OPTIMIZED BIODIESEL PRODUCTION BY USING ULTRASOUND ASSISTED TRANSESTERIFICATION

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FACULTY OF ENGINEERING
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ABSTRACT

In order to combat the world crisis of consuming fossil fuel energy, biodiesel has been an alternative to fossil fuel as the clean burning fuel. Despite the effort to make a more environmentally friendly biofuel, there are challenges that comes with it. The current commercial biodiesel in Malaysia utilizes only palm oil as the feedstock in which the feedstock is used in food industry as well, so there is a stiff competition in obtaining it. Waste cooking oil and jatropha oil are added to the palm oil feedstock to lessen the use of palm oil. Since jatropha oil is a promising aspect in Malaysia and also a nonedible oil there will not be a competition from the food industry. Moreover, to fully utilize the waste cooking oil from being disposed and gone to waste, the three feedstocks are being mixed together as a feedstock. The feedstock will be converted into biodiesel through an ultrasonic assisted transesterification. Due to its efficiency, time and energy saving method compared to the conventional method. The physicochemical properties of viscosity, density, acid value, higher heating value, flash point, oxidation stability, and fatty acid methyl ester content of the biodiesel were being studied and compared to commercial biodiesel and biodiesel standard EN14214. The results proved that compared to the palm oil biodiesl, the density at 15°C of WC50J15P35 biodiesel has improved by 0.9%, the acid value improved by 13.6%, the higher heating value improved by 0.3%, the oxidation stability improved by 24%, and lastly, the flash point has improved by 1.6%. Meanwhile the obtained kinematic viscosity at 40°C is 4.504 mm^2/s, The FFA content is 0.22, and the percentage yield is 91%.

ABSTRAK

Bagi menangani krisis dunia dalam penggunaan tenaga bahan bakar fosil, biodiesel telah menjadi alternatif kepada bahan bakar fosil sebagai bahan bakar yang bersih. Walaupun usaha untuk membuat bahan bakar yang lebih mesra alam, terdapat beberapa cabaran yang datang bersama usaha tersebut. Biodiesel komersial semasa di Malaysia dibuat hanya menggunakan minyak sawit sebagai bahan dasar yang dimana minyak sawit juga digunakan didalam sektor pemakanan juga, jadi disitu terdapat satu persaingan yang sengit untuk mendapatkan minyak sawit. Buangan minyak masak dan minyak jatropha telah ditambah ke dalam minyak sawit sebagai bahan dasar untuk mengurangkan penggunaan minyak sawit. Minyak jatropha adalah satu aspek yang menjanjikan di Malaysia dan juga minyak yang tidak boleh dimakan, tidak akan ada persaingan dari industri pemakanan. Selain itu, untuk menggunakan buangan minyak masak sepenuhnya dari dibuang begitu sahaja, ketiga-tiga bahan dasar telah dicampurkan untuk menjadi satu bahan dasar. Bahan dasar tersebut ditukar kepada biodiesel melalui proses transesterifikasi yang dibantu ultrasound. Kaedah tersebut dipilih oleh kerana kecekapan, kaedah penjimatan masa dan tenaga berbanding dengan kaedah konvensional. Sifat fizikokimia kelikatan, ketumpatan, nilai asid, nilai pemanasan yang lebih tinggi, titik nyala, kestabilan pengoksidaan, dan kandungan metil ester asid lemak biodiesel sedang dikaji dan dibandingkan dengan standard biodiesel dan biodiesel komersial EN14214. Hasilnya, membuktikan bahawa perbandingan dengan biodiesel dari minyak sawit, ketumpatan pada 15°C biodiesel WC50J15P35 telah meningkat sebanyak 0.9%, nilai asid meningkat sebanyak 13.6%, nilai pemanasan yang lebih tinggi meningkat 0.3%, kestabilan pengoksidaan meningkat sebanyak 24%, dan terakhir, kilat mata telah meningkat sebanyak 1.6%. Sementara itu, nilai yang diperoleh, kelikatan kinematik pada suhu 40°C ialah 4.504mm^2/s, kandungan FFA ialah 0.22, dan peratus yang diperoleh adalah 91%.

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LIST OF SYMBOLS AND ABBREVIATIONS

CO2 : Carbon dioxide

FFA : Free fatty acid

KOH : Potassium hydroxide

BSFC : Brake specific fuel consumption

LHV : Low heating value

EU : European Union

SOx : Sulphur oxide

WCO : Waste cooking oil

GHG : Green house gasses

NaOH : Sodium hydroxide

CaO : Calcium oxide

FAME : Fatty acid methyl ester

PLPO : Processed liquid palm oil

PD : Petroleum diesel

COME : Cottonseed oil methyl ester

PO : Palm oil

JO : Jatropha Oil

CHAPTER 1: INTRODUCTION

1.1 Research Background

Since way back in the late 18th century after the industrial revolution, energy has been a vital part for maintaining economic growth and the source of living for humankind. However, the main source for energy in the world has been derived from fossil energy. As shown in Figure 1.1, the world's primary energy consumption as of 2019, oil is the highest form of energy consumed. Renewable energy is the least consumed. The effect from this is that the earth is currently facing double crisis, one is energy crisis, and another is pollution to the environment. Whilst the reduction of unsustainable sources such as carbon fuels for power generation and transportation fuel has causes a huge number of harmful emissions and hazardous substance exposed the atmosphere, such as carbon monoxide, carbon dioxide, nitrogen oxide, sulphur oxide, and unburned hydrocarbon.

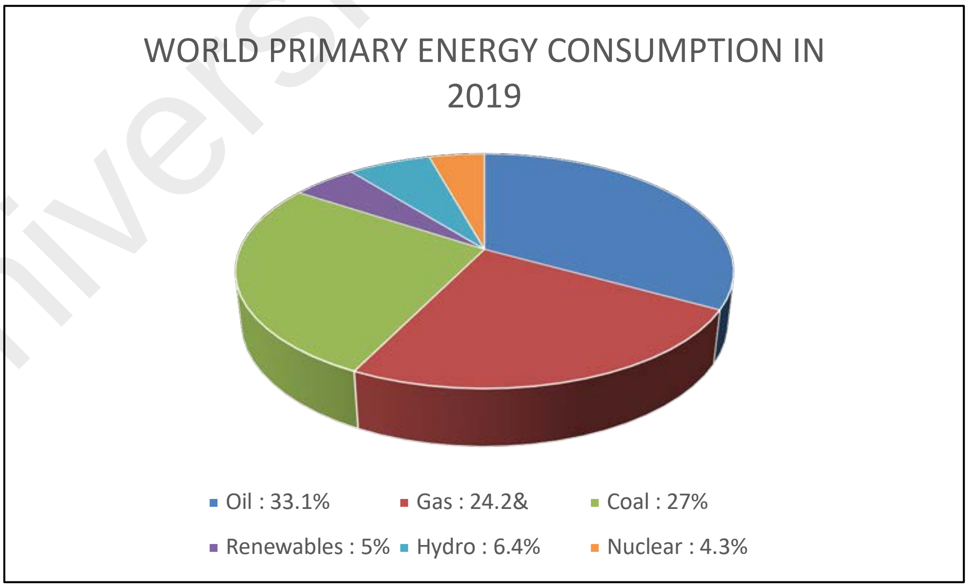

Figure 1.1: Statistical Review of World Energy

(Looney, 2020)

To combat this situation, a suitable alternative source of energy which is known as biofuel is the center of attention to researches around the globe where many ongoing experiments are being conducted in order to create a high efficiency biofuel with the intention to replace or substitute the declining source of fossil fuel completely. Thus, biofuel is the answer to the complexities faced by almost every country which causes global warming and also to be able to support the future energy demand.

Biodiesel is currently being produced from various types of feedstocks include animal fats, vegetable oils, and seeds. It is produced by a process called transesterification. This process is widely known and happen by turning triglycerides into fatty acid alkyl ester with a catalyst. Since biodiesel is made from such feedstocks, it is renewable and biodegradable. Biodiesel also contains very little sulfur, polycyclic aromatic hydrocarbons, and metals (Vasudevan & Briggs, 2008).

Due to the increasing use of fossil fuels in automobiles and industrial sectors over the years, the world faced severe problems like environmental pollution, ozone layer depletion, global warming. Despite that, the biodiesel prospect has attracted the world as the alternative fuel due to its good oxidation characteristics and lubricating nature. Referring to Figure 1.2, in 2020, it was estimated the consumption of biodiesel is 846 million litres. Indicating a slight drop compared to previous year. Although the majority of the biodiesel usage is in the transportation sector, the government intended to use it in industrial sector to heat boilers and generate electricity.

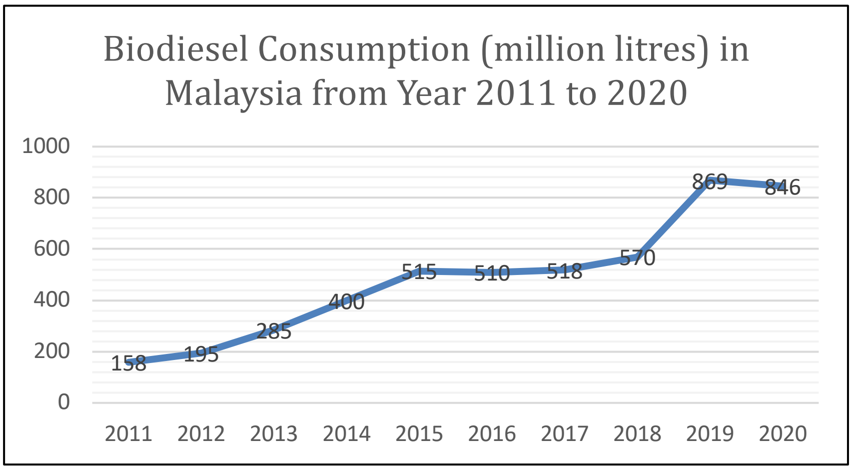

Figure 1.2: Biodiesel Consumption in Malaysia from Year 2011 to 2020

(Wahab, 2021)

There are a lot of advantage of using biodiesel as an alternative fuel. One of it being easy to use, which requires no vehicle modification or any fueling equipment needed. Apart from that, the proven power generation, performance and cost effective made it a very useful fuel. Also, the effect on environment is tremendous as it helps in reducing the global warming by lowering the emission of CO_2. Lastly, compared to petroleum, biodiesel is less hazardous and easy to keep, it reduces the use of foreign oils and helps the community by keeping energy dollars at home (Firoz, 2017).

1.2 Problem Statement

A different blend of feedstocks will produce a different quality of biodiesel, so when blending the feedstocks, the qualities that the biodiesel will produce must be considered. The variant feedstock can be chosen from refined vegetable oils to rendered animal fats. Refined vegetable oils are divided into two groups, one is edible vegetable oil namely corn, soybean, sunflower and palm oils, while the other one is non-edible vegetable oils namely Jatropha curcas, Sterculia foetida, and Calophyllum inophyllum oils. Recently, algae have become another source of feedstock.

Among all these feedstocks mentioned above, recycled cooking oil or also known as waste cooking oil are the most attractive due to the sustainability, availability, and its inexpensiveness for biodiesel production. Also, by using waste cooking oil, the amount of waste cooking oil disposal into the landfill will be reduced because these oils can be recycled into a cleaner and more useful product which is biodiesel.

The fatty acid of unsaturated and saturated composition in biodiesel played a major role to the effects of fuel physicochemical properties such as the density, kinematic viscosity, and higher heating value, to name a few. In a study, by blending feedstocks of tung, coconut, and palm, it was reported that the blended samples showcased improvement in physicochemical properties such as saturation level, oxidation stability, and iodine value (Chen, Chen, & Luo, 2012).

One of the ways to decrease the biodiesel production costs is to utilize inedible inexpensive feedstock with high content of fatty acids. Contrasting to edible oil as feedstock such as Palm oil, the demand is high in food industry. That makes it less ideal. The major factor of providing a competitive biofuel in the market will be determined by the sustainability and availability of the inexpensive and the sufficient supplies of it. The fact that Jatropha curcas has no competition in food uses makes it an ideal biodiesel feedstock. It grows in tropical and subtropical climates across the rising countries including Malaysia.

Another matter is that the conventional transesterification process has some disadvantages. The biodiesel produced from the conventional transesterification have poor storage stability and cold flow properties. Also, it requires different steps such as oil extraction, purification, and transesterification which all increases the total cost. The time required for the process is long and high catalyst consumption. To commercialize biodiesel, conventional transesterification is non practical due to high cost and the process and operating conditions needed to be improved.

