes. The split injector was maintained at 250 °C. The MS detector was set-up according to the following parameters:

Interface : Direct to ion source, temperature 290 °C

Ionization : 70eV, electron impact at 175 °C

Scan descriptor : m/z 50- m/z 250 in 0.73s

The identification of the compounds was confirmed by referring a NIST database and published mass spectra library. This study only focused on acid and ester content (wt. %) from the bio-oil using GCMS.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Proximate and ultimate analysis of feedstock

The summary of the proximate and ultimate analysis of CSF is presented in Table 4.1. The elemental composition of chicken skin is in agreement with elemental composition reported by Liew et al., (2013). Carbon and hydrogen elements are important for the composition of fatty acids and organic substances that forms chicken skin. The moisture and ash content of CSF obtained were 0.07 % and 0.6 % respectively. The ash content is lower than the ash content flock and broiler manure reported by Seung-Soo and Foster (2007) because most of the chicken fat was evaporated during the test. The higher heating value (HHV) of the chicken fat was 37.80 MJ/kg was also significantly higher than manure because chicken fat contains higher acid fat that can be converted to bio-oil product.

Table 4.1: Elemental composition of CSF.

Sample	**Moisture (%)**	**Ash (%)**	**Element**				**HHV (MJ/kg)**
			C	H	N	O	
CSF	0.07	0.6	71.67	9.71	0.29	18.33	37.80
Flock[1]	22.81	22.80	37.15	5.33	3.13	34.67	15.14
Broiler[1]	33.35	21.45	39.62	5.05	3.35	34.05	15.75

[1] Results obtained from Kim and Foster (2007)

4.2. Kinetic study of chicken skin waste decomposition

4.2.1. Thermal Behavior Analysis

The results of thermogravimetric analysis (TGA) were expressed as a function of conversion X, which is defined as:

$$X = \frac{W_0 - W}{W_0 - W_\infty} \tag{4.1}$$

Where W_0 is the initial mass of sample; W is the mass of the pyrolyzed sample; W_∞ is the final residual mass. The degree of conversion versus temperature for dynamic experiments at the heating rate 5, 10, 15 and 20 °C/min for CSF are shown in Figure 4.1

In the differential rate of conversion, dX/dt was obtained from differential thermogravimetric analysis (DTA). Figure 4.2 shows the first small peak between 110 to 160 °C/min for the heating rate of 5, 10, 15 and 20 °C /min respectively. The first weight loss in the samples was attributed to desorption of moisture as bound water on the surface and the pores of samples.

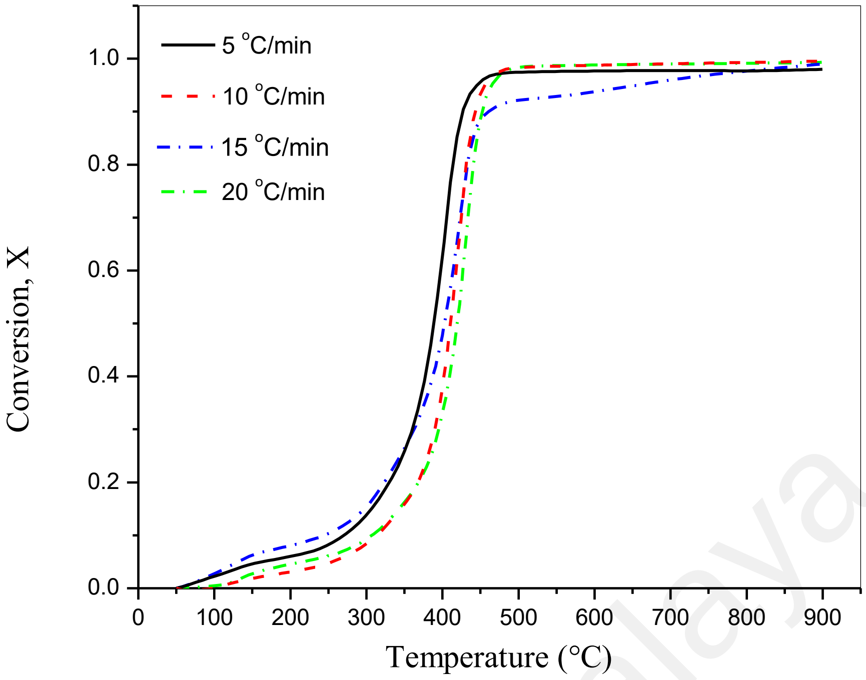

Figure 4.1: Conversion of CSF at heating rate 5, 10, 15 and 20 °C /min.

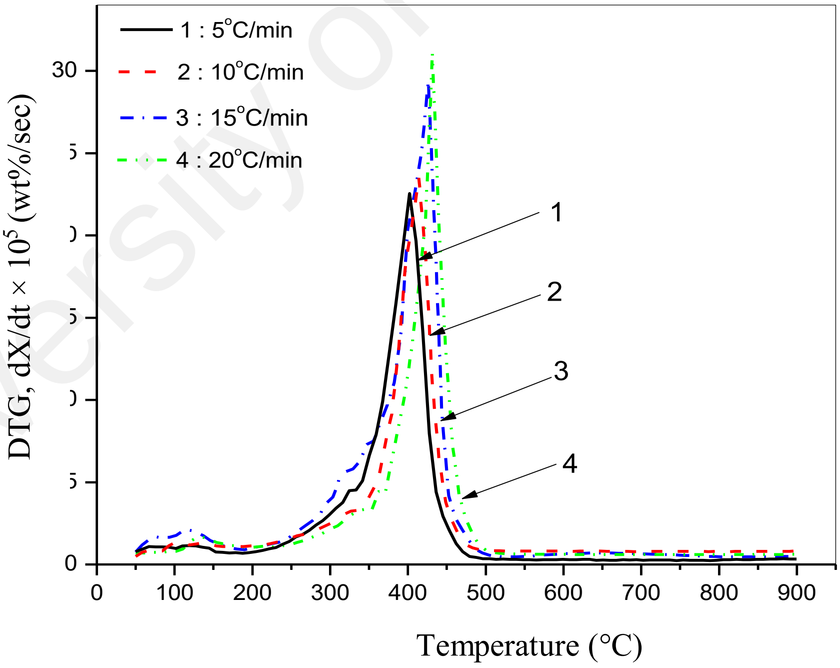

Figure 4.2: DTG curves of CSF at heating rate 5, 10, 15 and 20 °C /min.

All heating rates shows decomposition of fatty acids continued at 180 °C until 320 °C in the second weight loss except the 20 °C /min heating rate shows decomposition temperature from 180 °C until 380 °C The third decomposition peak of CSF is observed from 420 °C to until 440 °C for the all heating rates in Figure 4.2. The highest decomposition rate for CSF in this step occurred at around 400 °C and 420 °C for 5 °C /min and 10 °C /min respectively while slightly higher decomposition around 430 °C and 440 °C for the heating rate of 15 °C /min 20 °C /min (440 °C) respectively. The major decomposition of CFS usually occurred around 400 °C to 440 °C during third weight lost due to decomposition of fatty acids components that represents the major content of CSF. The decomposition temperature at this step is slightly higher for the heating rates of 15 °C/min and 20 °C/min compared to heating rates of 5 °C/min and 10 °C/min as higher heating rates increase the CSF cracking process even during decomposition under inert gas flow. Based from DTA analysis, the maximum rates of conversion for all heating rates are similar with all heating rates since the heating rates shows significant peaks at 180 °C to 380 °C and 420 °C to 440 °C respectively. After 440 °C, all fats are totally decomposed and bio-char remains until at the end of DTG analysis.

