

**OPTIMISATION AND RESPONSE SURFACE
METHODOLOGY STUDY OF LAURIC ACID AND
PALM FATTY ACID DISTILLATE INTO
METHYL ESTERS BY CATALYTIC
ESTERIFICATION**

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UNIVERSITI SAINS MALAYSIA

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ESTERIFICATION**

by

SIVAJOTHI A/P NADARAJAH

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AFS	Ammonium Ferric Sulphate
AFS-CS	Ammonium Ferric Sulphate-Calcium Silicate
ANOVA	Analysis of Variance
AOCS	American Oil Chemists' Society
ASTM	American Society of Testing and Materials
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCD	Central Composite Design
CCDC	Cambridge Crystallographic Data Centre
CO ₂	Carbon Dioxide
DOE	Department of Energy
EIA	Energy Information Administration
EN	European Standardisation
EPA	Environmental Protection Agency
ETAAS	Electrothermal Atomic Absorption Spectroscopy
FAME	Fatty Acid Methyl Esters
FAO	Food and Agriculture Organisation
FFA	Free Fatty Acid
FID	Flame Ionisation Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry

GHG	Greenhouse Gas
HEFA	Hydroprocessed Esters and Fatty Acid
HT	Hydrothermal
HVO	Hydrotreated Vegetable Oil
IPCC	Intergovernmental Panel on Climate Change
JCPDS	Joint Committee on Powder Diffraction Standards
LA	Lauric Acid
MPOB	Malaysian Palm Oil Board
NH ₃ -TPD	Ammonia-Temperature Programmed Desorption
OEM	Original Equipment Manufacturer
PFA	Palm Fatty Acid
PFAD	Palm Fatty Acid Distillate
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TGA/DTA	Thermogravimetric Analysis/Differential Thermal Analysis
THF	Tetrahydrofuran
WCO	Waste Cooking Oil
XRD	X-ray Powder Diffraction
XRF	X-ray Fluorescence

**KAJIAN PENGOPTIMUMAN DAN METODOLOGI PERMUKAAN
RESPON BAGI ASID LAURIK DAN SULINGAN ASID LEMAK SAWIT
KEPADA METIL ESTER SECARA PENGESTERAN BERMANGKIN**

ABSTRAK

Biodiesel telah menerima banyak perhatian di seluruh dunia disebabkan oleh keupayaannya untuk mengurangkan pencemaran udara alam sekitar dengan mengurangkan penggunaan bahan api fosil dan mengelakkan daripada kesan gas rumah hijau yang menjadikan iklim lebih panas. Kajian ini menyelidik esterifikasi asid lemak bebas dengan menggunakan kedua-dua mangkin asid homogen dan heterogen di bawah keadaan tindak balas yang sederhana. Kajian ini terbahagi kepada tiga bahagian. Pertama, pengesteran asid laurik dengan mangkin asid homogen baru iaitu amonium ferik sulfat (AFS), digunakan untuk mendapatkan keadaan reaksi optimum untuk menghasilkan penukaran metil ester yang terbaik dengan menggunakan dua kaedah pemodelan iaitu konvensional dan statistik untuk metodologi permukaan tindak balas (RSM). Kaedah konvensional dan statistik digunakan untuk menentukan hubungan antara masa tindak balas, nisbah molar metanol kepada asid laurik dan jumlah mangkin untuk menentukan keadaan optimum untuk proses pengesteran. Berdasarkan kajian ini, keadaan tindak balas optimum yang dicapai untuk pengesteran asid laurik adalah masa tindak balas 2 jam, nisbah molar 10:1 metanol kepada asid laurik dan 8 wt.% jumlah mangkin AFS pada 65 °C untuk memberikan kadar penukaran metil ester tertinggi sebanyak 97%. Kedua, kalsium silikat sisa dari kilang batik telah ditambahkan kepada ammonium ferik sulfat melalui kaedah pengisitepuan untuk menghasilkan mangkin asid heterogen yang murah, iaitu amonium ferik sulfat-kalsium silikat (AFS-CS) dalam nisbah jisim 2:1. Keadaan tindak balas untuk

pengesteran asid laurik dioptimumkan dengan menggunakan kaedah analisis konvensional dan statistik untuk memberikan penukaran metil ester maksimum sebanyak 100% dalam masa tindak balas 2 jam, 4 wt.% jumlah mangkin AFS-CS dan nisbah molar 15:1 metanol kepada asid laurik pada 65 °C. Akhirnya, sulingan asid lemak sawit diesterifikasi dengan menggunakan AFS-CS di bawah keadaan tindak balas yang dioptimumkan iaitu dalam masa tindak balas 2 jam, 12 wt.% jumlah mangkin AFS-CS dan nisbah molar 15:1 metanol kepada sulingan asid lemak sawit pada suhu tindak balas 65 °C untuk menghasilkan metil ester maksimum sebanyak 80%. Oleh itu, kedua-dua mangkin baru (AFS dan AFS-CS) ini sesuai digunakan untuk pengesteran minyak sisa dengan kandungan asid lemak bebas dan kandungan lembapan yang tinggi.