1.3 Objectives of Research

The main objective of this research is to study the improvement that can be provided by the stated combination mixture into a biodiesel. The more specific objectives are:

1. To produce ternary biodiesel via ultrasound assisted transesterification
2. To investigate the physicochemical properties of the produced ternary biodiesel

1.4 Scope of Research

This thesis focuses on the optimized biodiesel production from waste cooking oil, Jatropha curcas oil, and Palm oil by using ultrasound assisted reactor. This study mainly focused on the sample WC50J15P35 only. The characteristics of biodiesel produced were studied. The characteristics that were studied are kinematic viscosity at 40°C, density at 15°C, acid value, FFA content, higher heating value, oxidation stability at 110°C, flash point, and gas chromatography.

Other than that, the method used was ultrasound assisted transesterification with KOH as the catalyst. The research was done in a certain period of time which was within 28 weeks. There were limits in terms of time and experiments but the data in the results is enough to compare with the published literature.

CHAPTER 2: LITERATURE REVIEW

In this chapter, the literature related to the production of biodiesel has been reviewed. The description of different kind of feedstocks used to produce biodiesel were discussed and also the processes involved which are the pre-treatment, transesterification, and post treatment of biodiesel conversion process. Other than that, the comparison between conventional equipment and advanced equipment that can be used to produce biodiesel were reviewed as well.

2.1 Introduction

In today's world of developing countries, the population, industry, and civilization have demanded more the consumption of clean fresh air and energy. It has always been fossil fuel as the main source, and due to that there is a lot of disadvantages of when consuming that type of energy. The release of harmful gasses by the fuel when burning making it unsustainable and unrenewable. As a result, there is a lot research has been conducted on this matter to overcome this problem which leads to the revelation of biodiesel. For more than ten years, the production of biodiesel has increased as the solution to this problem (Mahlia et al., 2020).

Asia is headlining in energy consumption with 41% and up to 2040 among other countries around the world. This matter is increasingly concerning especially in the transportation sector because it relates with the environmental pollution. Most of the transport consumes fossil fuels that releases harmful gasses to the air. Reaching the year 2030 the transportation industry would contribute half of greenhouse gas emissions (Mujtaba, Masjuki, Kalam, Ong, et al., 2020). To counter this critical issue regarding the environmental pollution, biodiesel will be an alternative to fossil fuels.

2.2 Biodiesel As an Alternative to Fossil Fuel

There is a lot of pros of fuel properties in using clean fuel as compared to fossil fuels. Those advantages include the huge cetane number, smooth lubricant, decrease harmful gasses released, flash point, and the inexpensiveness of getting it. While in contrast, animal fats are unhealthy and can be dangerous to human health, thus making it more ideal to be utilized in different sectors such as fuel compared to the food and beverage industry. But due to the properties of animal fats that are solid and very viscous at room temperature, it limits the use as fuel in diesel engines. It causes low pressure, incomplete combustion, low vapor-air mixture, low atomization, and accumulation of harmful substances in the engine. To improve these properties, there are many processes that can be done like micro-emulsion, dilution, pyrolysis, and transesterification methods are used to improve the properties of animal fats, but the most widely used among those processes is the transesterification method.

The effects of biodiesel in engine performance and exhaust emissions were examined, and a decrease in engine torque and an increase in BSFC value were observed by adding biodiesel into diesel fuel (Simsek & Uslu, 2020). Unlike the usual diesel, biodiesel has an enough amount of oxygen and less amount of carbon, with the similar hydrogen content of a usual diesel. Due to that, the LHV is usually lower, the stoichiometric air-to-fuel ratio has a typical value of 12.5 and the combustion is generally improved. Also, biodiesel has a very little amount of phosphorus and sulphur, thus SOx emissions are almost negligible and the temperature of the flue gases at the stack can be considerably reduced, since acid condensation is not a problem of a huge issue (Carraretto, Macor, Mirandola, Stoppato, & Tonon, 2004).

Even though diesel is convenience in a daily life, it releases unpleasant odour, in which contain a lot kind of toxic air pollutants including hydrocarbons, carbon monoxide, nitrogen oxides and smoke. To make the air quality better, diesel engines are subjected to severe emission regulations. To control emissions, the factors that are important are the octane number, aromatic content and type, sulphur content, distillation temperature, and density of the fuel. Neat biodiesel fuel contains 10.5% oxygen content which significantly reduces the exhaust smoke emission density at high loads and speeds in direct injection diesel engine (Choi & Oh, 2006).

In early 2019, government of Malaysia introduced a ten percent blend mandate (B10) which saw the production of biodiesel projected at 1.69 billion liters and the demand from the EU and China for low-cost palm oil biodiesel as the supporting factor. As of now, Malaysia government intend to introduce a B20 mandate in 2020. Although the exact plan is not yet finalized but consultation with stakeholders is ongoing and a special committee to monitor the transition to a B20 mandate has been formed.

With the introduction of B10 mandate, the total calendar year 2019 consumption of biodiesel is forecast at 940 million liters, up to 42% compared to previous year. With no year-over-year increase in the size of the diesel pool, the usage increase is entirely due to the blend rate hike. From the first six months of 2019, the exports reached 367 million liters, about 35% higher than 271 million liters recorded during the same period of 2018. Thus, based on this pattern and expectation of perpetual demand especially from EU and China, the total exports of 2019 are forecast to reach 750 million liters (Wahab & Verzani, 2019).

2.3 Feedstock for Biodiesel

Biodiesel is a renewable fuel made from different kinds of feedstocks which includes vegetable oils, animal fats, and recycled cooking oils. Different feedstocks produce certain biodiesel with distinct qualities. The biodiesel then is often blended with petroleum diesel in percentage ranging from 5% to 20% biodiesel (B5 – B20). Biodiesel has high potential as the main energy source in the future, as a fuel substitution for petroleum-derived diesel and can be used directly in existing diesel engine without any modifications.

As of now, 95 out of 100 percent of the globe biofuel is made originally from edible oil that is easily available in a large scale from the agricultural industry. However, without a proper planning of the continuous and large-scale production of biodiesel from edible oil it will cause a negative impact to the world. The food supply will deplete and bring imbalance to the economy. As a solution to this problem, the use of non-edible oil or waste edible oil will help to bring balance to the problem situation.

The important measure to take to the sustainability of a feedstock for biodiesel production is the oil yield from the crop itself. In biodiesel production industry, oil crop with larger oil yield is more effective and preferable because it can reduce the production cost. Generally, the cost of raw materials accounts about 70 to 80 percent of the total production cost of biodiesel (Gui, Lee, & Bhatia, 2008).

Apart from that, another criterion in selecting oil feedstock in producing biodiesel is the composition and properties of the oil itself.

2.3.1 Waste Cooking Oil

Biodiesel has now considered as one of the main alternative fuel to fossil-based fuel for diesel engines. While manufacturing biodiesel from plant oil is relatively easy and possesses many environment benefits, there are many feedstocks can be chosen from and one of it being waste cooking oil. What makes biodiesel all the more attractive is that it can be derived from waste cooking oil in large quantities in public eateries. Cooking oil is plant, animal, or synthetic fat.

The amount of WCO produced annually by any region is very huge. Thus, making the disposal of WCO problematic due to the ways of exposing may contaminate environmental water. Even though a lot of developed countries have set policies that penalize the disposal of waste oil through the water drainage, still there are being violated. The production of biodiesel from WCO is one of the better ways to utilize it efficiently and economically but still the biodiesel obtained from WCO may not replace diesel fuel completely. It can partly decrease the dependency on petroleum-based fuel.

The thermal performance of esters of WCO closely resemble the performance of esters of fresh oil. At higher load operation of esters of WCO fueled engine suffers nearly 2% brake thermal efficiency loss. And also the hydrocarbon emissions of WCO-biodiesel fuel were observed to be approximately 35% lower than baseline diesel operation (Sudhir & Sharma, 2007).

The parameters and characteristics of waste cooking oil are essential in determining the quality and suitability of biodiesel that will be produced. The kinematic viscosity of 39.74-56.04 (± 4.904) mm2 /s, saponification value of 198.0-205.5 (± 2.853) mg KOH/g, flash point value of 198-290 (± 44.321) ºC, moisture content of 0.02 to 0.51 (± 0.0712) % and free fatty acid value of 0.52-4.74 (± 0.047) %. From the comparison with ASTM D6751, samples show a very high values for each parameter and transesterification need to be done so that all the values can be reduce and biodiesel can be produced (Alias, Javendra, & Shahrom, 2018).

In a conducted study of the impact of ternary blends of biodiesel towards the diesel engine performance, it showed that the ternary blend of Pongamia biodiel, Waste Cooking Oil biodiesel and diesel, has resulted in a higher 25% loading in Brake Thermal Efficiency and Brake Specific Fuel Consumption compared to either only Pongamia biodiesel and Waste Cooking Oil biodiesel (P. Kumar, Sharma, & Dwivedi, 2016).

Although, biodiesel is widely known as a clean sustainable power source with its non-toxicity, biodegradability, and superior efficiency, several feedstocks have proven impractical or infeasible due to its extremely high cost of their usage. For example, in India with a population of over 1.27 billion people generates millions of gallons of used cooking oil and organic waste every day which is disposed of without use and is a potent bane to the environment (Jha & Das, 2017).

2.3.2 Jatropha Oil

Jatropha (Jatropha Curcas L.) is also known as physic nut or laxative nut, is cultivated in tropical and subtropical region across the world. The trees can be adapted to arid conditions and can easily grow several meters tall and live for up to 50 years. They produce toxic substances that protect them against animals and other pests. Jatropha seeds can have an oil content of up to 43 percent. It is considered high quality because the composition is similar to rapeseed.

Due to its constituents, Jatropha is not suitable for human consumption and it is instead being used in a wide range of industrial products. Also, other parts of the plant such as leaves, stems, root or plant juice are also valuable raw materials. Hence, it is a really good source for feedstock. Having to not compete with food industry.

As the fluctuation in fossil fuel prices and the increasing awareness of environmental degradation have prompted the search for alternatives from renewable energy sources. In Malaysia, palm oil is considered as the most valuable commodity crop and gives a high economic return to the country. However, palm oil has been more useful in the food industry making it not an ideal feedstock for biodiesel production. Therefore, attention is shifted to non-edible feedstock Jatropha.

Jatropha is an inedible oil-bearing crop that can be processed into biodiesel. It has a high-seed yield that could be continually produced for up to 50 years. Furthermore, its utilization will have zero impact on food sources since the oil is poisonous for human and animal consumption (Hamzah, Khairuddin, Siddique, & Hassan, 2020).

Due to the excess use of petroleum diesel, the GHG emission increases day by day which is responsible for global climate change. To reduce the GHG, biodiesel is the best choice for its total emission characteristic. Jatropha has a greater carbon stocking ability than other cotton crop which would be helpful for environment. On an average it accumulates 900kg carbon per hector per year. But the yield hypotheses had a significant impact on the GHG emission (Sarker, 2016).

Table 2.1: Characterization of Biodiesel Produced

Property	Unit	Limit (ASTM D6751)	Results
Specific gravity	Kg/L	0.95 max	0.90
Kinematic viscosity	c.s.t	1.9 – 6.0	4.93
Cloud point	°F	40 max	37
Flash point	°F	130 min	138
Cetane number	-	40 min	52
Water by distillation	% vol	0.5 max	Trace
Free glycerin	% mass	0.02 max	0.05
Total glycerin	% mass	0.24 min	0.32
Ash content	% wt	0.1 max	Not determined
Carbon residue	% wt	15 max	Not determined
Gross calorific value	Cal/gm	10600min	Not determined

Source: (Folaranmi, 2013)

Flash point is one of the most vital fuel properties and it indicates at which temperature it will burn with a source of ignition. As shown in Table 2.1 above, it shows that biodiesel produced from jatropha has a high flash point of 138ºF which is higher compared to the standard of only 130ºF. It indicates that jatropha biodiesel is far way safe and secured for usage and keeping.

2.3.3 Palm Oil

Palm oil is a vegetable oil derived from the mesocarp of the fruit of the oil palms. It is naturally reddish in color because of its high beta-carotene content. Also, it is not to be confused with palm kernel oil derived from kernel of the same fruit, or coconut oil derived from the kernel of the coconut palm. The fatty acid composition of neat palm oil biodiesel is as in Table 2.2.