4.2.2. Kinetic analysis of CSF

Thermogravimetric analysis (TGA) has been widely used in the last decade for assessing the thermal stability of polymeric materials. The shapes of the TGA curves are determined by the kinetic parameters of the pyrolysis such as activation energy, Arrhenius frequency factor and reaction order. The intercept (ln(A.(1 –X)n)) can be determined from Figure 4.3 in every conversion. When the apparent order is determined at 0, the pre-exponential factor of A can be obtained using equation as follows:

$$\ln (A.(1 - X)^n) = \ln A + n \ln(1 - X) \qquad (4.2)$$

The variant of apparent activation energies as a conversion function for CSF is shown in Table 4.2. The range of apparent activation energies for 5 °C /min was between 44.60 kJ/mol and 78 kJ/mol and these changed with conversions.

Table 4.2: Conversion and apparent activation energy for different heating rates.

Heating rate (°C /min)	**Conversion (%)**						
	10	**20**	**30**	**40**	**50**	**60**	**70**
5	44.60	31.39	73.42	100.99	86.05	76.34	78.00
10	40.53	58.58	122.00	130.23	72.14	68.92	65.65
15	79.54	19.01	58.82	70.97	122.04	134.23	56.54
20	39.08	23.91	116.40	101.26	99.56	150.55	130.74

The apparent activation energies increase with the increasing conversion up to 60%. The apparent activation energy for 10 °C /min increased sharply from 40.53 kJ/mol to 130.23 kJ/mol (10% to 40% conversion) and from 79.54 kJ/mol to 134.23 kJ/mol for 15 °C /min by increasing the conversion between 10% to 60%.

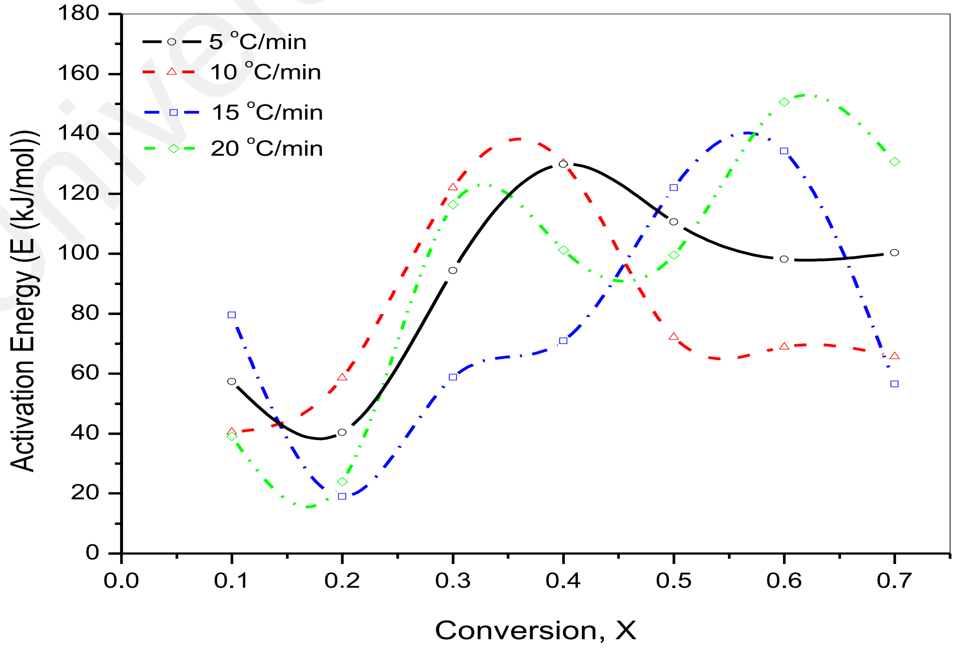

Figure 4.3: Calculated activation energies at different heating rate.

For 20 °C /min, the activation energies were between 39.08 kJ/mol (10 %) and 150.55 kJ/mol (60 %). After 60% conversion, the activation energies of all samples decreased because the entire element for CSF was completely decomposed.

Table 4.3: Pre-exponential factor with heating rate of 5, 10, 15 and 20 °C /min for CSF decomposition.

Heating rate (°C/min)	**Reaction order**	**Conversion (wt%)**						
		10	**20**	**30**	**40**	**50**	**60**	**70**
5	0th	1.19 x 10^{-2}	3.42 x 10^{-2}	8.45 x 10^{-2}	1.41 x 10^{-1}	1.71 x 10^{-1}	2.01 x 10^{-1}	1.74 x 10^{-1}
	1st	1.33 x 10^{-2}	4.28 x 10^{-2}	1.21 x 10^{-1}	2.34 x 10^{-1}	3.41 x 10^{-1}	5.03 x 10^{-1}	5.81 x 10^{-1}
10	0th	2.85 x 10^{-2}	5.36 x 10^{-2}	1.36 x 10^{-1}	1.89 x 10^{-1}	2.11 x 10^{-1}	2.40 x 10^{-1}	2.40 x 10^{-1}
	1st	3.17 x 10^{-2}	6.70 x 10^{-2}	1.94 x 10^{-1}	3.15 x 10^{-1}	4.21 x 10^{-1}	6.00 x 10^{-1}	8.00 x 10^{-1}
15	0th	6.91 x 10^{-3}	3.37 x 10^{-2}	5.35 x 10^{-2}	9.05 x 10^{-2}	1.50 x 10^{-1}	1.67 x 10^{-1}	1.93 x 10^{-1}
	1st	7.68 x 10^{-3}	4.21 x 10^{-2}	7.64 x 10^{-2}	1.51 x 10^{-1}	3.00 x 10^{-1}	4.17 x 10^{-1}	6.42 x 10^{-1}
20	0th	1.03 x 10^{-3}	3.41 x 10^{-3}	6.14 x 10^{-3}	1.00 x 10^{-2}	1.26 x 10^{-2}	1.90 x 10^{-2}	1.22 x 10^{-2}
	1st	1.15 x 10^{-3}	4.26 x 10^{-3}	8.77 x 10^{-3}	1.67 x 10^{-2}	2.51 x 10^{-2}	4.76 x 10^{-2}	4.07 x 10^{-2}

The pre-exponential factor (A), which can be obtained from Table 4.3, increased with the increase in conversion and heating rate. No devolution of bio-char was observed since pre-exponential factor were found to decrease at higher conversion and the apparent activation energy was less than 200 kJ/mol. It was reported by Kim (2007) that bio-char devolatilization was observed when the pre-exponential factor was found increased at higher conversion and the apparent conversion was more than 300 kJ/mol.

Overall, it was found the decomposition of CSF with minimum heating rate at 5 °C/min is comparable with other heating rates (10, 15, 20 °C/min) based from TGA and DTG analysis. This minimum heating rate also required low amount heating energy for CSF decomposition as the apparent activation energy showed around 30 kJ/mol to 100 kJ/mol. It was also reported that increasing heating rate from 5 °C/min to 15 °C/min significantly decreased the bio-oil yield and increased bio-char yield in lamb fatty slow pyrolysis due to the increasing of liquid phase cracking that reduced the condensation of long chain hydrocarbons (Ben Hassen et al., 2014). This trend was also reported in slow pyrolysis of sewage sludge and woody materials (Singh et al., 2012). Therefore, it was demonstrated that heating rate at 5 °C/min is the most efficient CSF decomposition compared to other heating rates.

4.3. Pyrolysis of chicken skin waste decomposition

4.3.1. Product analysis using GCMS

The pyrolysis experiment was performed at different heating temperature (450, 500 and 550 °C) at constant heating rate of 5 °C/min. At low temperature (450 °C), the yield of bio-oil and bio- char was 55 wt. % and 24 wt. %, respectively. The yield is calculated based from the equation 3.8 stated in Chapter 3 earlier. By increasing the pyrolysis temperature to 500 °C and 550 °C, the oil fraction is slightly increased to 65 wt. % and 68 wt. %, respectively. However, the yield of bio-char slightly reduced from 24 wt. % to 7 wt. % with the increasing temperature as shown in Figure 4.4.