**OPTIMISATION AND RESPONSE SURFACE METHODOLOGY STUDY
OF LAURIC ACID AND PALM FATTY ACID DISTILLATE INTO
METHYL ESTERS BY CATALYTIC ESTERIFICATION**

ABSTRACT

Biodiesel has received a great deal of attention worldwide attributed to its ability to ease the environmental air pollution by reducing the use of fossil fuel and avert the warmer climate greenhouse gas effect. This study investigates the esterification of free fatty acid using both homogeneous and heterogeneous acid catalysts under mild reaction conditions. This study is divided into three parts. Firstly, the esterification of lauric acid with a new homogeneous acid catalyst, ammonium ferric sulphate (AFS), was used to get optimised reaction conditions in order to produce the best methyl ester conversion by using both conventional and statistical modelling approach of response surface methodology (RSM). Both the conventional and statistical method was used to determine the relationship between reaction time, methanol to lauric acid molar ratio and catalyst amount to determine the optimum conditions for the esterification process. Based on this study, the optimum operating conditions achieved for esterification of lauric acid were 2 h reaction time, 10:1 molar ratio of methanol to lauric acid and 8 wt.% of AFS catalyst amount at 65 °C to give the highest conversion rate of methyl ester at 97%. Secondly, calcium silicate a waste from a batik factory was added to ammonium ferric sulphate via the impregnation method to produce an inexpensive heterogeneous acid catalyst, namely ammonium ferric sulphate-calcium silicate (AFS-CS) in 2:1 mass ratio. The reaction conditions for esterification of lauric acid was optimised by using both conventional and statistical analysis method which gave maximum methyl ester conversion of 100% within 2 h

reaction time, 4 wt.% of AFS-CS catalyst amount and 15:1 molar ratio of methanol to lauric acid at 65 °C. Finally, palm fatty acid distillate was esterified by using AFS-CS under optimised reaction conditions of 2 h reaction time, 12 wt.% of AFS-CS catalyst amount and 15:1 methanol to palm fatty acid distillate molar ratio at reaction temperature of 65 °C to produce maximum methyl esters conversion of 80%. Hence, these new catalysts (AFS and AFS-CS) are suitable to be utilised for the esterification of waste oils with high FFA and moisture content.

CHAPTER 1

INTRODUCTION

1.1 Background

There is a constant need for energy in our daily life. Energy is needed as it heats our home, lights the night, fuels our transportation and powers our machines particularly in the developing nations. In recent times, researchers found that global energy consumption is still highly dependent on fossil fuel. In 2018, the total energy use from the source of fossil fuel amounts to 80% and 72.2% in the United States and European Union respectively (World Bank Group, US). Fossil fuels sources such as coal, petroleum (oil) and natural gas are concentrated natural compounds found in the earth's outer layer. From these three fossil fuels, oil has the highest impact on society as a transportation fuel that moves both people and goods around the globe.

The fossil fuels are broadly exhausted at a rate significantly higher than it's recovery cycle. This leads to depletion of fossil fuels and eventually making the progress towards becoming a non-renewable natural resource. To meet this demand and supply deficit we have to switch from non-renewable energy sources to alternative and renewable energy resources. Therefore, the demand for renewable fuels and chemicals has increased many folds in the last few decades and expected to continue in the near future (Arumugam and Ponnusami, 2019). Transportation is the biggest and quickest developing energy sector covering around 33% of the world's total energy consumption (Gielen *et al.*, 2019). In 2017, petroleum-based energy used in the transportation sector in the United States represents around 92% of the gross transportation sector as shown in Figure 1.1 (U.S. Energy Information Administration). Ethanol and biodiesel are examples of biofuel which contributed around 5% and

natural gas contributed about 3%. Ethanol and biodiesel were some of the primary energies utilised in automobiles yet were later supplanted by petroleum gasoline and diesel fuel. Today, biofuels are added to gasoline and diesel fuel.

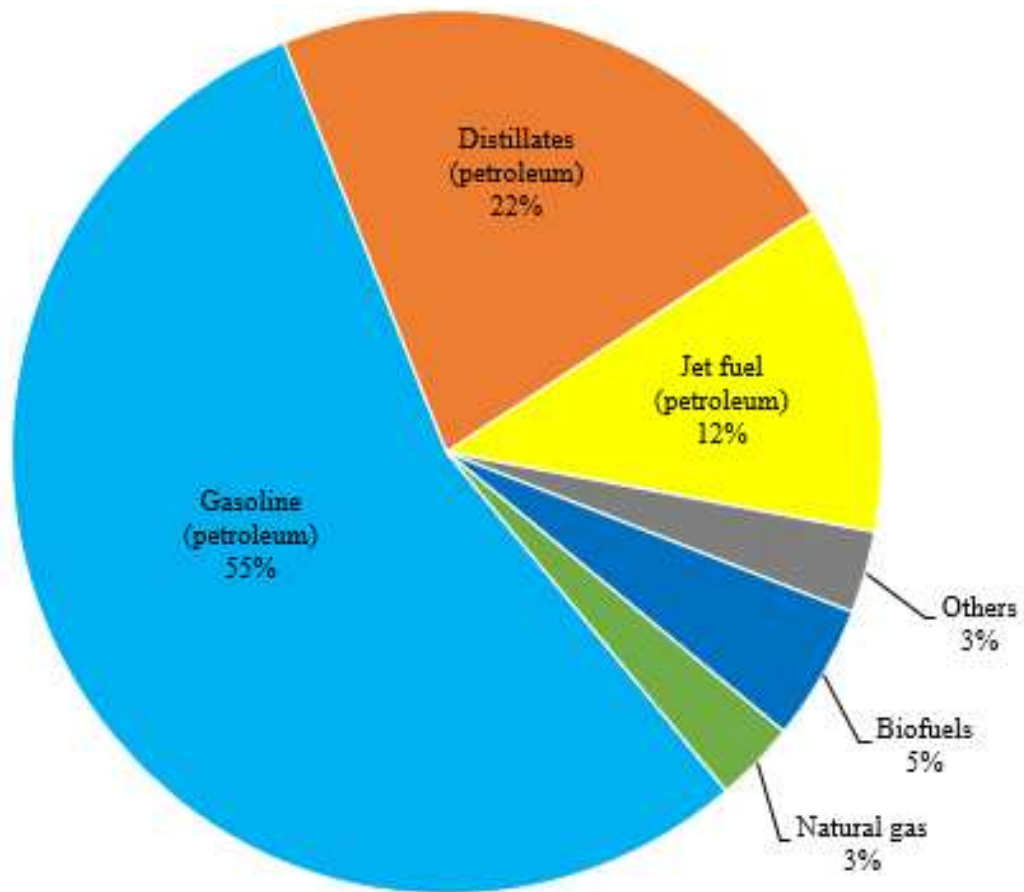


Figure 1.1 The U.S. transportation energy sources or fuels based on energy content in 2017 (adapted from U.S. Energy Information Administration)