Table 2.2: Fatty Acid Compositions of Palm Oil Biodiesel

Fatty Acids	POD100 (% mass)
Palmitic C16:0	35.9
Stearic	6.1
Oleic	46.1
Linoleic C18:2	11.9
Linoleic C18:3	-

Source: (Radhakrishnan, Devarajan, Mahalingam, & Nagappan, 2017)

In Malaysia, palm oil industry known to be the largest industry of crop due to its nurturing nature and high productivity rate within a short time. It is enough to be regarded as a renewable source of feedstock in the long run for commercial industry. Malaysia and also Indonesia are known for their huge palm oil plantation and production around the globe. Based on the current global vegetable oil demand, the production of crude palm oil es expected to reach 25.6 million tones by 2050 (Zulqarnain, Yusoff, Ayoub, Jusoh, & Abdullah, 2020). Figure 2.1 shows the palm oil production for Malaysia and Indonesia.

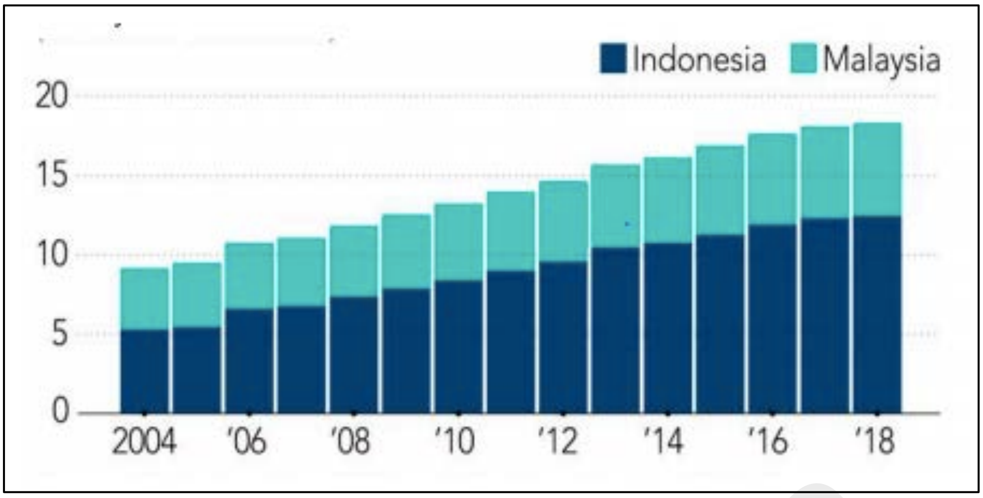

Figure 2.1: Palm Oil Production for Malaysia and Indonesia

(Zulqarnain et al., 2020)

Among other vegetable oils today, palm oil considered as the most promising source to make biodiesel as it has higher production yield, low fertilizer, water, and pesticide needed for the plantation. Furthermore, palm oil production takes less sunlight in terms of energy balance to produce a unit of oil as it produces more oil per hectare. From Table 2.3 we can see that palm oil was found to give the highest yield.

Table 2.3: Oil Yield for Major Non-edible and Edible Oil Sources

Type of oil		Oil yield (kg oil/ha)	Oil yield (wt %)
Non-edible oil	Jatropha	1590	Seed: 35-40 Kernel: 50-60
	Rubber seed	80-120	40-50
	Castor	1188	53
	Pongamia pinnata	225-2250	30-40
	Sea mango	N/A	54
Edible oil	Soybean	375	20
	Palm	5000	20
	Rapeseed	1000	37-50

Source: (Gui et al., 2008)

Compared to other vegetable oils in the market today, crude palm oil and refined palm oil tops the list. Known for its nutrients makes it suitable as vegetable oil itself for daily cooking. From a palm bunch, approximately 25 to 28 percent of crude palm oil can be obtained depending on the palm tree variety and also the age of the tree.

Table 2.4: Summary of Advantages and Disadvantages of Different Types of Biodiesels

Type of Biodiesel	Advantages	Disadvantages
First generation biodiesel (Palm, Sunflower, & Rapeseed oil)	• Feedstock can easily be produced by the existing infrastructure and technology.	• Requires large amount of inputs in terms of fertilizer, water, and land area thereby reducing net energy ratio.
Second generation biodiesel (Jatropha, Straw, Bagasse, & Trees)	• Feedstock can easily be produced by the existing infrastructure and technology. • Use of whole plant instead of only seeds or grains, and use of residues means more energy produced per hectare of land. • Marginal land can be used for planting of advanced feedstock such as Jatropha.	• Even though requires less amount of inputs but the land required for production is substantial. • The use of agriculture and forest residue degrades soil quality and also induces soil erosion.
Third generation biodiesel (Algae)	• Bioengineered algae utilized in this type of biodiesel is argued to be entirely renewable. • Algae is predicted to produce more energy per acre than. conventional crops • Algae can be grown using land and water unsuitable for food production, therefore reducing the strain on already stressed water resources. • Improves performance of first and second generation biodiesel when employed in integrated biodiesels. • Algae is predicted to produce more energy per acre than conventional crops.	• Requires new technology from the production of feedstock processing into final biodiesel product.
Fourth generation biodiesel (Solar Energy)	• Fourth generation biodiesel argued to be carbon negative rather than simply carbon neutral, as it locks away more carbon than it produces. • Synthetic raw materials to produce biodiesels is a possibility.	• Requires new technology from the production of feedstock to processing into final biodiesel product.

Source: (Acheampong, Ertem, Kappler, & Neubauer, 2017)

2.4 Biodiesel Production

2.4.1 Esterification

In every biodiesel plant today, the need to be multi-feedstock capable is not only a competitive advantage, but a business necessity. In a plant designed to use only refined oils, adding high Free Fatty Acid (FFA) pre-treatment opens up a world of new feedstock opportunities. Whether it's an animal fat-based feedstocks or the new emerging feedstocks such as Algae-oil, one thing in common is that these readily available, less expensive feedstocks all contain a significant amount of FFA which is too high for base transesterification. Figure 2.2 shows the biodiesel production cost which the highest cost is on feedstock with the percentage of 80.4.

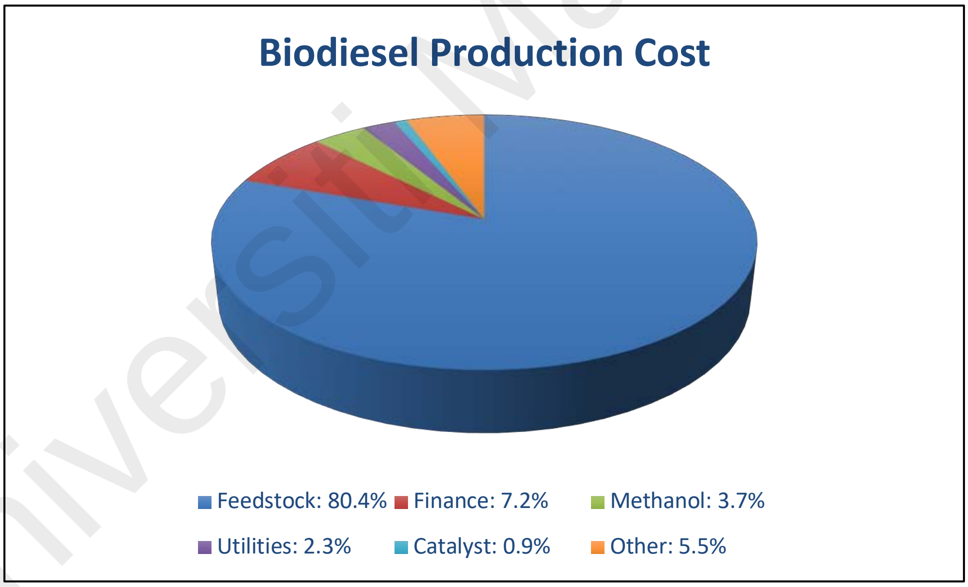

Figure 2.2: Biodiesel Production Cost

(SRS International, 2013)

Esterification increases the yield of biodiesel. Oil feedstocks that contain an excessive amount of Free Fatty Acids have to go through the process of esterification. The key to effectively preparing for the esterification process is to make sure the feedstocks have been sufficiently filtered by removing all contaminants and water. Upon filtration the feedstocks are fed to the acid or resin esterification process. The catalyst, sulfuric acid, is dissolved in methanol and then mixed with the pre-treated oil. Once the mixture is heated and stirred, the free fatty acids are converted to biodiesel. The final step of esterification is to dewater and feed the product to the transesterification process (SRS International, 2013).

The esterification reaction rate depends on the amount of the catalyst and the content of oleic acid in oil. The optimal quantity of the catalyst depends on the concentration of oleic acid. At a concentration of oleic acid of 0.162 mol/ L it is not expedient to increase the amount of the catalyst to more than 0.4 percent. A concentration is 0.346 mol/L limits the useful catalyst concentration to 0.5 percent. A concentration of 0.5012 mol/L, 1.017 mol/L or 1.948 mol/L to more than 1 percent (Sendzikiene, Makareviciene, Janulis, & Kitrys, 2004).

2.4.2 Transesterification

Biodiesel is getting more recognition and importance as an attractive alternative fuel due to its benefits to the environment without sacrificing the oil performance and also due to the depleting fossil fuel resources. In chemical terms, biodiesel is actually mono-alkyl esters of long chain fatty acids derived from feedstocks like vegetable oils and animal fats which is produced by the process of transesterification in which oil or fat is reacted with monohydric alcohol in the presence of catalyst.

The process of transesterification is affected by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants. In the present paper various methods of preparation of biodiesel with different combination of oil and catalysts have been described (Meher, Vidya Sagar, & Naik, 2006).

$$\underset{\text{Ester}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \underset{\text{Catalyst}}{\leftrightarrow} \underset{\text{Ester}}{RCOOR^2} + \underset{\text{Alcohol}}{R^1OH}$$

Figure 2.3: General Equation for Transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation shown in Figure 2.3 (Meher et al., 2006).

Table 2.5: Different Methods of Biodiesel Production

Method	Definition	Advantage	Disadvantage	Problems of using in engines
Direct use and blending	Direct use as diesel fuel or blend with diesel fuel.	• Liquid nature portability. • Heat content (80% of diesel fuel). • Readily available and renewability.	• Higher viscosity. • Lower volatility. • Reactivity of unsaturated hydrocarbon chains.	• Coking and trumpet formation. • Carbon deposits. • Oil ring sticking: thickening and gelling of the lubricating oil.
Micro-emulsions	A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles.	• Better spray patterns during combustion. • Lower fuel viscosities.	• Lower cetane number. • Lower energy content.	• Irregular injector needle sticking: incomplete combustion. • Heavy carbon deposits; increase lubrication oil viscosity.
Thermal cracking (pyrolysis)	The conversion of long-chain and saturated substance (biomass basis) to biodiesel by means of heat.	Chemically similar to petroleum derived gasoline and diesel fuel.	Energy intensive hence higher cost	
Transesterification	The reaction of a fat or oil with an alcohol in the presence of catalyst to form esters and glycerol.	Renewability; higher cetane number; lower emissions; higher combustion efficiency.	Disposal of byproduct (glycerol and waste water).	

Source: (Dennis Y.C. Leung, Wu, & Leung, 2010)

Nowadays, there are a number of methods currently available and have been adopted for the production of biodiesel fuel. The four primary ways to produce biodiesel are shown in Table 2.5 which are direct use and blending of raw oils, micro-emulsions, thermal cracking, and transesterification. The most commonly used method of converting oils to biodiesel is through the transesterification of animal fats or vegetable oils.

2.4.3 Catalyst Used in Biodiesel Production

In biodiesel production, there are three categories of catalysts used which are alkalis, acids, and enzymes. The one that has become more and more attractive recently is enzyme catalysts because it can avoid soap formation and the purification process is the simplest to accomplish. However, the downside of it is that the reaction time is longer and high in cost to be done, hence, it is less used commercially.

To counter the cost problem, some researchers developed new biocatalysts in recent years. An example is so called whole biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts (Matsumoto et al., 2001). Compared to enzyme catalysts, the alkali and acid catalysts are more commonly used in large scale biodiesel production.