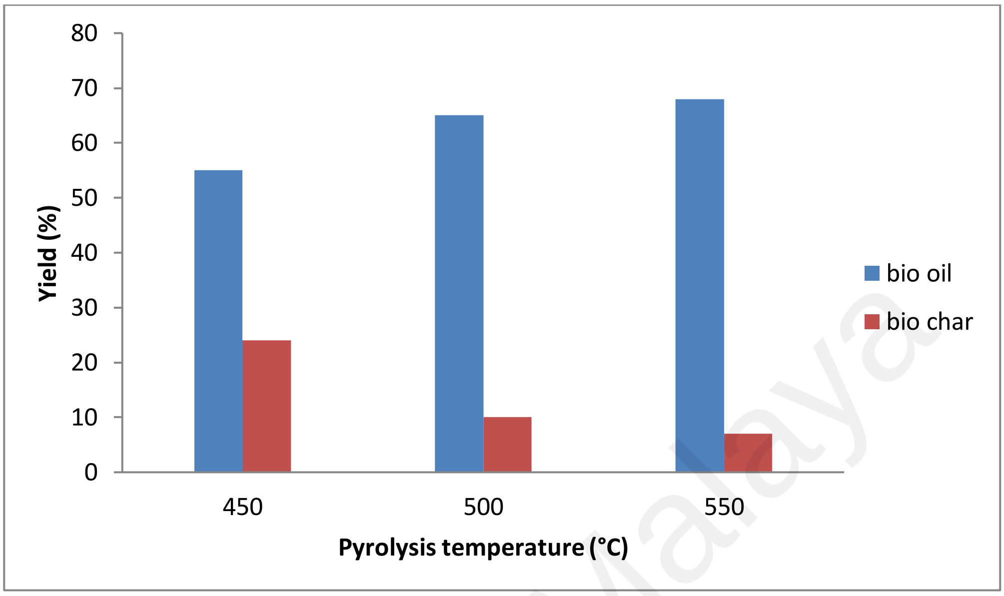

Figure 4.4: Effect of final temperature on pyrolysis products distribution.

It is found that no significant increase in bio-oil for pyrolysis temperature between 500 °C and 550 °C. This trend was also observed in other research groups for the pyrolysis temperature at 500 °C and 550 °C with no significant bio yield was found to increase in those temperatures with bio-char slightly reduced at a higher temperature. (Li et al., 2007; Takuya et al., 2012). They have studied using various types of organic wastes with different parameters in slow pyrolysis. Ben Hassen-Trabelsi and co-worker (2014) investigated the effect of experimental parameter on the quality and the distribution of waste animal fats pyrolytic bio oil. The group indicated that the temperature of 500 °C and heating rate of 5 °C/min were the most suitable condition to achieve high yield from 58% to 77.9%. Meanwhile, Wisniewski et al., (2010) studied waste fish pyrolytic bio oil by fast pyrolysis at 525 °C in continuous pilot plant reactor and found 72- 73 % bio-oil yield. Kim et al., (2009) investigated the pyrolysis characteristics in the pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. Poultry litter comprised relatively huge fractions of ash which are rich in potassium, phosphorus, calcium, and magnesium. The pyrolysis between 450 °C and 550 °C produced 15% to 30% viscous brown bio oil yield respectively. It is concluded that the temperature is one of the main points to increase the bio-oil yield and reduce the bio-char yield. As mentioned in the introduction, the purpose of the slow pyrolysis is to maximize the yield of bio-oil as well as to minimize the activation energy. Others who worked with similar triglyceride wastes concluded that by increasing the heating rate from 5 °C/min to 20 °C/min, the amount of residue decreases. The residue was about 34% with a heating rate of 5 °C/min while fewer residues (29%) form at a higher heating rate (20 °C/min). At the same time, the maximum velocity of weight loss changes also increased by increasing the heating temperature (1.8%/min to 10.95%/min) (Li et al., 2007). Thus, the pyrolysis temperature of 500 °C and the heating rate of 5 °C/ min are the efficient CSW decomposition parameters in this study.

Table 4.4 shows the major components of bio-oil products indicating the presence of theses compound families: fatty acid methyl ester (Palmitic acid methyl ester, Oleic acid, Dichloroacetic acid, 4-hexadecyl ester methyl ester), carboxylic acid (Propanoic acid, Acetic acid, Palmitic acid) ; alkanes (Tetradecane, Heptadecane) ; alkenes (1-Pentadecene, 8-Heptadecene) and cyclic hydrocarbons (Cyclohexane, Cyclopropanol) and alcohol (Pentadecyl alcohol, Hendecanoic alcohol).

Table 4.4: Compounds identified in the CSF pyrolytic bio-oil

No.	**Name of compound**	**Yield (%)**
1	Propanoic acid	0.14
2	Ethanoic acid	1.79
3	Hexadecanoic acid	2.60
4	Dodecyl alcoho	10.28
5	Hexadecanoic acid methyl ester	3.50
6	9-octadecenoic acid, methyl ester	3.03
7	Dichloroacetic acid, 4-hexadecyl ester	1.07
8	1,2-Benzenedicarboxylic acid, diisooctyl ester	10.18
9	8-Heptadecanol	0.28
10	Decanedioic acid, didecyl ester	0.87
11	n-Heptadecanol	3.13
12	1-Hexadecanol	3.59
13	Oleylalcohol, trifluoroacetate	6.11
14	Hendecanoic alcohol	6.91
15	Cyclohexane, octyl	0.90
16	Cyclohexanepropanol	2.30
17	Pentadecyl alcohol	3.82
18	Tetradecane	18.86
19	1-Pentadecene	12.29
20	8-Heptadecene	2.56
21	Heptadecane	3.00
22	2-Pentadecanone,6,10,14-trimethyl	2.80

Many other compounds (i.e.: ketone and aldehydes) were also found but in small amounts. Ben Hasen et al., (2014) studied the composition from pyrolysis of triglycerides material and they discovered that fatty materials pyrolysis produces several compounds including alkanes, alkenes, aromatics, alcohol, ketone and carboxylic acids. Liew et al., (2013) studied the pyrolysis of waste CSFs into potential hydrocarbon chemicals and bio-oils claimed that majority of the chemical composition of bio-oil consisted of aliphatics, carboxylic acid, alcohol, ketone, ester, aromatic, anhydride, ether and aldehyde.

The similar bio-oil composition that mostly consisted of carboxylic acids and alcohols was also observed in the pyrolysis of dissolved air flotation (DAF) skimming from chicken waste. It was reported that the preliminary triglycerides cracking produced carboxylic acid compounds and further thermal decomposition of triglycerides produced alcohol compounds via saturated oxygenated hydrocarbons decarbonylation (Smith et al, 2009). Huge amount of alkane and alkene were found was due to facile decarboxylation of carboxylic acid from CSW under high pyrolytic temperature (Maher, et al, 2007). Carboxylic acid such as 9-octadecenoic acid is compound of interest because this compound can be converted to alkyl esters (bio-oil) via esterification process

Meanwhile, molecular compositions of bio-oil from lignocellulosic biomass are relatively different because the chemical substance is related to the original polymer itself which is cellulose, hemicellulose and also lignin. So, phenolic compound (phenols, furan, and furfural) and fatty acids, alkanes, alkenes, amides and aldehydes were normally found (Piyarat et al., 2012). The GCMS result demonstrates the fraction of pyrolytic bio-oil displays a variety of chemical substances. Generally, acid value of bio-oil shows the existence of free fatty acid. The content of acidic components in the bio-oil should be reduced to avoid corrosion of combustion boilers and turbines. To counter this limitation, pyrolytic bio-oil has to be upgraded before it can be used in many applications such as conventional transport fuel (diesel, kerosene, methane or LPG).