1.2 World Energy Outlook

In 2018, the world energy demand is still rallying upon fossil fuels (35% oil, 29% coal and 24% gas) despite renewable energy (5%) and nuclear power (7%) are the world's quickest developing types of energy (Thangaraj *et al.*, 2019). Based on the New Policies Scenario, between now and 2040, the global energy demand will increase at least by one-fourth mainly in developing nations, with India being the leading country. Asia will be the next nation to consume the highest level of energy, which makes up half of global development in natural gas, 60% of the increase in wind and solar, more than 80% of the increase in oil and more than 100% of development in coal and nuclear power. In 2030, the demand for natural gas is expected to grow vividly in the industry sector which will overwhelm coal to become the second-largest fuel in the energy mix. The demand for oil will keep growing because of its use in the petrochemical sector. However, the use of oil in vehicles will reach the highest point around 2025 (International Energy Agency, 2018).

Today, petroleum and other liquids continue to be the biggest source of energy, yet the offer of world marketed energy decreases from 33% in 2015 to 31% in 2040. On a global basis, liquid utilisation increases in the industrial and transportation sectors and decreases in the electric power sector. Natural gas is the world's quickest developing fossil fuel, expanding by 1.4% per year compared with liquid's 0.7% per year and practically no development in coal usage which is 0.1% per year (U.S Energy Information Administration, 2017).

The world energy consumption relates in various ways due to fluctuation in supply, demand and innovation trends. The combination of inexpensive renewable energy innovations, digital application and the increasing aspect of electricity is an essential vector for change, in order to meet the world's sustainable development goals.

The electricity sector is encountering a vivid change since its creation more than 100 years ago. The world's final consumption is moving towards 20% and is set to increase further. Reductions in innovation cost and policy support are prompting fast development in reliable renewable sources of creation, placing the power sector at the forefront of emissions reduction endeavours. In 2017, more electricity was generated from renewable sources than coal in the European Union. Due to the huge success in Britain and Germany, the wind generation increased by 19% in 2017. In Malaysia, coal added up to 47% of fuel contribution to power stations while solar-based was only 0.2% in 2015 (Carbon Brief, 2018). Moving forward, the government in Malaysia has set up a climate change centre to tackle this problem. A new goal has been established whereby 2030, 20% of electricity will be generated from renewable sources (Smart Energy International, 2018).

1.3 Petroleum Diesel

Petrodiesel is processed from crude oil, a non-renewable energy source with broad differences in colour, from clear to tar-black, and viscosity from that of water to almost a solid (Adipah, 2019). Crude oil contains a complex mixture of hydrocarbons consist of various chain lengths and physical and chemical properties. The hydrocarbon can be divided into 5 groups consisting of three predominant groups (paraffins, aromatics and naphthenes) and two minor groups (alkenes, dienes and alkynes) (OTM, 1999). Crude oils are made out of 80 to 90% hydrogen saturated

aliphatic alkanes (paraffins) and cycloalkanes (naphthenes). Aromatic hydrocarbons and alkenes (olefins) contain 10-20% and 1%, respectively, of crude oil composition (ATSDR, 1995). Hydrocarbons containing up to 4 carbon atoms are gaseous in nature, whereas those with 5 to 19 carbon atoms are normally found in liquid form, and those with a carbon composition of more than 19 are found as solids.

Petroleum derived diesel is made out of 64% hydrocarbons, 35% aromatic hydrocarbons, and 1-2% olefinic hydrocarbons (ATSDR, 1995). The composition of petroleum hydrocarbons (PHCs) varies slightly depending upon its source, but the toxic properties are consistent. Chemicals such as benzene and polycyclic aromatic hydrocarbons (PAHs) are highly toxic components of high concern (Abdel-shafy and Mansour, 2016). PAHs are organic compounds that are mostly colourless, white or pale yellow solids. It has been proved that PAHs can cause carcinogenic and mutagenic effects and are potent immune-suppressants (CCME, 2010).

1.4 Biofuels

The worldwide energy demand is increasing very quickly and with depletion of fossil oil reserves coupled with environmental pollution and global warming, issues have led to the urgent need to develop alternative energies from renewable energy resources (Boonyuen *et al.*, 2017). The world urgently needs to move away from its dependence on fossil fuels which has a direct influence on global climate change (Perera, 2018; Woodward, 2019).

The idea of utilising substitute fuels is not new in its nature and it has existed for a long time. Substitute for diesel motor fuels that have been studied over the years extends from coal to peanut oil. At the request of the French government, the French Otto Company ran the diesel engine with peanut oil during the 1900 Paris World Fair.

In the year 1937, a Belgian patent conceded to G.Chavanne shows the early presence in the utilisation of ethyl esters derived from palm oil (Knothe *et al.*, 1997).