Homogenous and heterogenous catalyst are under the alkali and acid catalysts. Due to the low cost of raw materials, sodium hydroxide and potassium hydroxide are usually used as alkali homogenous catalysts and alkali-catalysed transesterification is most commonly used commercially. The alkali-catalysed transesterification process is carried out under a low temperature and pressure environment, making these materials the most economic. Also, the conversion rate is high with no intermediate steps. However, the alkali homogenous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield, therefore, they should be properly handled (D. Y.C. Leung & Guo, 2006).

In other case, some heterogenous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. Those solid heterogenous catalysts can stimulatingly catalyse the transesterification and esterification reaction that can avoid the pre-esterification step, hence, making these catalysts particularly useful for those feedstocks with high free fatty acid content (Kulkarni, Gopinath, Meher, & Dalai, 2006).

Table 2.6: Advantages and Disadvantages of Different Types of Catalysts Used in The Biodiesel Production

Type		Example	Advantages	Disadvantages
Alkali	Homogeneous	NaOH, KOH	High catalytic activity, low cost, favourable kinetics, modest operation conditions.	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable.
	Heterogeneous	CaO, CaTiO3, CaZrO3, CaO–CeO2, CaMnO3, Ca2Fe2O5, KOH/Al2O3, KOH/NaY, Al2O3/KI, ETS-10 zeolite, alumina/silica supported K2CO3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes.	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost.
Acid	Homogeneous	Concentrated sulphuric acid	Catalyse esterification and transesterification simultaneously, avoid soap formation.	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity.
	Heterogeneous	ZnO/I2, ZrO2=SO2 4, TiO2=SO2 4, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, NafionNR50	Catalyse esterification and transesterification simultaneously, recyclable, eco-friendly.	Low acid site concentrations, low micro-porosity, diffusion limitations, high cost.
Enzymes		Candida antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, non-polluting, easier purification.	Expensive, denaturation.

Source: (Dennis Y.C. Leung et al., 2010)

Table 2.6 classifies the three categories of catalysts with their advantages and disadvantages. The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages. Moreover, methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapours which are colourless and odourless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production (Ma & Hanna, 1999).

2.4.4 Conventional Method

Biodiesel, the most known alternative for fossil fuel and the most promising renewable energy that is produced through transesterification of feedstock oils. The transesterification process significantly depends on the reaction’s parameters such as reaction time, temperature, molar ratio, catalyst amount, and stirrer speed. Among the parameters of the conventional way of producing biodiesel, the temperature and stirring have a significant impact on mass transfer during the transesterification process.

In conventional heating or also known as wall heating, heat is transferred through thermal conduction and convection, through the wall of the targeted object, to reach its internal materials. By using this method, the sample results in a non-uniform temperature and higher thermal gradients as heat is transferred through the other mediums before it reaches the internal sample. The heating effect is heterogeneous and it is highly dependent on the materials’ properties, such as thermal conductivity, specific heat capacity, and density (Gude, Patil, & Deng, 2012).

The influence of baffles, different stirring speeds, and two types of impellers (turbine and blade) in a mechanical mixing stirrer reactor gave an optimized outcome of biodiesel. The baffles improved mixing and stirring by enhancing contact between the reactants. However, baffles had no influence or even elicited undesired effects on transesterification. Turbine impeller was more effective than paddles. Higher stirring speed promoted better transesterification yields. The optimal conditions for biodiesel production were turbine impeller in the absence of baffle and stirring speed of 350 rpm (Peiter et al., 2020).

To overcome the immiscibility of triglycerides and methanol, current industrial production of biodiesel uses the batch system with a mechanical stirrer with the help of potassium hydroxide (KOH) as a catalyst. The utilization of a static mixer gives a more rigorous stirring process can enhance the mixing rigorousness and reduce the requirement of catalysts in order to obtain the necessary reaction conversion. Experimental results with 0.3% and 0.5% of catalysts could reach a reaction conversion of 84.97% (w w-1) and 93.05% (w w-1). The increase in the number of modules is expected to increase the conversion to the necessary level. Transesterification reaction of palm oil by using the static mixing reactor resulted in 41.15% methyl oleate, 36.55% methyl palmitate, 9.45% methyl linoleate, and 4.05% methyl stearate as the main products. The viscosity and density of the mixed fatty acid methyl ester at the outlet of the static mixing reactor was found to be 4.99 mm2 s -1 and 851.66 kg m3 -1 (Tulliza, Hartulistiyoso, Kusdiana, & Tambunan, 2018).

In the presence of KOH, the reaction was carried out. The optimum conditions for mixed oil biodiesel production were a catalyst concentration of 1.0% w/w of oil, a reaction temperature of 70oC, a reaction time of 30minutes 6:1 methanol to oil molar ratio at 400rpm. The methyl ester content under these optimum conditions was 95.10%, and all the measured properties of mixed oil biodiesel met the ASTM standards (K V Yathish, 2013).

With stirring speeds of 200–800rpm, a catalyst concentration (KOH) of 0.25–1 wt% of oil (in gram), different total flow rates of the oil and MeOH, and on the production performance of the 5-stage continuous reactor for transesterification of vegetable oil. Using a molar ratio of oil:methanol of 1:7 and a reaction temperature of 65 °C, it showed that a high stirring speed increased the reaction rate, but an excessive stir speed decreased the reaction rate and conversion to biodiesel. Furthermore, a higher catalyst percentage significantly increased the reaction rate and production capacity. A catalyst percentage of 1 wt% of oil gave the best conversion; 99.04 ± 0.05% (G. Kumar et al., 2010).

2.4.5 Advanced Method

In the production of biodiesel, it offers a triple-facet solution which are economic, environmentally friendly, and waste management. The new process technologies developed years before made it possible to produce biodiesel from waste cooking oil comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price due to its availability. Making biodiesel from waste cooking oil having the same possibilities to be utilized.

Transesterification is an increasingly important process and well established but there are a few considerable inefficiencies in existing transesterification processes. There is an imperative need to improve the existing biodiesel production methods from both economic and environmental viewpoints and to investigate alternative and innovative production processes.

2.4.5.1 Microwave Irradiation-assisted Transesterification

While conventional method has been used for a long time, microwave assisted methods have been proved to be a promising way of transesterification process. The method is rapid, energy efficient, cost saving, and environmentally friendly to produce biodiesel. Numerous test and optimization research with different feedstocks have been conducted in recent years to maximize the advantages of microwaves for biodiesel production. Not only in transesterification, but also in the oil extraction process in order to produce a greener and better-quality biodiesel.

Microwave heating utilizes the ability of certain materials between solids or liquid to transform electromagnetic energy into heat energy. There are two components involved in microwave method which are electric field and magnetic field. They will interact differently with the material under different mechanisms, and they are responsible for the microwave dielectric heating and magnetic loss heating. Most of the heating effects are microwave dielectric heating (Sun, Wang, & Yue, 2016).

However, there are superior benefits of microwave magnetic field heating for certain magnetic dielectric and conductive powder materials (Cheng, Roy, & Agrawal, 2002). The magnetic loss in the microwave heating of ferrites is up to approximately 4 times greater than the dielectric loss (Peng, 2012).

It was proved that microwave irradiation has superior benefits over the conventional heating method in biodiesel production. By using microwave assisted method, the reaction time has reduced from 2 hours to only 6 minutes and at the same time it produces a higher biodiesel conversion yield which is 4.1% higher than the conventional method (Duz, Saydut, & Ozturk, 2011). The energy consumption of microwave heating which is 288kJ, is lower than the conventional method which is 3150kJ. Other than that, it enhances the reaction time, producing higher yield, and consuming less energy, lastly produces less by-product, which resulted in a simplified downstream process and eventually reduces the time taken for product separation (Patil, Gude, Reddy, Muppaneni, & Deng, 2012).

Table 2.7: Comparison Between Three Types of Heating Methods for Biodiesel Production

Characteristics/Parameter	**Conventional Heating**	**Supercritical Heating**	**Microwave Heating**
Reaction time	1 to 2 hours (Long)	Less than 1 hour (Short)	0.05 to 0.1 hour (Very short)
Reaction temperature	40°C to 100°C	250°C to 400°C	40°C to 100°C
Reaction pressure	Atmospheric	35MPa to 60Mpa (High)	Atmospheric
Catalyst required	Yes	No	Yes/No
Heat losses	High	Moderate	Low
Energy form	Electrical energy to thermal energy	Electrical energy to thermal energy	Electrical energy applied through microwave
Process efficiency	Low	Moderate	High
Catalyst removal	Yes	No	Yes
Soap removal	Yes	No	Yes
Advantages	Simple to operate, uses low energy source	Short reaction time, easy product separation	Short reaction time, cleaner products, energy efficient
Limitations	High energy requirement, saponified products	High capital costs, pressure vessel safety	May not be efficient with feedstock containing solids

Source: (Nomanbhay & Ong, 2017)

2.4.5.2 Ultrasound Frequency-assisted Transesterification

In today's world, biodiesel is primarily produced in batch reactors for a large-scale production. Ultrasonic biodiesel conversion allows for the continuous inline processing. By using ultrasonification, the biodiesel yield can achieve in excess of 99%. Plus, its reactors can reduce the processing time by less than 30 seconds compared to the conventional method which is up to 1 to 4 hour batch processing. Moreover, ultrasonification reduces the separation time from 5 to 10 hours (using conventional agitation) to less than 60 minutes.

Not only that, the ultrasonification does also help to decrease to amount of catalyst required by up to 50% due to the increased chemical activity in the presence of cavitation. The amount of excess required is reduced too when using ultrasonification. Another benefit is the resulting increase in the purity of the glycerin (Hielscher Ultrasonics, 2021).

A fatty acid methyl ester (FAME) conversion rate using ultrasonic method was conducted with two step transesterification process. The results show that 97.4% by weight of mahua biodiesel could be achieved compared to conventional method of transesterification led to comparatively lesser yield of biodiesel approximately 93% (Bahadur, Goyal, Sudhakar, & Bijarniya, 2015).

The transesterification yield was apparently high by the use of the ultrasonic method compared to magnetic stirring mechanism. With the help of cavitation phenomenon which reduces the activation energy involved in the reaction, the chemical reaction is accelerated. Along with bubble collapse that affects the liquid-liquid phase, resulting in improvement in mass transfer of the mixture and enhancement in rate of reaction between molecules.

Table 2.8: Compilation of Studies with Typical Parameters in Ultrasound-assisted Transesterifications

Feedstock	Alcohol type; molar ratio	Catalyst type; (%)	Frequency; power	Time (min); conversion (%)
Canola oil	Methanol 6:1	NaOH; 0.5	20 kHz; 200 W	30; 87
Sunflower oil	Methanol 7:1	NaOH; 2	24 kHz; 200W	20; 95
Coconut oil	Ethanol 6:1	KOH; 0.75	24 kHz; 200W	7; 98
Canola oil	Methanol 5:1	KOH; 0.7	20 kHz; 2000 W	50; 99
Synthetic oil	Methanol 6:1	NaOH; 0.5	40 kHz; 840 W	20; 98
Soybean oil	Ethanol 10:1	NaOH; 0.3	40 kHz;	30; 91.8
Oleic acid	Ethanol 3:1	H_2SO_4; 5	40 kHz; 700 W	120; 90
Fish oil	Methanol 9:1	H_2SO_4; 2	40 kHz; 60 W	90; 98.2
Waste cooking oil	Methanol 6:1	KOH; 1	20 kHz; 200 W	40; 89
Cottonseed oil	Methanol 6:1	KOH; 1	40 kHz;	5; 96
Palm acid	Methanol 7:1	H_2SO_4; 5	22 kHz; 120 W	200; >90
Waste cooking oil	Methanol 9:1	H_2SO_4; 3	40 kHz; 200 W	60; 99.9
Jatropha oil	Methanol 7:1	H_2SO_4; 4	210 W	60; 96.4

Source: (Oliveira, Baesso, Moraes, Alvarenga, & Costa-Félix, 2018)

In a commercialized equipment, the ultrasonic probe has high power output capability as it concentrates energy delivering. Usually, the setup of this equipment has a distance of about 5cm between the transducer which used for irradiation and the tip of the horn. The ultrasonic energy is supplied to the liquid through the horn immersed in it. Figure 2.4 showed an example of the ultrasonification setup of the process.