4.3.2. Proposed decomposition pathway

The main product produced from slow pyrolysis in this research work can be categorized into solid and liquid phases. The proposed slow pyrolysis reaction pathway from chicken skin fat is described in Figure 4.5.

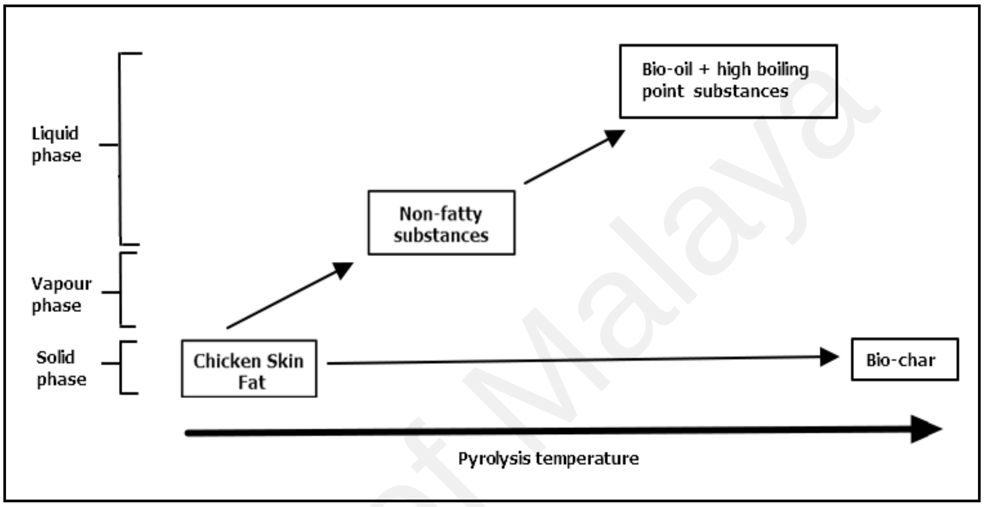

Figure 4.5: Proposed slow pyrolysis reaction of chicken skin fat.

The slow pyrolysis of chicken skin fat (CSF) was performed under nitrogen gas flow. Bio-char is the main solid product in slow pyrolysis typically contains high ash and low carbon contents (Ben Hassen et al., 2014). Bio-char is not evaporated and remains as solid even at high reaction temperature. At present time, bio-char is considerd as a pyrolysis waste since it is difficult to convert bio-char into other useful renewable energy.As the activation energy of CSF is relatively low compared to plant biomass, CSF is easily evaporated at around 150 °C to 250 °C during reaction and produced non-fatty substances in liquid phase upon condensation. The hydrocarbon cracking during pyrolysis is increasing with the increasing of pyrolysis temperature (Inguanzo et al., 2002). High boiling point of bio-oil and other boiling point substances produced from the cracking process are evaporated at higher temperature which is around 250 to 350 °C. It is assumed chicken skin fat pyrolysis also produced low volatile gasses such as

CO_2, CO, H_2 as part of the product in slow pyrolysis reaction based on the findings by Ben Hassen and co-workers.

4.4. ZSM-5 catalyst characterization

ZSM-5 catalyst used for esterification reaction in this research work were characterized using fourier transmission infra-red (FTIR), nitrogen physisorption technique, powder x-Ray diffraction (XRD) and thermal gravimetric analysis (TGA)/differential gravimetric analysis (DTG) analyses.

4.4.1. FTIR

The study of the vibration spectra by FTIR was carried out for both uncalcined and calcined ZSM-5. This technique can detect the chemical and structural changes that happened and the frequency bands will be the fingerprint band for both samples. Characterization by FTIR spectroscopy also can identify the functional groups of the sample.

In Figure 4.5 the FTIR absorption spectra for the ZSM-5 from 4000 to 400 cm^{-1} are presented. Both uncalcined and calcined ZSM-5 displayed intense band near 1630 cm^{-1} that present to the deformational vibrations of water molecules. The bands at 1216 cm^{-1} and 1063 cm^{-1} indicate the external and internal asymmetric stretching of the siloxane groups. The band at 792 cm^{-1} corresponds to the symmetric stretching of siloxane groups. The band at 540 cm^{-1} represents the internal flexion of tetrahedrons and the band at 438 cm^{-1} corresponds to presence of siliceous material (Li, 2003; Narayanan, 2014). The details about the FTIR characterization is described in Table 4.5

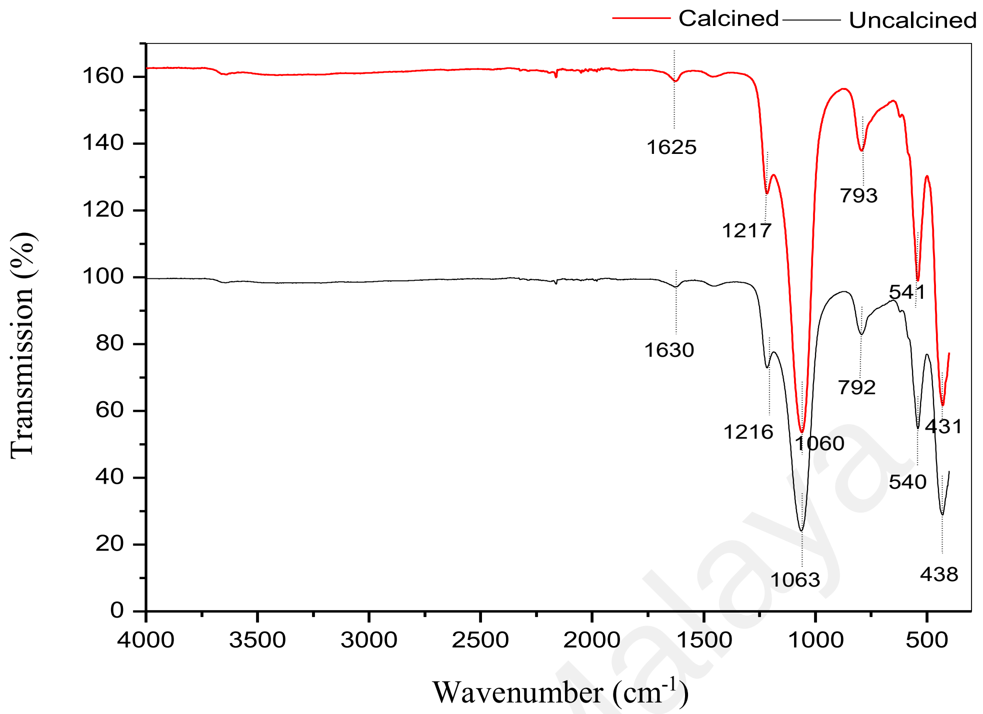

Figure 4.6: FTIR spectra of uncalcined and calcined ZSM-5

Table 4.5: FTIR adsorption band position and observations.