Research for a cleaner environment and worldwide energy security has caused a colossal increase in production and utilisation of biofuels, particularly as a substitute for transport fuels, over the past 10 years. Nevertheless, fossil fuels still continue to be the leading source of transport fuels and are accountable for vast CO₂ emissions. Worldwide carbon emission from fossil fuels has fundamentally expanded since 1990. The CO₂ emissions have expanded by around 90% since 1970, with outflows from fossil fuel burning and industrial processes contributing around 78% of the total greenhouse emissions increment from 1970 to 2011. Agriculture, deforestation and other land utilise changes have been the second biggest contributors (IPCC, 2014).

Biodiesel is the main and first economic scale fuel to have met America's EPA definition as a leading biofuel since it decreases ozone-depleting substance outflows by over half compared with petrol diesel (Ayetor *et al.*, 2015).

1.5 Biodiesel

In a near foreseeable future, biodiesel is envisaged to be a feasible substitute for fossil fuel as the production process of biodiesel is both renewable and sustainable (Zahan and Kano, 2018). Biodiesel is an eco-friendly fuel that is comprised of long-chain fatty acids of mono-alkyl esters derived from animal fats or vegetable oils using catalytic reaction (Hajjari *et al.*, 2017). The nature of biodiesel which has high oxygen content, aromatic free and sulphur free results in much cleaner combustion, prompting significantly lower discharge of environmentally destructive components compared to petroleum-based diesel fuels. Moreover, biodiesel offers the likelihood of generating energy without increasing the CO₂ released into the environment, which means the

CO₂ produced during the combustion can be reabsorbed by the plants via photosynthesis (Debnath and Giner, 2019). In addition, biodiesel has extraordinary lubricity characteristics which can prolong the engine life. In addition, it improves the lubricity of diesel amid sulphur content reduction when biodiesel is blended with diesel (Fazal *et al.*, 2019; Balajii and Niju, 2019).

Biodiesel production has drawn great attention in recent years. The most energy-efficient and easiest way to produce biodiesel is by catalytic transesterification of triglyceride with methanol to produce fatty acid methyl ester (FAME). Besides that, other techniques, for example, pyrolysis, dilution with hydrocarbons and emulsification methods are also under consideration (Mariod and Salaheldeen, 2017). In the meantime, transesterification of triglyceride produces glycerol as a by-product which has an economical value (Kolyaei *et al.*, 2016).

1.6 Problem Statements

Biodiesel is envisaged to be a feasible substitute for fossil fuel as the production process of biodiesel is both renewable and sustainable. However, the production of biodiesel derived from plant-based feedstock is not economical in the long run as this creates competition for food resources, thus increases the price for plant-based feedstock. Over-exploitation of farmlands for the production of plant-based feedstock for biodiesel instead of producing food for consumption is also a worrying trend and the indirect emission of carbon dioxide during exploitation of new land for fuel crops has also led to a long carbon payback time.

The current trend sees the shift to utilise low quality and cheap feedstocks such as waste oils and animal fats as these feedstocks are abundant and inexpensive to acquire. However, traditional transesterification process using homogeneous base

catalysts is found not suitable for processing these types of feedstocks. This is due to the high FFA and moisture content in the waste oils or animal fats which will cause saponification during the reaction and hence, lower the conversion of methyl esters. In order to overcome this situation, an acid catalyst is used to lower the FFA content before the transesterification process. Strong acid catalysts that are less susceptible to the influence of FFA can simultaneously esterify and trans-esterify low-quality feedstocks simplifying biodiesel production from low cost and high FFA content feedstocks.

Still, another matter of concern when using homogeneous acid catalysts in biodiesel production is that the catalyst will be consumed in the reaction and hence cannot be reused or recycled. The biodiesel produced using homogeneous acid catalysts also requires many purification steps resulting in higher production costs. Therefore, the focus is shifted to using a heterogeneous acid catalyst for biodiesel production from waste oils or animal fats.

1.7 Research Objectives

The overall aim of this study was to evaluate the use of the homogeneous and heterogeneous acid catalyst for esterification of FFA to produce methyl ester. The thesis also focuses on the synthesis and characterisation of both homogeneous and heterogeneous catalysts. Thus, the specific objectives of this research are as follows:

1. To evaluate the potentials of a new homogeneous acid catalyst, ammonium ferric sulphate (AFS) for esterification of lauric acid by using conventional and statistical modelling approach named response surface methodology (RSM) and the water tolerance of the catalyst.

2. To evaluate the potentials of a new heterogeneous acid catalyst, ammonium ferric sulphate-calcium silicate (AFS-CS) for esterification of lauric acid by using conventional and statistical modelling approach named response surface methodology (RSM) and the water tolerance, reusability and leaching of the catalyst.
3. To optimise the reaction conditions for esterification of palm fatty acid distillate (PFAD) using AFS-CS catalyst and the physical and chemical properties of the PFAD.

CHAPTER 2

LITERATURE REVIEW

2.1 Feedstock for Biodiesel

In 2017, the production of conventional transport biofuels derived from sugar and starch-based ethanol, oil crop biodiesel and hydrotreated vegetable oil also known as first-generation biofuels reached 143 billion litres with average development growth of around 2.5% a year foreseen throughout the following five years. The interest for hydrotreated vegetable oil (HVO), otherwise called renewable energy and hydroprocessed esters and fatty acids (HEFA) biojet fuel is relied upon to develop due to the characteristics of this energy where the fuel can conceivably be utilised unblended without modifying the engines, routine maintenance or fuel supply infrastructure. Currently, waste and residue feedstocks are used for the production of HVO and HEFA which further supports decarbonisation. Therefore, production is expected to develop as new technologies and investments are made to boost the capacity of existing plants. Production is basically located in Europe, Singapore and the United States (International Energy Agency, 2019). Generally, around 6-8% of biodiesel and HVO are generated from waste oil and animal fat feedstocks compared to overall biofuel production.