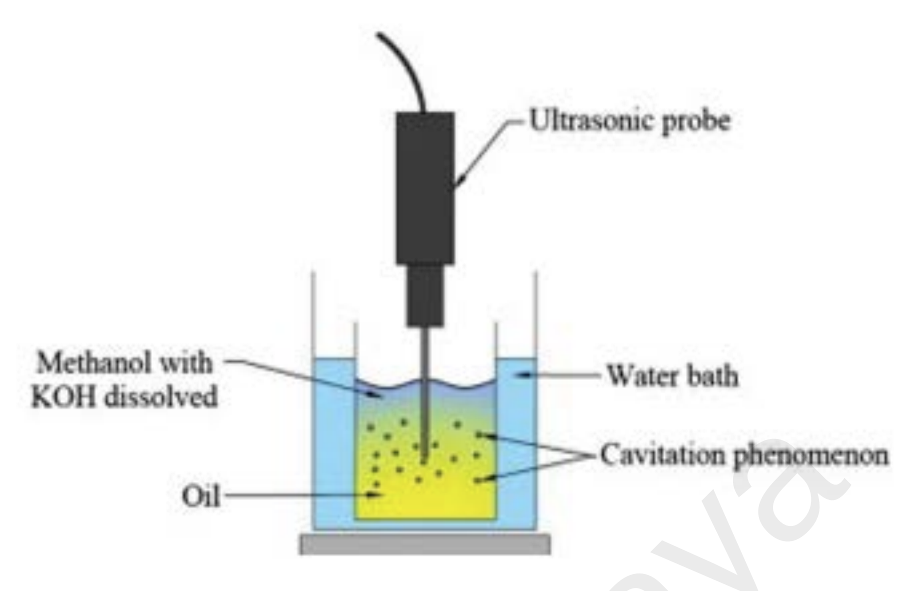

Figure 2.4: Schematic Representation of The Reaction Using Ultrasonic Probe

(Sáez-Bastante et al., 2014)

An ultrasonic processor of 24 kHz 200W, or also known as ultrasonic probe was used in a transesterification reaction of canola oil with ethanol. After 30 minutes of the reaction, a conversion of 87% was obtained to a molar ratio of 6:1 and 0.5-1% of the sodium hydroxide. Then, a comparison between the ultrasonic method and methods of agitation of magnetic and mechanical was carried out with the conclusion of the ultrasound obtains lower energy costs (Lifka & Ondruschka, 2004).

Another experiment of biodiesel production using ultrasonic probe at a low frequency of 24kHz 200W with sunflower oil as the feedstock and methanol at a molar ratio alcohol/oil of 7:1 and 2% sodium hydroxide. In just 2 minutes of reaction, it reached 95% yield. Meanwhile, while using ethanol with the same reaction parameters, the ultrasound led to high ester yields about 98%. Compared to mechanical stirring, it gave only 88% yield in 40minutes of reaction even after 4 hours of reaction time (Georgogianni, Kontominas, Pomonis, Avlonitis, & Gergis, 2008).

The same equipment used in as described above, in the transesterification of coconut oil to produce biodiesel. Resulting in 98% conversion was obtained in 7 minutes of reaction at a molar ratio of 6:1. The ultrasonicator probe was used as an alternative to the usual production process and resulted in high conversion (D. Kumar, Kumar, Poonam, & Singh, 2010).

A pilot scale plant was developed for biodiesel production from canola oil catalyzed by hydroxide potassium. An ultrasonicator probe was used at low frequency of 20 kHz. After only 50 minutes of reaction, a maximum conversion of more than 99% was obtained with a methanol to oil molar ratio of 5:1 with a 0.7% catalyst concentration. With the conclusion of the optimization of ultrasonic power and mode of delivery can be carried out to minimize energy consumption while attaining high conversions (Thanh et al., 2010).

A study performed transesterification reaction in ultrasonic bath shown a conversion result of greater than 90% (Santos, Malveira, Cruz, & Fernandes, 2010). An experiment of producing a biodiesel using an ultrasonic bath with frequency of 40 kHz. The conducted study profile of methyl esters of different vegetable oils produced under ultrasonic irradiation with conventional heating were compared. It turned out the profile of methyl esters in the presence of potassium hydroxide was quite similar for both procedures. The highest conversion obtained was 98% after only 20 minutes of reaction at an alcohol to oil molar ratio 6:1 (Stavarache, Vinatoru, & Maeda, 2006).

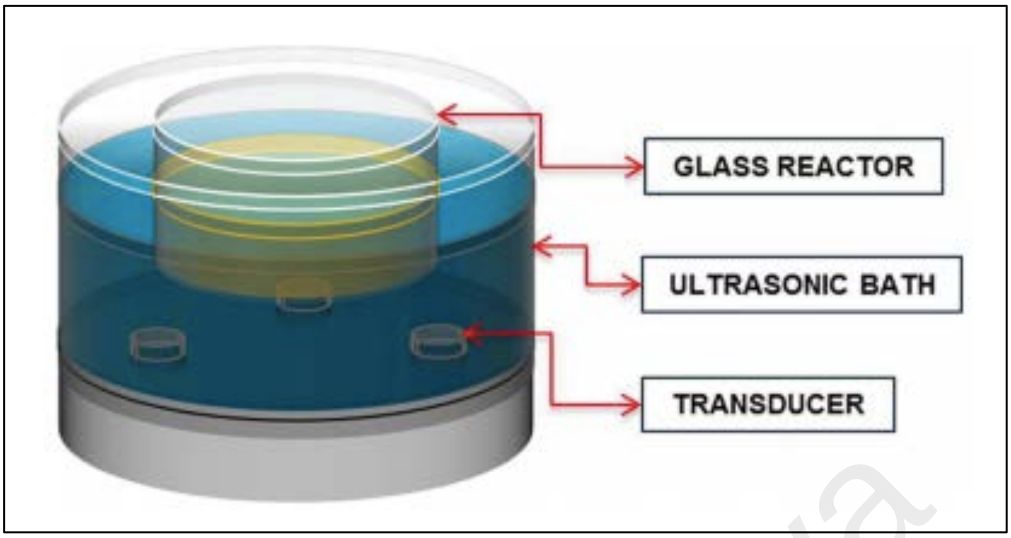

Figure 2.5: Schematic Representation of The Reaction Using Ultrasonic Bath

(Oliveira et al., 2018)

In a research of producing biodiesel in an ultrasonic bath with low frequency of 40 kHz using soybean oil as the feedstock and ethanol. After 30 minutes of reaction, the conversion which is 91.8% was greater than the conversion obtained using the conventional process (Rodrigues, Mazzone, Santos, Cruz, & Fernandes, 2009). Another reaction was carried out in an ultrasonic bath operating at low frequency of 40 kHz 700 W. The conversion obtained was 90% after 120 minutes of reaction using oleic acid and ethanol at an alcohol to oil molar ratio of 3:1 (Hanh, Dong, Okitsu, Nishimura, & Maeda, 2009).

Other than that, in a research using ultrasonic bath operating at low frequency of 40 kHz 60 W, fish oil as feedstock and methanol. The reaction was carried out by an ultrasound-assisted method at an alcohol to oil molar ratio of 9:1 and a catalyst concentration of 2.0%. A higher methyl ester yield was achieved as compared to mechanical stirring with the result of yield equal to 98.2% in 90 minutes of reaction (Santos et al., 2010).

Soon in 2009, there is a development of the ultrasound-assisted method in producing biodiesel. The use of ultrasonic transducer was introduced and applied in the reaction media. By using this method, there is no separation between the transducer and the liquid surface making the wave propagation is more confined.

A waste cooking oil was used as feedstock to produce biodiesel via low frequency ultrasonic reactor at 20 kHz with power of 200 Watt. The molar ratio of alcohol to oil of 6:1, catalyst concentration of 1% and the temperature of 45 Degree Celsius. The effect of power was studied, and the obtained conversion was around 66% at a power of 150 Watt. But when the power is increased to 200 Watt, the conversion was also increased to about 89%. When further increased from 200 Watt to 250 Watt, resulted in lower conversion due to the cushioning effect which results to decrease the transfer of energy into the system (Hingu, Gogate, & Rathod, 2010).

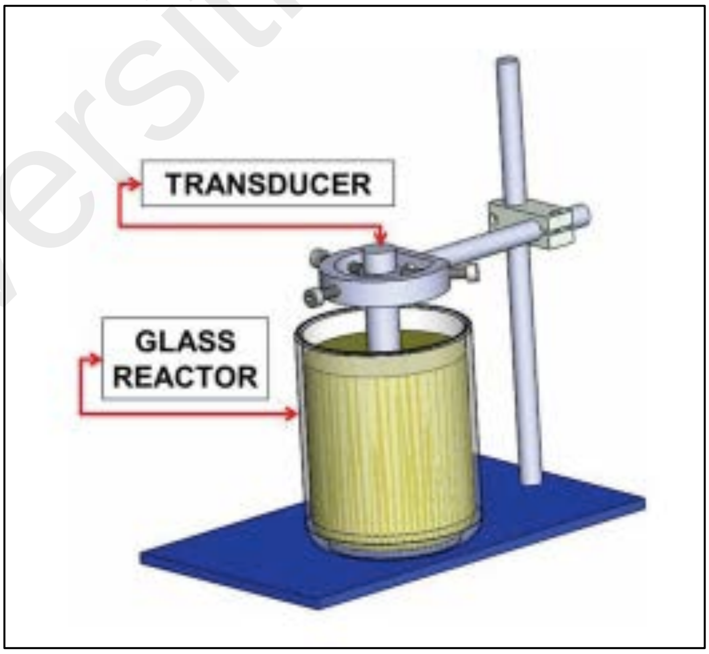

Figure 2.6: Schematic Representation of The Reaction Using Ultrasonic Transducer

(Oliveira et al., 2018)

In an experiment to perform the transesterification of a crude cottonseed oil by using transducer powered by function generator was carried out with methanol and in alcohol to oil molar ratio of 6:1 in the presence of base catalyst. Just only after 60 minutes of reaction, using low frequency of 40 kHz, a yield of approximately 90% was obtained. Even though four different frequencies were investigated which are 400 Hz, 4 kHz, 40 kHz, and 400 kHz, but there were no remarkable differences in the formation of the cavitation bubbles at the examined frequencies (Fan, Wang, & Chen, 2010).

2.5 Biodiesel Standard

A criterion that proves a certain biodiesel's long-term success is the quality of the final product which is the biodiesel. The usage without any technical problem would be the desirable one. It all depends on the chemical and physical characteristics. Given the fact that most engines operate using diesel so the characteristics of biodiesel should be near the characteristics of diesel fuel. The quality standards of biodiesel are continuously updated due to the evolution of compression ignition engines, the stricter emission regulations, reevaluation of the eligibility of feedstocks used for the production of biodiesel, etc. The current quality standards regulations varies from region to region including the characteristics of the existing diesel fuel standards, the most used type of diesel engines most common in the region, the emissions regulations governing those engines, the development stage, and the climate properties of the region (Montero & Stoytcheva, 2012).

In a study conducted where fuel properties of processed liquid palm oil/petroleum diesel blend in relating to Malaysian standard on diesel fuel were discussed, stated that generally, the fuel properties of PLPO/PD blends are very similar to those of petroleum diesel. Blending PLPO up to 10% in petroleum diesel does not change the fuel properties of petroleum diesel much with the resultant fuel properties of the blends still heavily dependent on the fuel properties of petroleum diesel. Table 2.9 depicts the fuel properties of the blends from a study conducted using PLPO from different palm oil refineries in Malaysia. From this study, B2 and B5 of the PLPO/PD blends can meet all the requirements of MS123:1993 (Foon, May, Liang, Ngan, & Basiron, 1994).