Wave number (cm^{-1})	**Observation**	
	Uncalcined ZSM-5	**Calcined ZSM-5**
1630	H-O-H bending motion of free water	Reduced band observed
1216, 1063	Asymmetric stretching of the siloxane group	Asymmetric stretching of the siloxane group with reduce band
792	Symmetric stretching of siloxane groups.	Symmetric stretching of siloxane groups with increase band
540	Internal flexion of the tetrahedrons	Internal flexion of the tetrahedrons with increase band
438	Siliceous material	Siliceous material

4.4.2. Nitrogen physisorption technique

The textural properties of ZSM-5 catalyst were determined using nitrogen physisorption technique. It is demonstrated that ZSM-5 used is classified as type IV isotherm. Figure 4.7 shows adsorption and desorption of nitrogen gas during nitrogen physisorption analysis. At low relative pressure (P/P0) a moderate amount of nitrogen becomes physisorbed until saturation. This increase is caused by multiple condensations of nitrogen inside the pores as filling of the pores takes place over a wide range of relative pressures (P/P0 = 0.15-0.95). At relative pressure, the nitrogen uptake by the sample increases further and desorption of nitrogen afterwards. It is demonstrated the ZSM-5 catalyst used is classified as type IV isotherm based on IUPAC nomenclature with the pore size around 2 to 50 nm or mesopore size range.

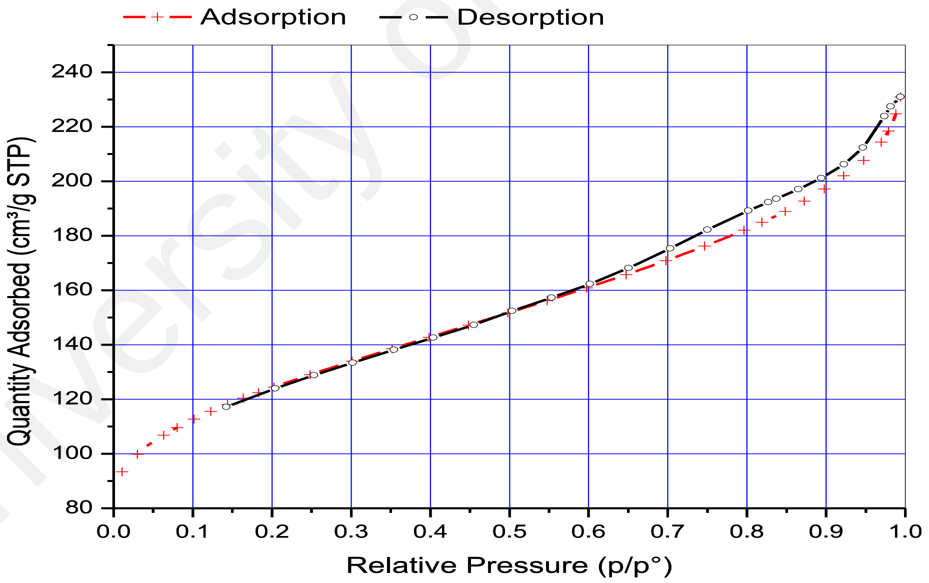

Figure 4.7: BET surface area and pore volume for ZSM-5.

The adsorption data in the range of P/P^0 0.15-0.95 are used for the calculation of the surface area of the material using Brunauer, Emmett and Teller (BET) method. From the isotherm curves, pore size distribution is calculated using Barret, Joyner, Halenda (BJH) method. The value of surface area, pore size and pore volume in Table 4.6.

Table 4.6: The surface area, pore size and pore volume of ZSM-5 catalyst

Textual Properties	Properties value
Surface Area	436.8 m^2/g
Pore size	4.4 nm
Pore volume	0.4 cm^3/g

The surface area supplied by the manufacturer, which is 425 m^2/g is not much different compared to the surface area testing performed in this research. The slight difference is observed possibly due to the different pretreatment temperature prior to nitrogen chemisorption test. The pore size of 4.4 nm showed in Figure 4.7 is within the range of mesopore size range.

4.4.3. Powder XRD analysis

ZSM-5 catalyst used in this work was calcined at 800 °C for 5 hours. Figure 4.8 shows the diffactograms of calcined and uncalacined of ZSM-5 catalyst. Both calcined and uncalcined diffractograms shows the similar patterns exhibiting the characteristic diffraction peaks at 2ϴ around 8.05 °, 8.92 °, 23.21 °, 23.99 ° and 24.46 ° which are indexed to the MFI topology (ICDD 42-0024). This MFI topology is usually the signature of ZSM-5 in powder XRD analysis. However, calcined ZSM-5 has high intensity peak compared to uncalcined ZSM-5. This observation shows that calcination can increase the crystallinity of ZSM-5 catalyst.

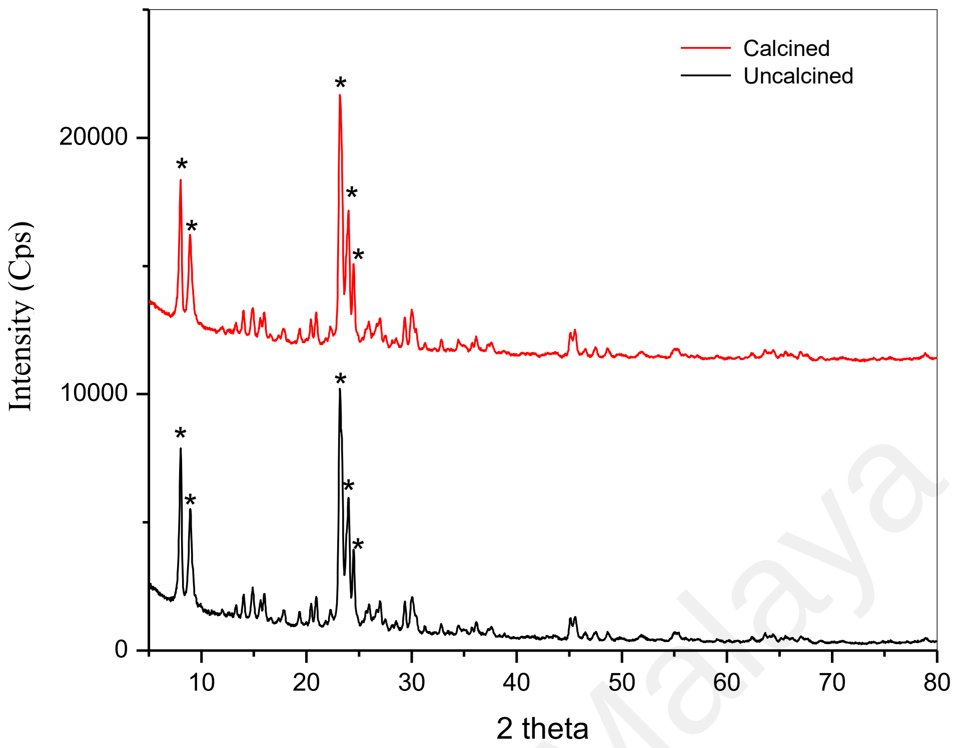

Figure 4.8: X-ray diffraction pattern of uncalcined and calcined ZSM-5.

Widayat and Annisa (2017) studied the production process of ZSM-5 and the effect of time and temperature on the crystallinity and the morphology of ZSM-5. They claimed that by increasing the temperature, the cryctallinity would improve and the best calcination parameter was 800 °C at and hold for 5 hours.

4.4.4. TGA/DTG analysis

The ZSM-5 thermal degradation can affect the surface properties, crystal lattice and further heating can break down the lattice structure. Figure 4.9 shows the TGA analysis of zeolite ZSM-5 catalyst.

