AGRO-BASED CATALYST SYSTEMS FOR CONVERTING PALM BASED OILS WITH HIGH FATTY ACIDS AND WATER CONTENTS INTO METHYL ESTERS

by

SHANGEETHA A/P GANESAN

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

August 2012

ACKNOWLEDGEMENTS

I would like to express my sincere and heartfelt gratitude to my supervisor, Professor Dr. Boey Peng Lim for his incessant guidance, constructive comments, relentless motivation, inspiration and advices. His incomparable supervision and approach in disseminating knowledge and ideas has certainly made me a better person in these endeavour of higher degree. Due appreciation also goes to Dr. Melati Khairuddean, my co-supervisor for her encouraging words, guidance and positive comments. My deepest and genuine gratitude also goes to Dr. Gaanty Pragas Maniam, my mentor and ex-laboratory mate for his sharing of knowledge and brotherly advices.

My sincere thanks to Universiti Sains Malaysia (USM) for the financial support through the Incentive for Postgraduates (1001/PKIMIA/823022) and USM-RU-PRGS (1001/PKIMIA/844128) and Institute of Postgraduate Studies (IPS) for the IPS research grant (308.AIPS.415401) as well as Ministry of Higher Education for awarding me the MyPhD scheme.

My appreciation also goes to Vignesh, Toh Ruh Hong and Navan for sharing their helpful ideas and knowledge. I would also like to thank my laboratory mates Pui Nyuk, Suren, Francis, Siew Ee, Sze Xooi, Sau Lai as well as Angeline, Kavitha and others for their support and company. My thanks to Mr. Chow, En. Ali, Ms. Ami, Mr. Karuna and Ms. Faizah for their assistance and also to the staff of School of Chemical Sciences, USM. Special credits go to my family members; especially my dad, mom, sister and brother-in-law for their continuous support, encouragement and trust in me to excel.

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
AAS	Atomic Absorption Spectroscopy
BJH	Barrett-Joyner-Halenda
BA	Boiler ash
BA-CaO	Boiler ash-calcium oxide
BET	Brunauer, Emmett and Teller
CaO	Calcium oxide
CCD	Central Composite Design
DOE	Department of Energy
DOT	Department of Transportation
EPR	Electron Paramagnetic Resonance
EPA	Environmental Protection Agency
FAME	Fatty acid methyl esters
FA	Ferric-alginate
FFA	Free fatty acids
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
G-block	α-L-Guluronic acid
GHG	Greenhouse gas
H_o	Hammett acidity function
H_-	Hammett basicity function
KBr	Potassium bromide
KOH	Potassium hydroxide
LA	Lauric acid

MPOB	Malaysian Palm Oil Board
MPOWCF	Malaysia Palm Oil Wildlife Conservation Fund
M-block	β-D-Mannuronic acid
MS	Mass spectrometer
MeOH	Methanol
OPA	Oil palm ash
PORIM	Palm Oil Research Institute of Malaysia
POME	Palm oil methyl esters
PFAD	Palm fatty acid distillate
PAH	Polycyclic Aromatic Hydrocarbon
RBD-PO	Refined, bleached and deodorized palm oil
RSPO	Roundtable on Sustainable Palm Oil
RSM	Response Surface Methodology
SAC-13	Niafon/SiO_2
SBC	Spent bleaching clay
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analaysis
TG-DTG	Thermogravimetry-differential thermogravimetry
TCLP	Toxicity Characteristics Leaching Procedure
TLC	Thin layer chromatography
UNFCCC	United nation's Framework Convention on Climate Change
WCO	Waste cooking oil
XRD	X-ray diffraction

SISTEM MANGKIN ASAS TANI UNTUK MENUKAR MINYAK ASAS KELAPA SAWIT YANG MEMPUNYAI KANDUNGAN ASID LEMAK DAN AIR YANG TINGGI KEPADA METIL ESTER