Table 2.9: Fuel Properties of Processes Liquid Palm Oil (PLPO)/Malaysian Petroleum Diesel (PD) Blends

Property	Unit	PLPO/PD blends		Malaysian petroleum diesel	MS123:1993	
		B2	B5		Min.	Max.
Density at 15°C	kg/litre	0.8395 – 0.8448	0.8419 – 0.8459	0.8380 – 0.8420	-	-
Viscosity at 40°C	mm^2/s	3.974 – 4.184	4.136 – 4.549	3.918 – 3.974	1.5	5.8
Flash point	°C	77.0 – 81.0	75.0 – 81.0	77.0	60	-
Cloud point	°C	14 -16	14 - 16	14 – 16	-	18
Pour point	°C	9 - 12	9 - 12	12	-	15
Sulphur content	mg/kg	0.18 – 0.19	0.17 – 0.18	0.19 – 0.21	-	0.5
Carbon residue (on 10% distillation residue)	% mass	< 0.1 – 0.1	0.1	< 0.1	-	0.2
Cetane number	-	50.6 – 61.8	54.8 – 61.5	55.2 – 61.2	45	-
Cetane index	-	51 - 57	55 - 56	51 - 57	47	-
Ash content	% mass	0.001 – 0.007	< 0.001 – 0.006	0.001 – 0.005	-	0.01
Basic sediment and water	mg/kg	< 0.01	< 0.01	< 0.01	-	0.01
Copper strip corrosion (3 hour at 100°C)	rating	1a	1a	1a	-	1
Distillation temperature at 90% recovery	°C	365.4 – 369.0	363.7 – 367.8	365.4 – 365.9	-	370
Water by distillation	% volume	< 0.05	< 0.05	< 0.05	-	0.05
Colour	-	1.0 – L1.5	1.0	L1.0 – 1.5	-	2.5
Gross calorific value	MJ/kg	45 - 47	44 - 47	45 - 47	-	-

Notes:
B2: 2% processed liquid palm oil + 98% petroleum diesel.
B5: 5% processed liquid palm oil + 98% petroleum diesel.
MS123: 1993: Malaysian Standard for Diesel Fuel.

Source: (Foon et al., 1994)

In a conducted research, a cottonseed oil was converted into biodiesel by alkali catalysed transesterification reaction at different catalyst concentration, catalyst type, temperature, methanol to oil molar ratio and agitation intensity designing an optimized protocol. It was found that optimum catalyst type was NaOCH3, catalyst concentration 0.75%, temperature 65 °C, methanol to oil molar ratio 6:1 and agitation intensity 600 rpm. Those optimum parameters produced excellent yield of 96.9%. The important fuel properties of COME were compared well with ASTM D6751 and EN 14214 specifications (Rashid, Anwar, & Knothe, 2009).

Table 2.10: Properties of Cottonseed Oil Methyl Esters (COME) with Comparison to Biodiesel Standards

Property	COME	ASTM D6751	EN 14214
Cetane number	54.13 ± 1.52	47 min	51 min
Kinematic viscosity (mm^2/s; 40°C)	4.07 ± 0.04	1.9-6.0	3.5-5.0
Oxidative stability (h)	1.83 ± 0.12	3 min	6 min
Lubricity (HFRR; μm)	139.5 ± 2.6	-	-
Cloud point (°C)	7.00 ± 0.11	Report	-
Pour point (°C)	6.00 ± 0.15	-	-
Cold filter plugging point (°C)	1.00 ± 0.12	-	-
Flash point (°C)	150 ± 3.00	93 min	120 min
Sulfur content (%)	0.011 ± 0.001	0.05 max	-
Ash content (%)	0.013 ± 0.001	0.02 max	0.02 max
Acid value (mg KOH/g)	0.16 ± 0.03	0.50 max	0.50 max
Copper strip corrosion (50°C, 3 h)	1a	No. 3 max	No. 1 min
Denstiy (25°C), kg/m^3	875 ± 15.7	-	860-900
Methanol content (%)	0.175 ± 0.002	-	0.2 max
Free glycerin (%)	0.015 ± 0.001	0.020 max	0.020 max
Total glycerin (%)	0.229 ± 0.015	0.240 max	0.250 max

Source: (Rashid et al., 2009)

A study of Amygdalus pendunculata as a feedstock to produce biodiesel in China was conducted. The biodiesel produced from that feedstock confirmed the EN 14214, ASTM D6751, and GB/T20828 standards, except for those cetane number and oxidative stability. With the cold filter plugging point of 11 Degree Celsius and flash point of 169 Degree Ceslsius, the cold flow and transportation safety properties were excellent. Additives and antioxidants would be required to meet cetane number and oxidative stability specifications. The addition of 500 ppm tert-butylhydroquinone resulted in a higher induction period of 6.7 hours, bringing oxidative stability into compliance with all three biodiesel standards. In conclusion, most of the fuel properties of biodiesel prepared from the said feedstock above were in good compliance with the standards mentioned (Chu, Xu, & Zhang, 2013).

2.6 Research Gap

From the analysis conducted of the literature review, it has become apparent that there is certain limitation in the previous research or certain areas that have not yet been studied. In this case, the study of biodiesel produced from waste cooking oil, palm oil, and Jatropha have not been done yet. The prospect of having the three feedstocks combined is promising backed by the facts and data discussed in literature review.

In a conducted study, (Mofijur et al., 2012) has stated that the oil content in Jatropha is higher than soybean, linseed, and palm kernel which was found 18.35%, 33.33% and 44.6% whereas oil contents in Jatropha was reported at 66.4%. In addition, the properties of Jatropha oil solely depending on the geographical and climate condition which Malaysia has that can cultivate Jatropha curcas to be the main source of biodiesel production.

Other than the already existing B5 biodiesel in Malaysia derived from Palm oil, the area of study that haven’t conducted yet is the combination of waste cooking oil, palm oil, and Jatropha oil which has a promising properties and resources that could produce an optimized biodiesel in terms of properties and performance of the biodiesel.

CHAPTER 3: METHODOLOGY

In this chapter, the process carried out systematically to obtain accurate and convincing results were explained. The experiment includes important aspects starting with the feedstock selection of the oil mixture, physicochemical properties of esterified mixture, biodiesel production via ultrasound assisted transesterification, and the analysis of biodiesel physicochemical properties. The workflow is shown in the flow chart given in Figure 3.1.

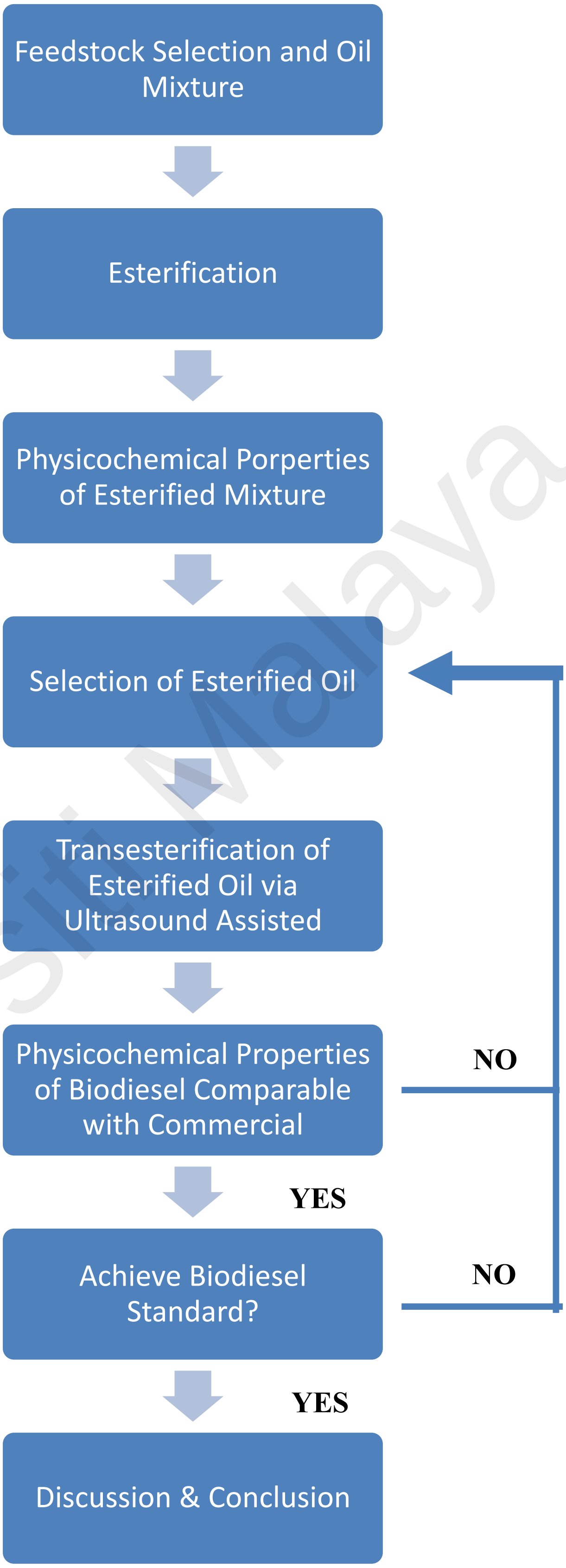

Figure 3.1: Workflow of Research

3.1 Feedstock Identification

3.1.1 Materials

The feedstock Jatropha curcas were purchased from Bionas (Kuala Lumpur, Malaysia). While, palm oil was purchased from Sime Darby Oils – Jomalina Refinery (Selangor, Malaysia), and lastly the waste cooking oil were obtained from various local restaurant in Petaling Jaya. In this research, all the chemicals were bought from It Tech Research (M) Sdn Bhd in Malaysia. The materials and chemical used are methanol, sulphuric acid, anhydrous sodium sulphate, potassium hydroxide pellets, FAME mix C_8 until C_{24}, and phenolphthalein solution. The purity of all the chemicals are more than 98.9%.

3.2 Experimental Setup

3.2.1 Acid-catalyzed Esterification of Feedstocks

All the feedstocks of waste cooking oil, jatropha oil, and palm oil were filtered and heated to remove impurities and water. Then the feedstocks are mixed based on the compositions in Table 3.1 below.

Table 3.1: Feedstocks and Its Composition

Feedstock	Composition
WC50J35P15	50% Waste Cooking Oil 35% Jatropha Oil 15% Palm Oil
WC50J30P20	50% Waste Cooking Oil 30% Jatropha Oil 20% Palm Oil
WC50J25P25	50% Waste Cooking Oil 25% Jatropha Oil 25% Palm Oil
WC50J20P30	50% Waste Cooking Oil 20% Jatropha Oil 30% Palm Oil
WC50J15P35	50% Waste Cooking Oil 15% Jatropha Oil 35% Palm Oil

The oil mixtures were being esterified using a double jacketed reactor fitted with a reflux condenser at 15°C with a homogenous acid catalyst which was KOH. The schematic diagram of the experimental set-up for esterification process is shown in Figure 3.2.

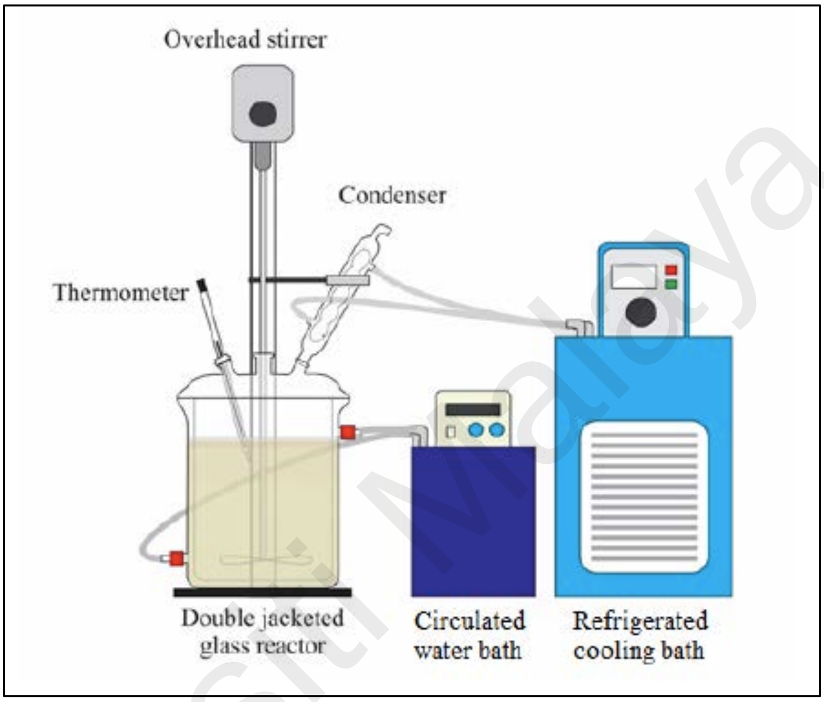

Figure 3.2:Schematic Diagram of The Experimental Setup for Esterification Process

(Jassinnee, 2019)

3.2.2 Base-catalyzed Transesterification of The Feedstock

The sample WC50J15P35 was used to prepare the biodiesel using Q500 Sonicator (QSONICA, Manufactured in Newton, CT, USA) ultrasound equipment as shown in Figure 3.3. The transesterification assisted by ultrasound was performed under the following operating conditions: time (40 minutes), duty cycle of (60%), Methanol to oil ratio of 60 vol./vol.%, potassium hydroxide was used as catalyst with a quantity of 0.70 wt.%.