The biodiesel produced from different feedstocks is not the same despite various innovations in biodiesel generation that have been discovered. Indeed, even physical and chemical properties of biodiesel from a similar feedstock may vary depending upon the types, method of oil preparation, water content, type or loading of catalyst, the molar ratio of alcohol and even reaction time. So, in order to safeguard consumers from accidentally buying substandard fuel, OEMs (Original Equipment

Manufacturer) have agreed formally that the biodiesel must meet either ASTM D-6751 (American Society for Testing and Materials) or potentially EN 14214 (European committee for standardisation) (Beckman and Junyang, 2009; ASTM, 2015).

Practically, any plant oil or animal fats can be utilised in biodiesel production. The selection of oil supply for feasible biodiesel production must be treated with caution from both technical and economic perspectives. In terms of technical aspects, a generally shorter carbon chain which is between C₁₆ - C₁₈ is used in biodiesel. This is because longer carbon chain FAME will result in long haul debris build-up within engines due to incomplete combustion (Labatut and Pronto, 2018). Furthermore, biodiesel produced from oil sources with a straight and saturated fatty acid carbon chain is favoured due to its high cetane number (Zahan and Kano, 2018). In terms of economic aspects, the source of feedstock accounts for 80% of biodiesel production cost. Thus, it is important to consider the cost of biodiesel feedstock including the base stock, geographic zone and inconstancy in crop growth due to the difference in the climate. Generally, biodiesel feedstock can be classified into four main categories, namely plant oils, algae oil, animal fats, and waste oils.

2.1.1 Plant Oils

Plant oils can be classified into edible oils and non-edible oils. Various plant oils such as palm oil, palm kernel, canola, sunflower and coconut oil have been studied as feedstock for biodiesel production. In order to serve as a potential feedstock for biodiesel production, the plant source should contain high oil content with favourable fatty acid composition. These plants should be able to grow easily with low material input such as water, pesticides, and fertilizers so that the cost of feedstock can be reduced. In order to continue cultivating the source, they should have a definite

developing season. They should be able to develop on grounds that are not attractive for agriculture or cultivate in the off-season of regular ware crops in order to minimise the land rivalry with the development of food (Moser, 2009).

Traditional feedstock for biodiesel production is produced from edible plant oils, for example, rapeseed oil in Europe, soybean oil in the US, palm oil in Southeast Asia and coconut oil in the Philippines (Murugesan *et al.*, 2009). Amongst the most produced vegetable oil around the world is palm oil. In 2013, palm oil supplied 50 million tonnes of oil which represents more than 30% of worldwide oil production. Indonesia and Malaysia are the two major palm oil producer which produce 85% of world production (FAO, 2013). Both the flesh and the seed of the palm fruit produces oil. Crude palm oil is derived from the outer pulp of the fruit whereas palm kernel oil, another source of oil derived from the palm kernel. At room temperature, crude palm oil is semisolid. Palm kernel oil is high in saturated fatty acid namely, lauric acid and myristic acid which is less prone to oxidation (Mancini *et al.*, 2015). Vast scale biodiesel production from edible oils may lead to the global shortcoming for the food supply and demand market. Thus, create a negative impact on our planet particularly deforestation and annihilation of the environment in countries such as Malaysia, Indonesia, and Brazil where more forest has been cleared for plantation reasons (No, 2011). In order to support the constant expanding demand for biodiesel, plantation of oil crops has been significantly expanded in the previous years. In the long run, with the usage of biodiesel as an alternative fuel for petrol-based diesel fuel, this may prompt the exhaustion of edible oil supply around the world.

To overcome this problem, non-edible oils (second-generation biofuels) were used for biodiesel production. In India, non-edible oil such as jatropha and karanja oil are exploited as a substitute feedstock for biodiesel production so as to lessen the reliance on imported crude material (Patel and Sankhavara, 2017). Generally, jatropha tree grows widely in the tropical and subtropical region and depending on the variety, its seed contains high oil content of up to 43-59 wt.% (Souza *et al.*, 2018). Karanja tree can grow well in a humid tropical region and the seed contains oil ranging from 30-40 wt.% (Harreh *et al.*, 2018). Karanja oil is reddish-brown and it is rich in unsaturated oleic acids (45-70 wt.%) as the major fatty acids whereas jatropha oil contains 34 wt.% of saturated fatty acids (Syed, 2017). In terms of low-temperature operability, Karanja oil is better than jatropha oil due to its high content of oleic acids (Demirbas *et al.*, 2016). The fatty acid composition of some common vegetable oils is shown in Table 2.1.

Table 2.1 Fatty acid composition of some common vegetable oils (Thomas, 2000; Mittelbach and Remschmidt, 2004)

Vegetable oil	Fatty acid composition (wt.%)							
	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C _{18:1}	C _{18:2}	C _{18:3}	Others
Edible oils								
Soybean oil	-	-	12	3	27	52	6	-
Sunflower oil	-	-	7	5	19	68	1	-
Rapeseed oil	-	-	4	1	65	22	8	-
Palm oil	-	1	45	4	40	10	-	-
Cotton seed oil	-	1	22	3	19	54	1	-
Coconut oil	51	18	9	3	6	2	-	capric acid (6), caprylic acid (5)
Rice bran oil	-	-	15	2	43	39	1	-
Corn oil	-	-	2	11	28	58	1	-
Peanut oil	-	-	11	2	48	30	2	-
Non-edible oils								
Karanja oil	-	-	6	7	62	17	-	eicosanoic acid (3), dosocasnoic acid (4)
Jatropha oil	-	1	15	6	55	23	-	-
Rubber seed oil	-	-	10	9	25	40	16	-
Mahua oil	-	-	28	23	50	9	-	-
Tung oil	-	-	4	1	8	4	3	eleostearic acid (80)
Neem oil	-	-	16	10	50	16	8	-