ABSTRAK

Kajian ini berfokus untuk menghasilkan suatu sistem mangkin berkembar bagi mengesterifikasi asid lemak bebas dan mengtransesterifikasi trigliserida dengan metanol untuk menghasilkan metil ester. Sebagai langkah pertama, abu relau yang dihasilkan daripada sisa tandan kelapa sawit telah dianalisis dan seterusnya digunakan sebagai mangkin alkali 'pseudo-homogenan' bagi pengoptimuman transesterifikasi minyak olein sawit. Abu relau berjaya mengesterifikasi minyak olein sawit dalam keadaan yang sederhana (3% abu relau kering berasaskan berat minyak, 15:1 nisbah molar metanol kepada minyak sawit olein, suhu refluks metanol dan masa tindak balas 0.5 jam) untuk menghasilkan metil ester sebanyak 90%. Kalsium oksida (dikalsinkan pada suhu 900 °C, 2 jam) telah ditambahkan kepada abu relau untuk meningkatkan toleransi abu relau terhadap asid lemak bebas dan air semasa transesterifikasi minyak yang berkualiti rendah. Suatu campuran abu relau-kalsium oksida didapati mempunyai toleransi terhadap air 3% dan toleransi terhadap asid lemak bebas (berasaskan berat minyak) 4%. Kemudian, ferik-alginat telah digunakan sebagai mangkin asid heterogen bagi mengesterifikasi asid laurik kepada metil laurat. Keadaan tindak balas yang terbaik untuk mendapatkan 99% metil laurat telah ditentukan sebagai 0.16:1 nisbah berat ferik-alginat kepada asid laurik dan 15:1 nisbah molar metanol kepada asid laurik. Masa tindak balas telah ditetapkan selama 3 jam dan tindak balas dijalankan pada suhu refluks metanol. Keadaan optimum berkenaan telah digunakan untuk esterifikasi (dimangkinkan oleh ferik-alginat) dan transesterifikasi (dimangkinkan oleh abu relau-kalsium oksida) minyak yang mempunyai sehingga 20% (berasaskan berat minyak) asid lemak bebas kepada hampir 100% metil ester tanpa pemisahan hasil selepas esterifikasi acid lemak bebas.. Kalsium oksida memainkan dua peranan iaitu; menyerap air yang dihasilkan semasa esterifikasi asid lemak bebas dan sebagai spesis aktif untuk transesterifikasi trigliserida. Walau bagaimanapun, bagi minyak yang mempunyai kandungan asid lemak melebihi 20%, seperti dalam kes asid lemak sulingan sawit dengan keasidan 87.3%, hampir 100% metil ester telah diperolehi dengan kaedah pemisahan hasil selepas esterifikasi.

AGRO-BASED CATALYST SYSTEMS FOR CONVERTING PALM BASED OILS WITH HIGH FATTY ACIDS AND WATER CONTENTS INTO METHYL ESTERS

ABSTRACT

Present work focuses on producing a dual catalyst system to esterify fatty acids and transesterify triglycerides into methyl esters in the presence of methanol. Firstly, boiler ash sourced from waste empty fruit bunches of the palm oil industry was characterized and used as a pseudo-homogeneous base catalyst for transesterification of palm olein. Boiler ash successfully transesterified palm olein at mild reaction conditions (3 wt.% dried boiler ash, 15:1 methanol : oil molar ratio, methanol refluxing temperature and reaction time of 0.5 h) to produce 90% methyl esters. Calcium oxide (calcined at 900 °C for 2 h) was added to boiler ash in order to increase the free fatty acids and water tolerance of boiler ash for transesterification of low quality oils. A mixture of boiler ash-calcium oxide was found to be able to tolerate 3 wt.% water and 4 wt.% free fatty acids. Then, ferric-alginate was used as a heterogeneous acid catalyst to esterify lauric acid into methyl laurate. The best reaction conditions to achieve methyl laurate yield of 99% was found to be 0.16:1 ferric-alginate to lauric acid weight ratio and 15:1 methanol to lauric acid molar ratio. The reaction time and temperature was fixed at 3 h and methanol refluxing temperature, respectively. The optimized reaction conditions were employed for esterification (catalyzed by ferric-alginate) and transesterification (catalyzed by boiler ash-calcium oxide) to successfully convert oil containing up to 20% free fatty acids to almost 100% methyl esters without product separation after esterification of

free fatty acids. Calcium oxide played a dual role to absorb the water produced by the esterification of free fatty acids and also as an active species for transesterification of triglycerides. However, for oils with more than 20% fatty acids content, in this case palm fatty acid distillate of 87.3% acidity, almost 100% methyl esters yield was obtained with product separation after esterification reaction.

CHAPTER 1

INTRODUCTION

1.1 Global energy outlook

The global energy demand has been estimated to increase by 30% in 2040 compared to 2010 due to the ever expanding world population and economic output. Oil, gas and coal will continue to be the most sought after energy sources making up about 80% of total energy consumption in 2040. Of the three, oil will remain as the world's most desirable energy source. The energy demand for transportation is estimated to rise nearly 45% from 2010 to 2040. From this figure, 70% of increase in energy demand will be due to commercial transportation (ExxonMobil Corporations, 2012). The mounting consciousness on the necessities of a global energy future is a step in the right direction to ensure energy security, control of pollution from fuel combustion and addressing the challenge of climate change.

Currently, about 80% of global energy demand is met by fossil fuel. The combination of renewable energy and smart usage of fossil fuel can supply half of world's energy demand by 2050. According to Sven *et al.* (2007), it is economically viable to reduce global CO_2 emissions by almost 50% within the next 43 years. However, time is running out as drastic climate change is happening now largely due to human activities, namely burning of fossil fuel bringing about dire consequences if left unchecked.