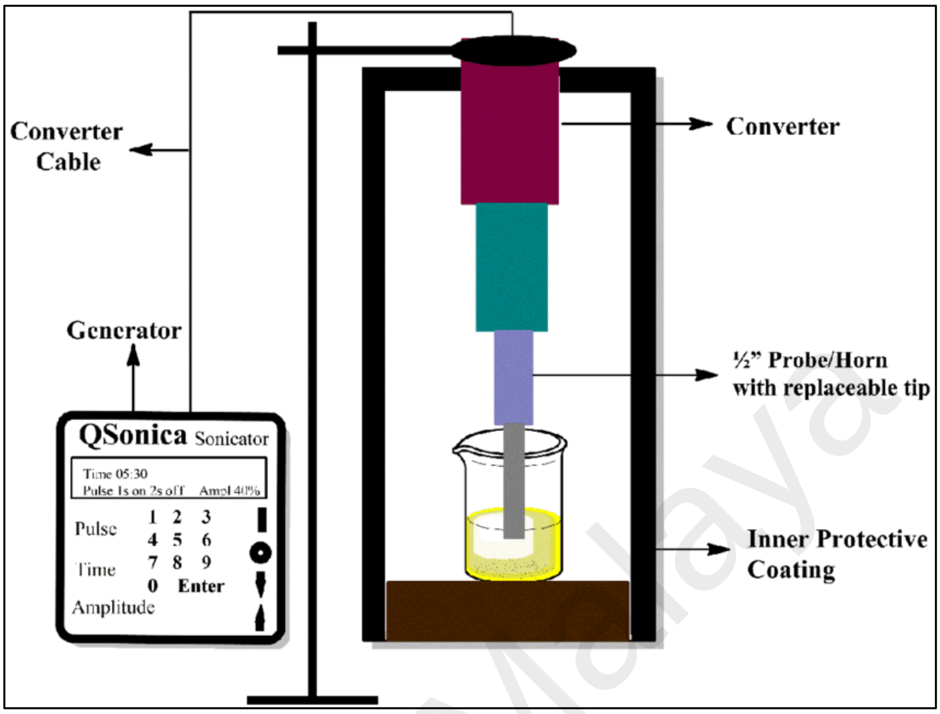

Figure 3.3: Ultrasound Equipment for Biodiesel Production

(Mujtaba, Masjuki, Kalam, Noor, et al., 2020)

The step to performing this method of transesterification started with placing the beaker filled with sample of 100ml of WC50J15P35 mixture and 0.633gram of KOH, in the inner protective coating. The position of the beaker is directly under probe horn tip. The tip is place in the sample of 1.5cm deep. Then the duty cycle of the generator was set to 60% before starting the process.

Right after the transesterification process, there are two layers of crude biodiesel and glycerol formed. The top layer is the crude biodiesel while the bottom layer is glycerine with water. The separation was done by letting it flow down a separation funnel. Then the washing step was done when the distilled water looks clear after several washes.

3.3 Physicochemical Properties of The Feedstock Oils and Feedstock Oil Mixtures

In order to determine the most suitable raw oil mixture for biodiesel production, the physicochemical properties of the waste cooking oil, Jatropha oil, and Palm oil were measured. The main criterion was density, acid value, FFA and oxidation stability of the mixture in order to choose the most suitable ratio. The results obtained shows that the combination of WC50J15P35 is the most favourable feedstock with superior physicochemical properties that is ideal for biodiesel production.

Table 3.2: Feedstock Oils and Feedstock Oil Mixtures Properties

Property (unit)	Feedstock oil			Feedstock oil mixture				
	WCO	**JO**	**PO**	**WC50 J35 P15**	**WC50 J30 P20**	**WC50 J25 P25**	**WC50 J20 P35**	**WC50 J15 P35**
Kinematic viscosity at 40°C (mm^2/s)	40.99	34.93	40.24	38.92	39.93	39.61	39.92	39.97
Density at 15°C (kg/m^3)	916.2	917.7	914.8	916.9	916.7	916.5	916.3	916.1
Acid value (mg KOH/g)	0.73	47.69	3.37	14.51	12.28	10.67	8.93	7.39
FFA content (wt%)	0.36	23.84	1.68	7.26	6.14	5.34	4.47	3.69
Higher heating value (MJ/kg)	41.97	41.78	42.03	41.90	41.93	41.94	41.95	41.96
Oxidation stability at 110°C (Hour)	10.86	1.73	17.57	1.79	2.47	2.88	3.47	5.08

Each of the feedstock's physicochemical properties were studied and tabulated. Based on Table 3.2, the density, acid value, FFA content decreased as the PO content increased. Meanwhile, the kinematic viscosity, higher heating value and oxidation stability increased as the PO content increased. Besides that, the oxidation stability of WC50J35P15, WC50J30P20 and WC50J25P25 are relatively low, therefore these crude oil mixtures were not suggested for further analysis. However, WC50J20P30 and WC50J15P35 oils give favorable oxidation stability values with 3.47 and 5.08 hour, respectively. The oil mixture of WC50J15P35 have the lowest acid number and FFA content among the crude oil mixtures, thus requires minimum conditions in acid catalysis esterification as a pre-treatment step to reduce the FFA content. Since palm oil is easily available in Malaysia, it will be good to utilize more of that instead of jatropha oil because jatropha is only new in Malaysia.

3.4 Measurement of The Physicochemical Properties

The physicochemical properties of the feedstocks WCO, JO, PO, and biodiesel WC50J15P35 were measured and analyzed. The list of equipment used to measure the physicochemical properties of the biodiesel is given in Table 3.3.

Table 3.3: List of Equipment Used to Measure the Physicochemical Properties of The Feedstock Oil Mixtures and Biodiesel

Property	Equipment
Kinematic Viscosity at 40°C	Stabinger viscometer TM SVM 3000TM (Anton Paar GmbH, Austria)
Density at 15°C	DM40 LiquiPhysics™ Excellence density meter (Mettler Toledo, USA)
Heating Value	6100 calorimeter (Parr Instrument Company, USA)
Acid Value	Rondo 20 Automated titrator (Mettler Toledo, USA)
Oxidation Stability at 110°C	873 Biodiesel Rancimat (115 V) (Metrohm AG, Switzerland)
Flash Point	PM 4 Pensky-Martens flash point tester (Anton Paar GmBH, Austria)
Gas Chromatography	Agilent Gas Chromatography (Agilent Technologies, USA)

3.4.1 Kinematic Viscosity

The equipment used to measure the kinematic viscosity is a Stabinger viscometer TM SVM 3000TM produced in Austria by Anton Paar and the method used was according to ASTM D445. The ASTM D445 method was used to determine the kinematic viscosity and dynamic viscosity at 40°C. A 10ml syringe was used to suck in the oil and placed at the identification tube holder and the eject the sample into the tube. The operation time of one sample was 10 minutes. The calibration fluids provided by the manufacturer were used to calibrate the viscometer at least once in 6 months to keep it in good condition.

3.4.2 Density

The equipment used to measure the density is a Stabinger viscometer TM SVM 3000TM produced in Austria by Anton Paar and the method used was according to ASTM D4052. The ASTM D4052 method was used to determine the density at 15°C. A 10ml syringe was used to suck in the oil and placed at the identification tube holder and the eject the sample into the tube. The operation time of one sample was 10 minutes. The calibration fluids provided by the manufacturer were used to calibrate the viscometer at least once in 6 months to keep it in good condition.

3.4.3 Calorific Value or Heating Value

The calorific value was measured using 6100 calorimeter manufactured in USA by Parr Instrument Company. The calorific value was measured referring to ASTM D240 standard test method. 0.5 g of methyl ester was measured into the crucible and placed in an oxygen bomb calorimeter, then the cover of the bomb was tightened, oxygen hose was connected to the bomb inlet valve, and oxygen gas with up to 40 atm was charged into the bomb. The secured oxygen bomb calorimeter was placed in the 2L circulating water system. A high precision electronic thermometer using a specially designed thermistor sensor sealed in a stainless-steel probe was fixed in the colorimeter cover. The operating time for each sample was approximately 6 min., the quantity of heat produced by complete combustion of a given mass of a sample is usually expressed in joules per kilogram. The measurements were taken with 0.0001 resolution over a 20°C to 40°C working range. The calorimeter produces reliable results with good repeatability with 0.05- 0.1 % precision.

3.4.4 Acid Value

To measure the acid value, Standard Method for Acid and Base Number by Colour-Indicator Titration of ASTM D974 was referred. In order to determine the acid number, the sample weight of 2gram is dissolved in a mixture of 100ml Titration solvent (containing 50% Toluene, 49.5% propan-2-ol, and 0.5% distilled water) and 0.5ml

Phenolphthalein indicator. The end point was indicated by the colour change of the sample by titrating Potassium Hydroxide (KOH).

3.4.5 Oxidation Stability

To measure the oxidation stability, 873 Biodiesel Rancimat (115 V) manufactured in Switzerland by Metrohm AG was used. The measurement was based on EN 14112 standard method. This test is really crucial to measure the biodegradability of the produced methyl ester. 7.5 g of sample was measured into a glass tube and placed in the oxidation stability equipment. 60ml of distilled water was poured into the robust glass beaker and covered with a built-in conductivity cell, the conductivity cell was placed in the measuring vessel. Air supply line allowed controlled air to pass through the sample via the rotation rate of the built-in pump.

3.4.6 Flash Point

For the flash point test, Petrotest PM4 Semi-Automatic Flash Point Tester was used referring to Pensky-Martens method. A brass test cup is filled to the inside mark with test specimen, fitted with a cover and heated, while the specimen is stirred at specified rates. An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash is detected. The flash point is the lowest temperature at which the application of an ignition source causes the specimen vapours to ignite. The temperature sensor used was Thomas Scientific Traceable Kangaroo Thermometer in order to track the temperature.

3.5 Gas Chromatopgraph

In this research, gas chromatograph was used to determine the FAME content, linolenic acid methyl ester content, glycerol content, and methanol content of WC50J15P35 methyl ester produced by using ultrasound assisted transesterification. The procedures, materials used, and analysis equations are presented in detail in the following sections.

3.5.1 Determination of The Fatty Acid Methyl Ester (FAME) Content and Linolenic Acid Methyl Ester Content According to The EN 14103:2011 Standard Test Method

For the WC50J15P35 methyl ester, gas chromatograph fitted with a flame ionization detector was used to determine the FAME content and linolenic acid methyl ester content according to the EN14103:2011 standard test method. This method is also suitable to determine the FAME content of biodiesels containing methyl esters between C_6 and C_{24} as well as to determine the linolenic acid methyl ester content ($C_{18:3}$). According to the EN 14103:2011 method, the FAME content should be greater than 90 (w/w) % whereas the linolenic acid methyl acid content should be within a range of 1–15 (w/w) %. This method is suitable for use with the gas chromatograph equipped with HP-INNOWax high-polarity column (length x inner diameter x film thickness: 30 m x 0.25 mm x 0.25 μm, stationary phase: polyethylene glycol). Helium gas was used as the carrier gas. The gas chromatograph was used to determine the FAME content and linolenic acid methyl ester content according to the EN 14103:2011 standard test methods as presented in Table 3.4. The FAME content and linolenic acid methyl ester content were determined using Equation (3.1) and Equation (3.2), respectively:

$$FAME\left(\left(\frac{w}{w}\right)\%\right) = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \qquad (3.1)$$

$$L\left(\left(\frac{w}{w}\right)\%\right) = \frac{A_L}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \qquad (3.2)$$

Table 3.4: Operating Conditions for The Gas Chromatography Measurements Used to Determine the FAME Content and Linolenic Methyl Ester Content in Biodiesel According to The EN 14103:2011 Standard Test Method

Parameters	Specifications
Capillary column	Agilent HP-INNOWax column Length x inner diameter x film thickness: 30m x 0.25 mm x 0.25 µm
Oven temperature	60 °C, hold for 2 min. 60 – 200 °C at 10 °C/min. 200 – 240 °C at 5 °C/min. 240 °C, hold for 7 min. Post-run at 225 °C for 0.5 min.
Carrier gas	Helium
Helium pressure	70 kPa
Flow rate	1.5 mL/min
Split flow	100 mL/min
Split ratio	100:1.5
Injector temperature	250 °C
Detector temperature	250 °C
Type of injector	Split/splitless
Type of detector	Flame ionization detector
Injection volume	1 µL
Flame ionization detector makeup gas	Helium
FAME standard	FAME mix C_8 – C_{24}, Brand: Sigma-Aldrich, Packaging size: 100 mg
Internal standard	Methyl nonadecanoate, C_{19}, Brand: Sigma-Aldrich, Purity: >99.5%

CHAPTER 4: RESULTS & DISCUSSION

4.1 Results

The results that were obtained from the experiment conducted are described, analyzed, and discussed in this chapter. The first thing is that the selection of the feedstock in this experiment is selected and discussed, followed by the esterification process. Then the physicochemical properties of the esterified feedstock were presented and discussed. Secondly, the feedstock undergone transesterification via ultrasound assisted process. The obtained biodiesel was analyzed and discussed as the optimized biodiesel produced and compared with the commercial and biodiesel standards.