2.1.2 Algae Oils

Another low-cost feedstock for biodiesel production is algae oil which produces high oil production from algae. The production of oil from algae is 200 times higher compared to the production of oil from plants per acre. Moreover, through photosynthesis algae can convert carbon dioxide and water into lipids and carbohydrates (Khan *et al.*, 2018; Khan *et al.*, 2017). Among the algae, microalgae the third generation of biofuels feedstock is the quickest developing photosynthesising living organisms which can complete a whole developing cycle every couple of days and the only supply that can be viably developed in the future (Felix *et al.*, 2019; Khan *et al.*, 2018; Medipally *et al.*, 2015). Microalgae reduce the cultivation area (per ha) when compared to feedstock production of first and second-generation biofuels. Furthermore, they can cultivate more quickly, grow in rough condition and can even live in wastewater inappropriate for human utilisation compared to the plant. The algae can be effectively grown with minimal care and require only daylight and basic nutrition (Khan *et al.*, 2018; Miranda *et al.*, 2015).

Currently, the production of microalgae is constrained to only small industries. Globally, the production of microalgae-based on the autotrophic process is only around 6000 tonnes (dry weight) per year. Basically, microalgae species are very rich in lipid where the oil level is around 40% – 60% (Saad *et al.*, 2019). Different type of microalgae species produces a different type of biofuels such as biodiesel, hydrogen, methanol, and ethanol. Some of the microalgae that produce biodiesel are shown in Table 2.2. Various technologies, for example, open pond system (Kiruthika *et al.*, 2014), closed photobioreactor system (Narala *et al.*, 2016) and raceway ponds system (Baldev *et al.*, 2018) have been deployed to economically develop microalgae to be utilised as feedstock for biodiesel production.

Mostly open pond systems such as a natural lake, lagoon, and artificial ponds are used for large scale of microalgae production (Khan *et al.*, 2018; Khan *et al.*, 2017; Borowitzka and Moheimani, 2013). The open pond system is easier to manage in terms of operation and construction compared to other systems. The drawback in these systems is that they tend to lose water by evaporation and likewise prone to contamination by undesirable species since the system is open to the atmosphere (Kiruthika *et al.*, 2014). Whereas, the photobioreactor system saves water, energy, and chemicals. It can also supply a controlled environment that can be custom fitted to the particular request of highly effective microalgae to achieve a consistently good yearly yield of algae oil (Kothari *et al.*, 2017).

Table 2.2 Biodiesel production from different microalgae species with different lipid content

Microalgae	Algae Type	Lipid (%)	References
<i>Arthrospira platensis</i>	Green	20	Baunillo <i>et al.</i> , 2012
<i>Chlorella vulgaris</i>	Green	36	Adamakis <i>et al.</i> , 2018
<i>Chlorella protothecoides</i>	Green	49	Li <i>et al.</i> , 2007
<i>Chlorococum sp.</i>	Blue-Green	31	Mahapatra and Ramachandra, 2013
<i>Haematococcus pluvialis</i>	Red	35	Damiani <i>et al.</i> , 2010
<i>Neochlorosis oleabundans</i>	Green	29	Gouveia and Oliveira, 2009

2.1.3 Animal Fats

Animal fats such as beef tallow, pork lard, chicken fat, fish oil, and insect oil can be used as a raw material for biodiesel production. Generally, animal fats are solid at room temperature due to the high percentage of saturated fatty acids compared to plant oils. Animal fats are less expensive than vegetable oils since it is considered as a by-product of poultry processing, hence making them suitable as feedstock for biodiesel production (Gaurav, 2019).

Globally, 24 billion chickens are killed every year and around 8.5 billion tons of poultry by-product is produced (Purandaradas *et al.*, 2018). Prior to biodiesel synthesis, the liquid fats and the solids (protein residue and suspended particles) need to be separated after melting the fats at 110 °C (Mata *et al.*, 2014). Since animal fats are high in free fatty acids (FFAs) content, most of the animal fats are synthesised using two-step process which is acid catalysed esterification to reduce the FFA and base catalysed transesterification of triglyceride (Bankovic-Ilic *et al.*, 2014). Alptekin and Canakci (2011) developed a two-step process on chicken fat to produce methyl ester. The base catalysed transesterification process was conducted after reducing the FFA level to less than 1%. The methyl ester produced meets both the ASTM D6751 and EN 14214 biodiesel standards when base catalyst potassium hydroxide and sodium hydroxide were used for 4 h reaction time at 60 °C.

Dias *et al.* (2009) used pork waste as raw material with sulfuric acid as a pretreatment step to reduce the FFA level via the esterification process then followed by the transesterification process with sodium hydroxide to produce 99.6 wt.% of biodiesel. Sathiyagnanam *et al.* (2012) employed the same material to produce methyl esters via the transesterification process and found that without any engine

modifications, the diesel engine can perform remarkably well on waste pork lard methyl esters. Fish oil is also another raw material that can be used to produce biodiesel. Waste fish oil was used to produce biodiesel by two-step esterification and transesterification process with acid-base catalyst. The results showed that the highest conversion of FFAs was achieved with 1.5% sulfuric acid, 15:1 methanol to oil molar ratio and 160 min reaction time. Whereas, maximum biodiesel conversion was achieved with 1% potassium hydroxide, 9:1 methanol to oil molar ratio and 60 min reaction time at 60 °C (Kara *et al.*, 2018). Zheng *et al.* (2013) found that yellow mealworm beetle can be used as an alternative feedstock for biodiesel production where 96.8% of methyl esters were produced by the two-step method which also meets the EN 14214 standard. The fatty acid composition of some common animal fats is shown in Table 2.3.