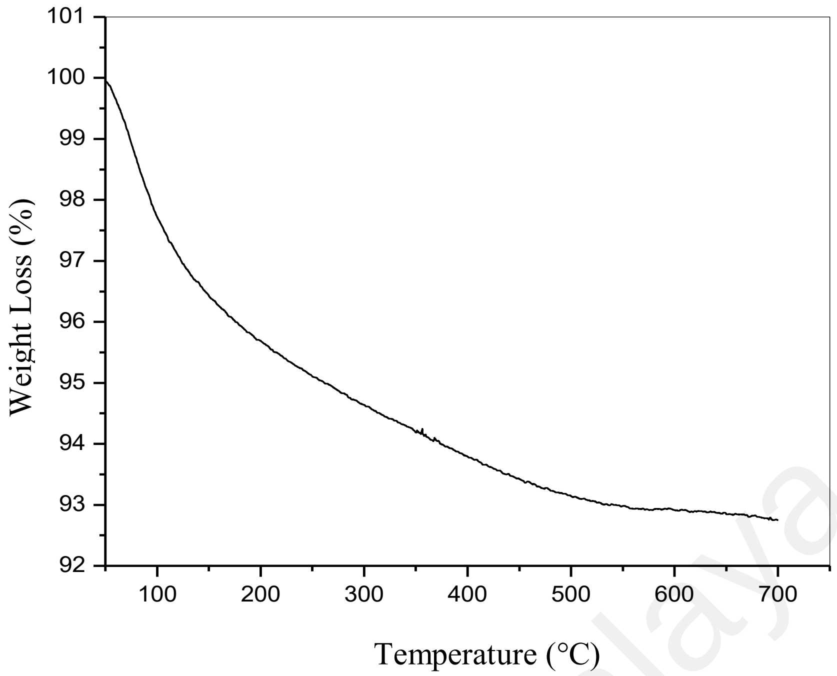

Figure 4.9: Thermal gravimetric analysis of ZSM-5 catalyst.

The catalyst weight loss was reduced significantly from 50 °C to 700 °C due to catalyst degradation. It is suggested ZSM-5 is very sensitive to the temperature as crystal lattice collapse easily after certain temperature. In order to observe the thermal degradation in detail, DTG graph has been prepared and depicted in Figure 4.10.

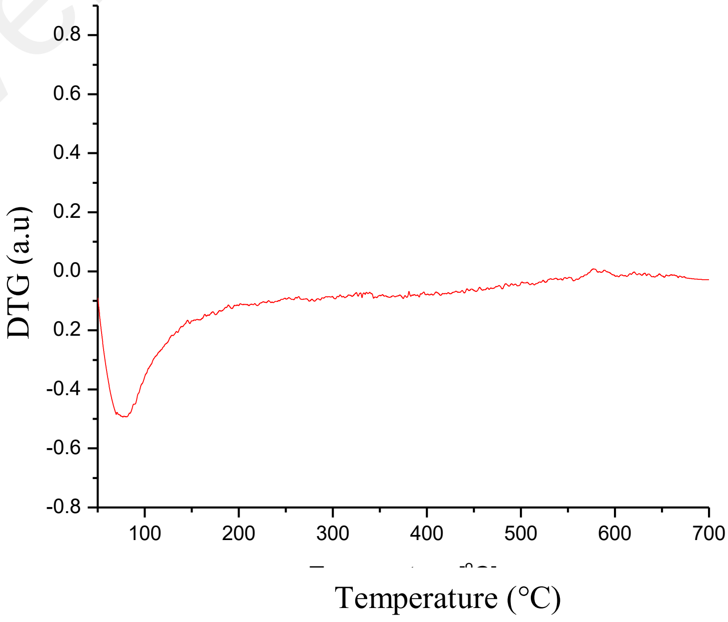

Figure 4.10: Differential gravimetric analysis of ZSM-5.

Figure 4.10 shows the exponential degradation of ZSM-5 started at 70 °C, an exponential degradation is observed because of the degradation of tetrapropyl ammonium hidroxyde (TPAOH) species that are forming the main component of ZSM-5 (Gabelica et al., 1984) The degradation reduces slowly from 150 °C until 200 °C before the weight loss of zeolite ZSM-5 is constant until the end of thermal analysis.

4.5. Crude pyrolysis bio-oil upgrading

The crude bio-oil produced from this research work was upgraded using esterification reaction using methanol and zeolite ZSM-5 catalyst using different process condition of temperature, reaction time, methanol to oil ratio and catalyst loading. The crude bio –oil were tested using 7 sets of proses condition in which classified into CSF01, CSF02, CSF03, CSF04, CSF05, CSF06, and CSF07. This product from esterification was compared with the crude oil from CFS pyrolysis and classified as CFS raw (CFSR). Crude bio-oil is a complex mixture that contain great amount of large size molecules of all oxygenated organics such as esters, ethers, aldehyde, ketones, organic acids and alcohols. Table 4.7 shows the pyrolysis process condition and Table 4.8 below shows the process condition for each sample ID.

Table 4.7: Pyrolysis process condition for CSFR.

Sample	**Reaction temperature (°C)**	**Heating rate (°C /min)**	**Reaction time (hour)**
CSFR	500	5	1

Table 4.8: Esterification process condition for CSF.

Sample	**Methanol – to-oil ratio (wt.% of oil)**	**Reaction temperature (°C)**	**Reaction time (hour)**	**Catalyst (wt.% of oil)**
CSF01	2: 1	80	1	0
CSF02	2: 1	80	2	0
CSF03	2: 1	80	3	0
CSF04	2: 1	70	3	0
CSF05	2: 1	60	3	0
CSF06	2: 1	70	3	2
CSF07	2: 1	70	3	4

The percentage area (%) of CSF was analyzed for relative contents of the compounds present in the CSF. Methanol to oil ratio were fixed from CSF01 to CSF08. The reaction temperature in the esterification was varied from 60 °C to 80 °C whereas reaction time is varied from 1 to 3 hours. No zeolite ZSM-5 catalysts were used in CSF01 to CSF05 whereas the catalyst loading was used in CSF06 (2 %) and CSF07 (4%). The bio-oil was calculated based from the amount of esters and acid compounds accumulated in the product. This method was used based from the work performed by Aziz et al. (2017) as the research group produced crude bio-oil from microwave pyrolysis prior to conversion of acid compound to ester compound via esterification process. The actual compounds obtained from this research work of upgraded bio-oil are enclosed in the Appendix A.

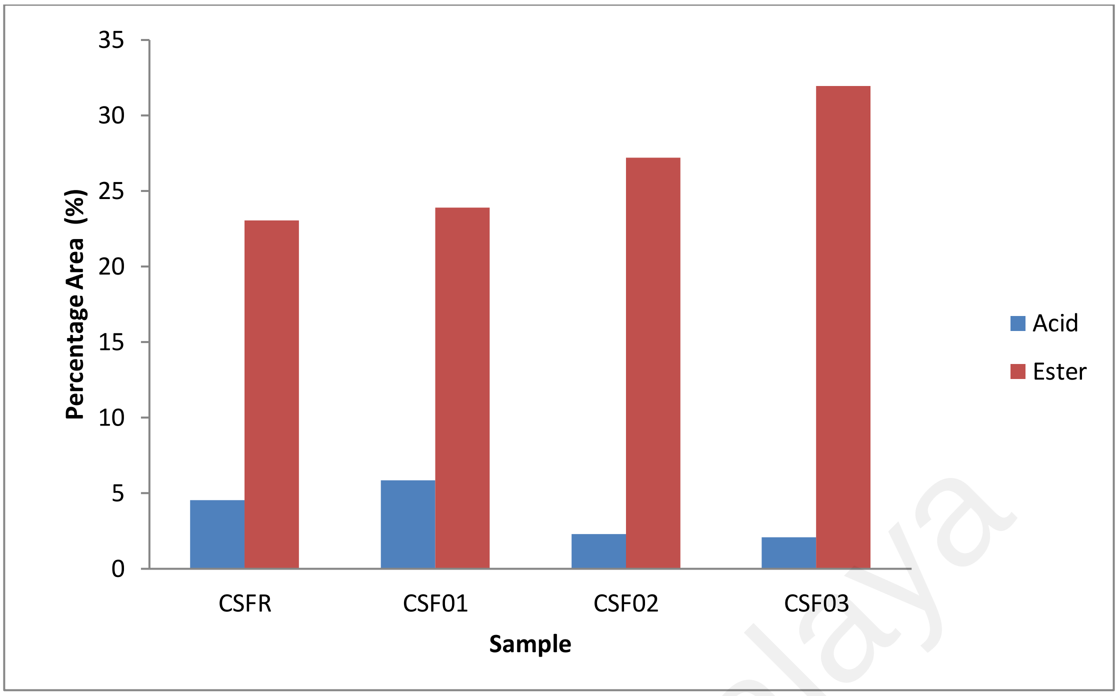

Figure 4.11: Effect of esterification with varying reaction time.