Table 4.1: Physicochemical Properties of WC50J15P35 Biodiesel

Property	Unit	WC50J15P35 biodiesel
Kinematic Viscosity at 40°C	mm^2/s	4.504
Density at 15°C	kg/m^3	870
Acid Value	mgKOH/g	0.44
FFA Content	wt%	0.22
Higher Heating Value	MJ/kg	40.01
Oxidation Stability at 110°C	Hour	19.85
Flash Point	°C	185

After the transesterification process have been conducted, the obtained biodiesel's physicochemical properties were measured. The biodiesel yield obtained were 91%. The data were tabulated in Table 4.2. The kinematic viscosity at 40°C is 4.5043mm^2/s, the density at 15°C is 877kg/m^3, the acid value 0.49mgKOH/g, the FFA content is 0.24wt%, the higher heating value is 40.31MJ/kg, the oxidation stability at 110°C is 19.85 Hour, and lastly the flash point is 181.1°C.

Table 4.2: Physicochemical Properties of the obtained WC50J15P35 Biodiesel Compared to Commercial Biodiesel and Biodiesel Standards

Property (Unit)	WC50J15P35 biodiesel	Waste cooking oil biodiesel	Jatropha oil biodiesel	Palm oil biodiesel	Biodiesel Standard (EN 14214)
Biodiesel Yield (%)	91	90	90	92.3	Min 96.5
Kinematic Viscosity at 40°C (mm^2/s)	4.504	5.3	4.8	4.415	3.5 – 5.0
Density at 15°C (kg/m^3)	870	897	880	878	860 – 900
Acid Value (mgKOH/g)	0.44	0.2	0.40	0.5	Max 0.50
FFA Content (wt%)	0.22	0.10	0.20	0.25	Max 0.25
Higher Heating Value (MJ/kg)	40.01	42.65	39.23	40.135	-
Oxidation Stability at 110°C (Hour)	19.85	5.22	3.27	16	Min 6
Flash Point (°C)	185	195.85	135	182	Min 101

Source: (Demirbas, 2009), (Udomsap, Nuwong Chollacoop, Udomsap, Chollacoop, Topaiboul, & Hirotsu, 2009), (Jain & Sharma, 2011), (Datta, Palit, & Mandal, 2014), (MPOB, 2011), (Kołwzan & Narewski, 2013)

4.2 Discussion

To compare the physicochemical properties of WC50J15P35 biodiesel with the commercial biodiesel and biodiesel standards, all the data of commercial biodiesels and biodiesel standards were tabulated in Table 4.2. The biodiesel standards used was EN 14214. First and foremost, based on the biodiesel standard, the biodiesel yield should be more than 96.4%, but the obtained result from the experiment only 91% were achieved.

While in other researches, the amount of biodiesel yield is 90% for waste cooking oil biodiesel and jatropha biodiesel and 92.3% for palm oil biodiesel. Considering the limitation of time given to conduct the experiment, the results could be improved with the amount of catalyst loading, molar to oil ratio, and reaction time.

The kinematic viscosity of WC50J15P35 biodiesel is 4.504mm^2/s which is lower than waste cooking oil biodiesel and jatropha oil biodiesel at 5.3mm^2/s and 4.8mm^2/s respectively. While higher by 2% compared to palm oil biodiesel which is at 4.415mm^2/s. The biodiesel standards stated the value must be within 3.5mm^2/s to 5.0mm^2/s. The value of viscosity must be at the lower region because if the value is high, it will lead to formation of oxidized polymeric compounds and this can lead to clogging of filters in engine due to the formation of gums and sediments.

Next up is the density of WC50J15P35 at 15°C which is 870kg/m^3. It is the lowest compared to the other biodiesels. Waste cooking oil biodiesel at 897kg/m^3, jatropha oil biodiesel at 880kg/m^3, and palm oil biodiesel at 878kg/m^3. While the biodiesel standard stated the density should be between 860kg/m^3 to 900kg/m^3. The lower the value of density is better because high density value indicate some impurities in the biodiesel.

For the acid value in biodiesel, it indicates the level of free fatty acid (FFA) present in biodiesel. The ideal acid value according to biodiesel standard EN 14214 should be maximum of 0.50. In this experiment, the acid value of WC50J15P35 is 0.44mgKOH/g, which is lower than palm oil biodiesel of 0.5mgKOH/g, but higher than waste cooking oil biodiesel at 0.2mgKOH/g and jatropha oil biodiesel at 0.4mgKOH/g. A high acid value can cause premature failure in engine as it can have a strong solvency effect on rubber seals and hoses in the engine. Not only that, it can leave deposits which can clog the fuel filter and drop fuel pressure.

The higher heating value for WC50J15P35 is 40.01MJ/kg which is lower than palm oil biodiesel at 40.135MJ/kg and waste cooking oil biodiesel at 42.65MJ/kg but higher compared to jatropha oil biodiesel at 39.32MJ/kg. The higher heating value is important value to define the energy content and the efficiency of fuels.

The oxidation stability is one of the most important properties of biodiesel. The degradation by oxidation yields oxidation products that will compromise fuel properties. In this research, the oxidation stability of WC50J15P35 biodiesel is 19.85 hours which is the highest among all other biodiesels. The waste cooking oil biodiesel is 5.22 hours, jatropha oil biodiesel 3.27 hours, and palm oil biodiesel at 16 hours. Whereas the biodiesel standard EN14214 stated that the minimum should be 6 hours.

Lastly, the flash point is also one of the most important properties of biodiesel to determine at which temperature the biodiesel burns when there is ignition source. In this experiment the flash point for WC50J15P35 biodiesel is 185°C which is higher than jatropha oil biodiesel at 135°C and palm oil biodiesel at 182°C, but lower than waste cooking oil biodiesel at 195.85°C. The biodiesel standard EN 14214 stated that the minimum temperature should be 101°C.

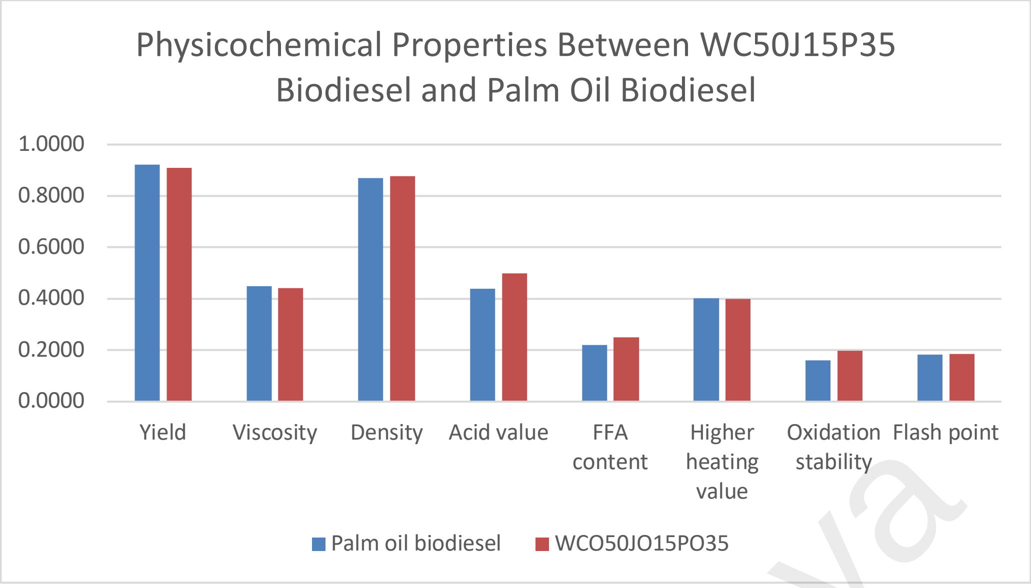

Figure 4.1: Physicochemical Properties Improvement Between WC50J15P35 Biodiesel and Palm Oil Biodiesel

The WC50J15P35 biodiesel's certain properties has improved compared to the current palm oil biodiesel physicochemical properties. Figure 4.1 indicates that the density at 15°C of WC50J15P35 biodiesel has improved by 0.9%, the acid value improved by 13.6%, the higher heating value improved by 0.3%, the oxidation stability improved by 24%, and lastly, the flash point has improved by 1.6%.

Table 4.3: FAME Content and Profile of WC50J15P35 methyl ester

FAME	Molecular formula	Carbon structure	FAME content in WC50J15P35 methyl ester (%)
Methyl laurate	$C_{11}H_{23}COOCH_3$	$C_{12:0}$	0.22
Methyl tetradecanoate	$C_{13}H_{27}COOCH_3$	$C_{14:0}$	0.79
Methyl palmitate	$C_{15}H_{31}COOCH_3$	$C_{16:0}$	32.77
Methyl palmitoleate	$C_{15}H_{29}COOCH_3$	$C_{16:1}$	0.26
Methyl stearate	$C_{17}H_{35}COOCH_3$	$C_{18:0}$	4.10
Methyl oleate	$C_{17}H_{33}COOCH_3$	$C_{18:1}$	43.28
Methyl linoleate	$C_{17}H_{31}COOCH_3$	$C_{18:2}$	13.76
Methyl linolenate	$C_{17}H_{29}COOCH_3$	$C_{18:3}$	0.23
Methyl erucate	$C_{19}H_{37}COOCH_3$	$C_{20:1}$	0.39
Saturated FAME (%)	-	-	36.87
Unsaturated FAME (%)	-	-	57.53
Total FAME (%)	-	-	96.00

The analysis of gas chromatograph was conducted to determine the FAME in WC50J15P35 biodiesel. The results in Table 4.3 above shows the FAME content for WC50J15P35 methyl ester is 96%. While the content of saturated FAME is 36.87% and the content of unsaturated FAME is 57.53%.

The tabulated results of FAME content from gas chromatograph shown in Table 4.3 indicates the dominant content is unsaturated FAME because the percentage is higher than saturated FAME. In literature, it was reported that fatty acids containing high content of unsaturated FAME will have a good cold flow property. Unsaturated FAME will reduce the acid crystals formed by saturated FAME in colder weather that will cause clogging of fuel filter thus causes improper engine operation.

Moreover, based on the biodiesel standard EN 14214, it stated that the limit of methyl linolenate or also known as linolenic acid content should be not more than 12%. In this study, the result shown in Table 4.3 above, the value of methyl linolenate is only 0.23%, which mean it complies with the standard.

CHAPTER 5: CONCLUSION & RECOMMENDATION

To sum it all up from this experiment, the feedstock WC50J15P35 has successfully converted to ternary biodiesel blend via ultrasonic assisted transesterification with a yield of 91%. Secondly, the physicochemical properties of the produced ternary biodiesel blend is better than current commercial palm oil biodiesel in Malaysia. The physicochemical properties were also complied with the biodiesel standard of EN 14214.

Despite the kinematic viscosity has lowered by 2%, the value is still in the biodiesel standard of EN 14214 range and considering the other properties has increased. The following are the recommendations for future study:

- The biodiesel yield could be higher with further experiment to be conducted by studying the effects of catalyst loading, methanol to oil molar ratio, and also the time reaction on the biodiesel yield.
- Further testing of the ternary biodiesel blend could also be conducted to run on diesel engine in real time but more time needed to complete the experiment.
- Engine performance test and exhaust emission study can be conducted on the produced biodiesel. This will provide more detailed study on the durability and degradation of the engine fuel properties to investigate the impact of using the ternary biodiesel blend.

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