Biodiesel from animal fats has a higher cetane number compared with biodiesel from virgin vegetable oils (Ahmia *et al.*, 2014). However, the fuel produced from fats has a bigger cold filter plugging point due to the high saturated fatty acid content (Sinh *et al.*, 2019) and it is prone to oxidation due to the absence of natural antioxidants (Varatharajan and Pushparani, 2018). Hence, during cold weather, the biodiesel produced from animal fats is not suitable to be used 100% pure in vehicles but can be used 100% pure in boilers for heat generation (Niculescu *et al.*, 2019).

Table 2.3 Fatty acid composition of some common animal fats (Thomas, 2000; Mittelbach and Remschmidt, 2004)

Animal fats	Fatty acid composition (wt.%)							
	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C _{18:1}	C _{18:2}	C _{18:3}	Others
Chicken fat	-	1	23	6	42	17	1	C _{16:1} (8), C _{20:1} (2)
Fish oil	-	11	20	3	15	2	1	C _{16:1} (15), C _{18:4} (4), C _{20:6} (12)
Beef tallow	1	3	27	17	42	3	1	C _{16:1} (4), C _{17:0} (2)
Lard	-	1	30	16	40	7	1	C _{20:4} (2)

2.1.4 Waste Oils

Waste oil such as used cooking or frying oil and trap grease provides a promising sustainable oil feedstock which is relatively inexpensive and even in some cases free of cost. The quantity of waste cooking oil produced in each country is tremendous and fluctuates depending on the usage of vegetable oil (Kulkarni and Dalai, 2006). There is about 1 million ton of waste cooking oil generated per year in Brazil. Whereas in Europe, about 0.7-10 million tons of waste cooking oil is produced annually (Hanisah *et al.*, 2013). The environmental and economic aspects become very appealing when waste oil is used as feedstock for biodiesel production as it helps to reduce pollutants besides a highly valuable product is also generated. Likewise, the cost of biodiesel production is decreased by 60-90% when waste oils are replaced with refined vegetable oil as a feedstock (Chhetri *et al.*, 2008).

At present, the low cost and a large amount of waste cooking oil are from residential and restaurants are gathered and used either as feed additive or discarded, causing environmental pollution. It is estimated that around 100 million gallons of waste cooking oil is generated per day in the United States and an average of 9 pounds of waste cooking oil produced per individual per year (Ebenaza and Vinoth, 2015). Normally, waste oils are high in FFA and water content with the presence of some solid materials which must be filtered prior to biodiesel conversion. Waste cooking oil with high water content will cause hydrolysis of triglycerides to form diglycerides and free fatty acid which will subsequently cause soap formation and slow down the transesterification process. It was found that the methyl esters conversion will significantly decrease if the water content is more than 0.5 wt.% (Guan *et al.*, 2009).

Since waste cooking oil is high in FFA and water content, Demirbas (2009) proved in his study that waste cooking oil can be converted to 99.6% of methyl esters by using supercritical methanol transesterification method which can eliminate the pre-treatment and operating costs. Dhanasekaran and Dharmendirakumar (2014) used two types of used frying oils namely sunflower oil and palm oil to produce biodiesel. The results showed that after the pre-esterification process, used frying sunflower oil gave a higher biodiesel yield of 94% when the oil was transesterified with 1.0 wt.% of potassium hydroxide catalyst, 7:1 methanol to oil molar ratio and 90 min reaction time at 60 °C. A similar study was conducted on waste cooking oil which was subjected to the acid catalyst (sulphuric acid) for the esterification process as a pre-treatment in order to reduce the FFA. After the transesterification reaction, the results revealed that the waste cooking oil can be converted into 94% of methyl esters in the presence of 1 wt.% of potassium hydroxide base catalyst at 50 °C (Sahar *et al.*, 2018). Canakci and Gerpen (2001) conducted the two-step process on yellow grease and brown grease

with 12% and 33% of FFAs respectively. In the first step (esterification) the acid level was reduced to less than 1%, then transesterification reaction was conducted with a base catalyst to produce a maximum methyl ester conversion of 75.12%.

Palm fatty acid distillate (PFAD) is a waste from refining crude palm oil which is yellowish in colour and semi-solid at room temperature. PFAD has been categorised as a low-quality feedstock in view of its high FFA content of roughly 85 wt.% with palmitic acid and oleic acid as the two major fatty acid composition. Hence, homogeneous and heterogeneous base catalysts are not suitable for the transesterification of PFAD as they can cause soap formation due to the neutralisation of FFA from PFAD (Atadashi *et al.*, 2012). Therefore, the acid catalyst is the better choice for the esterification process in order to lower the level of FFA in PFAD. A study conducted by Akinfalabi *et al.* (2019) showed that the optimum reaction conditions derived from esterification of palm fatty acid distillate are 2 wt.% of sulfonated kenaf seed cake (SO₃H-KSC) catalyst, 10:1 methanol to PFAD molar ratio and 90 min of reaction time at 65 °C were successfully applied on the esterification of PFAD to give 97.9% of methyl esters. Akinfalabi *et al.* (2019) used different sulphonation method on palm waste biochar as a catalyst to produce biodiesel from PFAD. The results showed that palm waste biochar-sulphuric acid (PWB-H₂SO₄) catalyst gave the highest methyl esters conversion of 96.1% when optimised reaction conditions of 9:1 methanol to PFAD molar ratio, 2 h reaction time and 2.5 wt.% of PWB-H₂SO₄ catalyst at 60 °C were employed. The fatty acid composition of some common waste oils is shown in Table 2.4.