Figure 4.11 shows the comparison between crude bio-oil (CSFR) and esterification products obtained with respect to acid and esters compounds. The pyrolysis experiment was performed for sample CSFR at 500 °C at constant heating rate (5 °C/min) for 1 hour produced 23.0% and 4.5% compound of esters and acids respectively. The esterification of CSF01 to CSF3 was compared according to the duration of esterification reaction. The effect of reaction time was investigated by studying esterification of the bio-oil and methanol under the following conditions: 2:1 ratio of methanol to bio-oil which is 6 g of methanol to 3 g of bio oil in 2.0 wt. % of solid zeolite catalyst (ZSM-5), reaction temperature 80 °C with 1, 2 and 3 hours. The ratio of methanol to bio-oil is based on the weight. Figure 4.11 shows longer reaction time after 2 hours has increased esterification conversion for the acid and esters compounds in upgraded bio-oil. The ester content was increased sharply from 23.7 % to 27.2% after 2 hours and started to attain a constant value which is 31.9% of ester content at 3 hours. The acid content also reduced from 5.85 % at 1 hour to 2.07 % at 3 hour. Piyarat et al. (2012) studied the effect of reaction time on the catalytic esterification of bio-oil and reported the increasing of reaction time have increased esterification conversion to esters compounds for the condition of 3.25:1 mole ratio of methanol to carboxylic acids in oil, 5 wt.% of Amberlyst15 and reaction temperature of 60 °C. It was further claimed in achieving conversion of 70.6% at 12 hours.

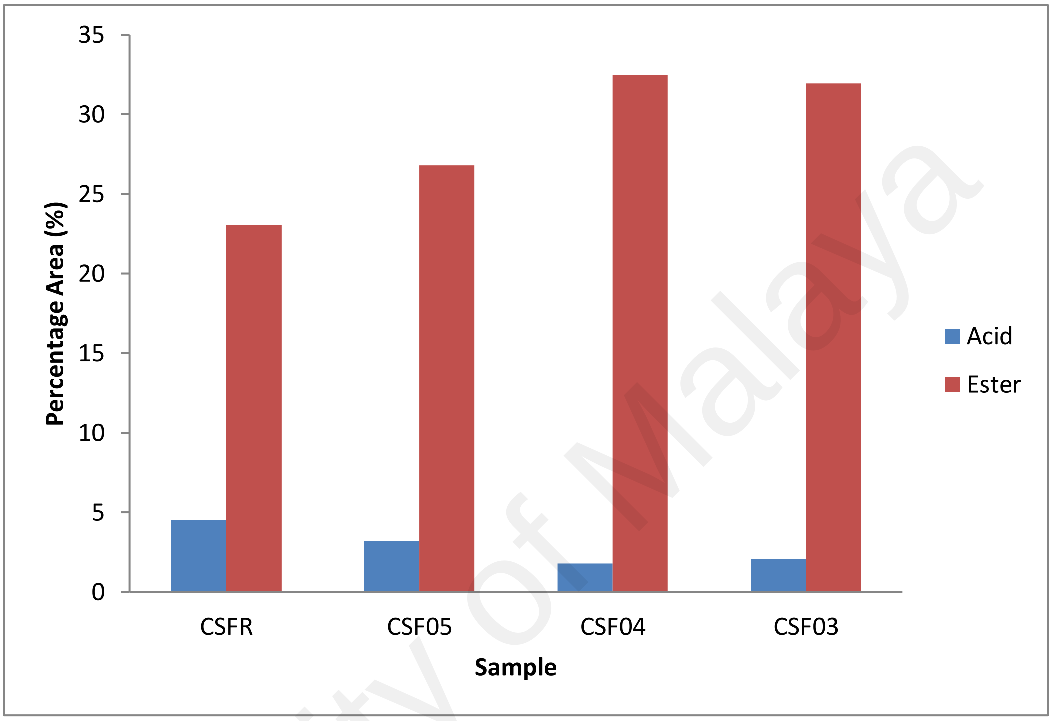

Figure 4.12: Effect of esterification with varying reaction temperature.

The esterification reaction was performed by varying reaction temperature at the process condition of 2:1 ratio of methanol to bio-oil, reaction time of 3 hours and reaction temperature from 60 °C (CSF05), 70 °C (CSF04) and 80 °C (CSF03). Figure 4.12 indicates the ester compound increased from 26.8 % at 60 °C to 31.5 % at 70 °C. When temperature reached 80 °C, the ester compounds shows constant value at 31.9 % with no increment of acid compounds compared to esterification temperature at 70 °C. This result shows that esterification reached maximum reaction temperature around 60°C and 70 °C. Prinsen et al., (2018) studied about catalytic activity of ZSM-5 for conversion of palmitic acid to methyl palmitate and they concluded 70 °C and 3 hours are sufficient condition for esterification.

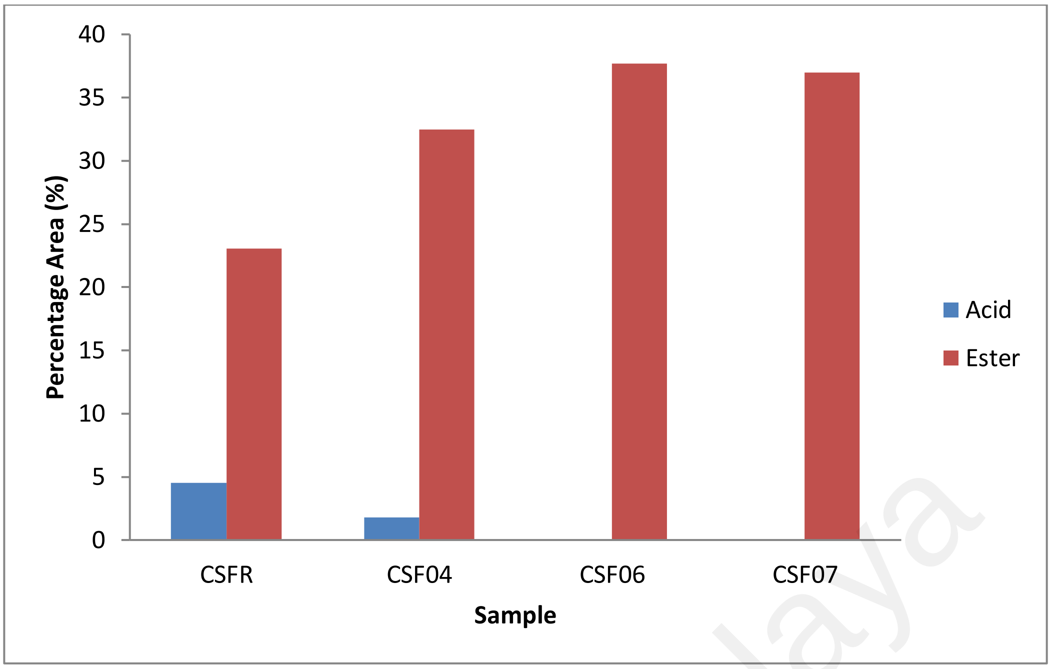

Figure 4.13: Effect of esterification with varying catalyst loading.