Table 2.4 Fatty acid composition of some common waste oils

Waste oils	Fatty acid composition (wt.%)							
	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C _{18:1}	C _{18:2}	C _{18:3}	Others
WCO ¹	-	-	9	4	45	40	-	>C ₂₀ (2)
PFAD ²	-	1	49	3	37	10	-	-
Yellow grease ³	-	2	23	13	44	7	1	C _{16:1} (4)
Brown grease ³	-	2	23	13	42	12	1	C _{16:1} (3)

¹Bautista *et al.*, 2009 ²Jumaah *et al.*, 2018 ³Canakci and Gerpen, 2001

2.2 Biodiesel Production by Transesterification

The most common technique used for biodiesel production is transesterification. Transesterification is a reversible chemical reaction where triglyceride from oil or fats will react with alcohol in the presence of a catalyst to produce fatty acid alkyl ester (biodiesel) and glycerol as a by-product as shown in Figure 2.1 (Leung *et al.*, 2010). In this reaction, the stoichiometric coefficient demonstrates that one mole of triglyceride reacts with three moles of alcohol to produce three moles of fatty acid alkyl ester and 1 mole of glycerol. Nevertheless, the reaction is carried out with an excess amount of alcohol in order to drive the equilibrium toward the product side (Singh, 2010). Methanol is the most common alcohol used in biodiesel production as it is the cheapest compared to other alcohols.

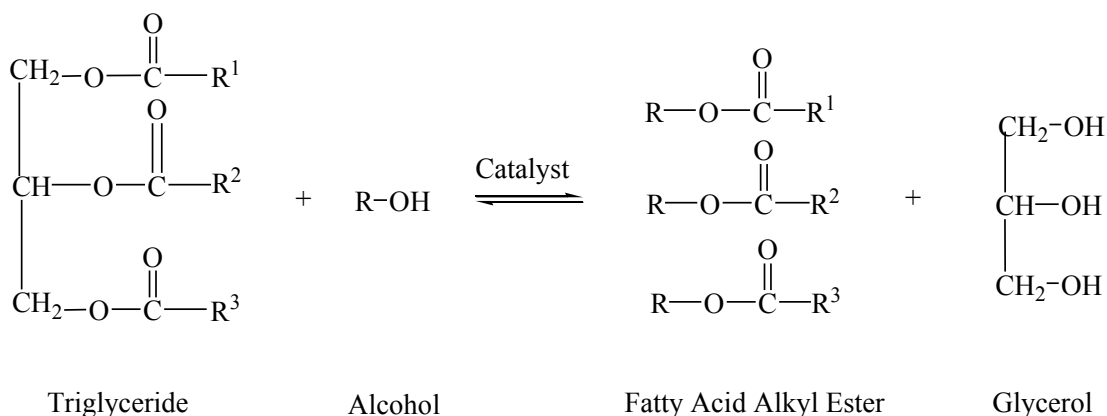


Figure 2.1 Transesterification of triglyceride with alcohol

Transesterification reaction can be carried in the absence of a catalyst but under supercritical conditions in order to increase the reaction rate. The major drawback of the supercritical procedure is that it requires extreme reaction conditions such as temperature, pressure excess methanol. A study conducted by Wei *et al.* (2013) found that optimal reaction conditions of 280 °C, 20 MPa pressure, 60:1 methanol to oil molar ratio and 90 min reaction time gave 97.8% of methyl esters conversion.

2.2.1 Homogeneous Catalyst

The other alternative is to use a homogeneous base catalyst. Sodium hydroxide, potassium hydroxide, and sodium methoxide are some of the most frequently used catalysts (Talha and Sulaiman, 2016). The main advantage of using a homogeneous catalyst is that it requires moderate reaction conditions (temperature, pressure and reaction time) to achieve high methyl esters conversion, thus it is economically favourably (Lam *et al.*, 2010; Atadashi *et al.*, 2013). However, the separation and purification of biodiesel from catalyst and glycerol are more costly and time-consuming (Zhang *et al.*, 2003a; Zhang *et al.*, 2003b). It also requires plenty of water for product washing which will increase the manufacturing cost and the catalyst is not

reusable (Boonyuen *et al.*, 2018). Besides, a homogeneous base catalyst is not suitable for transesterification if the oil or fat contains more than 2 wt.% of FFA as they can cause soap formation due to the neutralisation of FFA which will cause a reduction in biodiesel yield (Atadashi *et al.*, 2012). This triggers the researchers to shift their focus on developing a heterogeneous catalyst that is reusable and recoverable.

2.2.2 Heterogeneous Catalyst

The heterogeneous catalyst needs to satisfy a few criteria in order to be used in industrial application, they are:

- Inexpensive and easy to source or synthesis
- Feasible activity at moderate reaction conditions
- Can be reused and regenerated
- Stable in alcohol, triglycerides or methyl esters
- Thermally and mechanically stable

An ideal heterogeneous catalyst should be effective for a single step process which is simultaneous transesterification of triglycerides and esterification of FFA (Poonjarernsilp *et al.*, 2015). A heterogeneous catalyst is non-corrosive and can be easily separated from the product. Metal oxides (Liu *et al.*, 2013) and zeolites (Carrero *et al.*, 2011) are some of the most frequently used solid base catalysts. Catalyst support such as alumina (Ebiura *et al.*, 2005), silica (Suzuta *et al.*, 2012), zirconia (Kawashima *et al.*, 2008) and zinc oxide (Yan *et al.*, 2009) are used to improve the mass transfer limitation.