The esterification reaction was performed by varying catalyst loading with the process conditions of 2:1 ratio of methanol to bio-oil, reaction temperature of 70 °C and reaction time of 3 hours with catalyst loading at CSF04 (no catalyst loading), CFS06 (2% weight loading) and CSF07 (4% weight loading). Figure 4.13 shows the esterification reaction without catalyst shows 32.5% of ester yield. Nevertheless, increasing catalyst loading to 2% shows the increment of ester compound rise to 37% with no of acid yield is observed. However, no increment of ester compound shows when increasing the catalyst loading to 4%. The presence of mesoporous networks in ZSM-5 gives the benefits to improve the catalytic performances in terms of catalytic activity, desired product yield, and catalyst stability/reusability, due to the improved accessibility to active sites (Kamonlatth et al., 2017). Krishnamurthy et al., (2016) observed ZSM-5 can significantly improve catalytic performances of the esterification of benzyl alcohol and hexanoic acid due to its porosity. Wei et al., (2015) studied the effect of reaction time on ester yield and conversion and reported the adequate processing temperature is less than 100 °C with 2% of ZSM-5 loading. Catalyst loading of 2 wt. % was chosen as the optimized catalyst loading for extracting bio-oil.

CHAPTER 5: CONCLUSION

5.1. Conclusion

Chicken skin fat (CSF) can easily convert to crude bio-oil because fatty acids and non-fatty acids organic compounds in CSF were degraded at lower temperature compared to typical plant biomass waste because the plant biomass is largely consisted of cellulose, hemicellulose and lignin components in which required higher thermal degradation. In this study, a complete degradation kinetic study of CSF via TGA/DTG using model-free isoconversional methods has been presented. DTG pattern showed that the maximum rates of conversion for all heating rates demonstrated similar trend with the main thermal degradation occurred around 420 to 440 °C. After 60% conversion, the activation energies decreased because the entire element of CSF was completely decomposed. Despite similarity maximum rates of conversion for all heating rates (5 °C/min, 10 °C/min and 15 °C/min), the apparent activation energy at the heating rate of 5 °C/ min was much lower than other heating rates. CSF decomposition with low activation energy required low temperature and shorter degradation time to produce bio-oil products. Based from the findings from TGA/DTG kinetic study, this research work used the optimum process condition of temperature at 500 °C and heating rate of 5 °C/ min for the degradation and devolution of CSF to bio-oil in slow pyrolysis reaction.

The slow pyrolysis products were analyzed using GCMS analysis. It was found CSF bio-oils have large variety of organic compounds (alkanes, alkenes, cyclic hydrocarbon, aldehydes, alcohol, carboxylic acid, ester) indicating that this compounds have the potential to be used in industry as a special chemicals and feedstock for intermediate chemicals. Nevertheless, these bio-oils and organic compounds have to be upgraded to improve its physical and chemical properties.

The crude bio-oil from slow pyrolysis reaction was further upgraded in esterification reaction using zeolite ZSM-5 catalyst. The ZSM-5 catalyst is an acid catalyst with MFI topology has mesopores with surface area and pore volume of 436.8 m^2/g and 0.4 cm^3/g respectively. It was found catalytic esterification using ZSM-5 increased the yield of ester compounds. In this esterification reaction, increasing reaction time and reaction temperature had increased the bio-oil yield significantly. The application of 2 wt.% of ZSM-5 in esterification process condition of 2:1 ratio of methanol to bio-oil, temperature of 70 °C and reaction time of 3 hours improved the ester compound yield up to 32.5% with no acid yield was observed because the remaining acid compounds in bio-oil were converted to esters.

5.1. Research outlook

This purified bio-oil in this research work is not ready to be used for diesel engine fuel as this bio-oil has to be further purified to remove other impurities (such as alkanes, alkenes, aromatics, cyclic hydrocarbons, alcohols) and the water content has to be reduced significantly. Based on this research work, further developments are recommended as follows:

I. The fractionation process of bio-oil to produce bio-fuel (ester compounds) and special chemicals.
II. Bio-oil produced from fractionation is to be tested for standard physical ASTM testing prior to fossil fuel blending and conventional diesel engine testing.
III. Bio-char produced from this work has to be analyzed for the possible agriculture application such as fertilizer, soil filler and water retention in farming.

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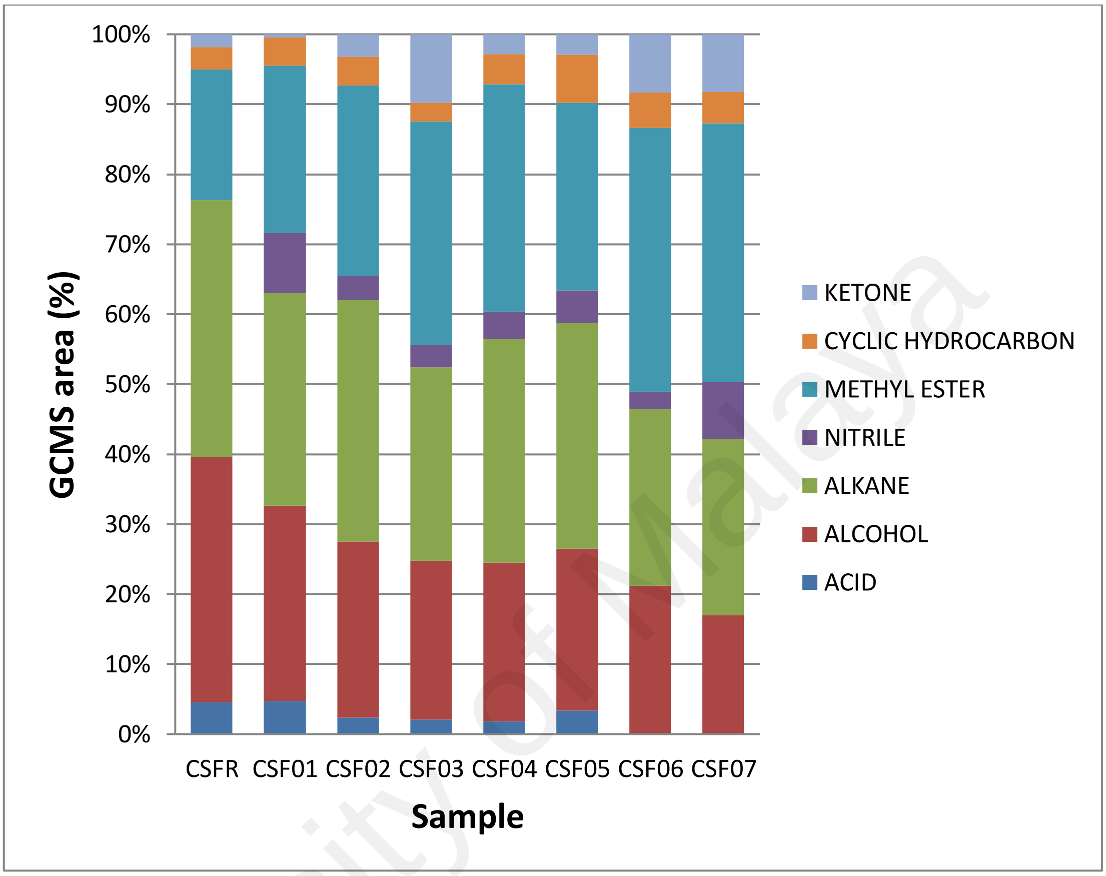
APPENDIX A



Compounds identified in the CSF pyrolytic bio-oil.