The Kyoto Protocol responded by committing its participants to reduce their greenhouse gas (GHG) emissions by 5.2% from their originally agreed upon level in 1990. The target period for the reduction was set from 2008-2012. The European Union followed suit by agreeing to increase its proportion of renewable energy from 6% to 12% by 2010 to reach its target of overall GHG reduction of 8%. For the second phase of the Kyoto Protocol, the signatories are negotiating the need for industrialized countries to reduce CO_2 emissions by 18% in the timeframe of 2013-2017 and 30% between the timeframe of 2018-2022 (Sven *et al.*, 2007).

According to the report by Sven *et al.* (2007), only with these reductions in CO_2 that the average increase in global temperature can be kept below 2 °C and otherwise the consequences will be catastrophic. Global warming aside, staggering increase in global energy demand, over-dependence on energy imports from a few countries and capricious oil and gas prices is intimidating to cause an immense stress on global economy. The principal GHG is CO_2, released by fossil fuel used in energy generation and transportation. When the atmosphere traps some of the sun's energy, warms the earth and moderates the climate; the process is known as 'greenhouse effect'. However, human activities such as burning of fossil fuels (oil, coal and gas) for energy and transport as well as deforestation contribute to the increase in greenhouse gases, thereby escalating global temperature and upsetting the climate.

The energy revolution report by Sven *et al.* (2007) also suggested five key principles to push ahead towards changing the way energy is produced, distributed and consumed. The principles are as follows:-

- Implement renewable solutions, especially through decentralized energy systems.
- Respect the natural limits of the environment.
- Phase out dirty, unsustainable energy sources.
- Create greater equity in the use of resources.
- Decouple economic growth from the consumption of fossil fuels.

1.2 Biodiesel

As the world is clamouring to prevent the effects of greenhouse gases (GHGs) from further damaging the environment, biodiesel is fast gaining momentum for expansion in terms of production and usage. This renewable energy will be able to reduce the demand for the damaging fossil fuel if produced on a larger scale thereby reducing the escalating price of diesel (Szulczyk & McCarl, 2010). Biodiesel is composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751. The history of biodiesel can be dated back to more than 100 years ago when Dr. Rudolph Diesel invented a diesel engine which ran on vegetable oils (Griffin, 1993).

In the most recent edition of WWF's The Energy Report 2011, the possibility of using 100% renewable energy by 2050 was suggested to inspire the governments and the industrialists to have a firm grasp of the idea in order to overcome challenges and fiercely move towards making the renewable economy a reality. The report recommended 10 points to achieve the 100% renewable energy future by 2050;

- Clean energy: Promote and develop existing and new renewable energy sources.
- Grids: Share and exchange clean energy through grids and trade.
- Access: End energy poverty; provide clean energy to all.
- Money: Invest in renewable, clean energy and energy-efficient products.
- Food: Stop food waste and make land available for nature, forestry and biofuel production.
- Materials: Reduce, reuse, recycle to minimize waste and save energy.
- Transportation: Promote the usage of public transport and research into alternative fuels.
- Technology: Promote research and development in energy efficiency and renewable energy.
- Sustainability: Develop and enforce strict sustainability criteria to ensure renewable energy is compatible with the environment.
- Agreements: Support climate and energy agreements to provide global guidance and cooperation on renewable energy.

1.3 Production and use of biodiesel around the world

United States was not to be left out of the race for the production and use of biodiesel. According to The National Biodiesel Board (2012), US National Biodiesel Board visions to reduce their dependence on petroleum, improve economics of local communities and to reduce harmful environmental impact by reducing vehicular emissions, net CO_2 and threats to water and ecology. Clean Air Act 1990 was implemented where its regulations required reduced sulphur content in diesel fuel and reduced diesel exhaust emissions.

In 2009, the US biodiesel production stood at over 500 million gallons with soybean oil making up major portion of the feedstock. The National Biodiesel Board (2012) claims that biodiesel has the best energy balance that stood at 3.2 units of energy gained for every 1 unit of energy put in for production. The energy balance grew to 4.56 due to improved farming and is expected to reach 5.44 by 2015. The board also reported that in 1998, 78% GHG reduction was achieved followed by 85% in 2010. Producers of biodiesel that meets American Society of Testing and Materials (ASTM) standard are issued Certified Biodiesel Markerter. In 2004, tax exemption was given for biodiesel. Since biodiesel does not contain sulphur, it meets the 2006 Ultra Low Sulphur Diesel Standard. Biodiesel is registered with Environmental Protection Agency (EPA) as both fuel and fuel additive.

Europe is the world's largest biodiesel user and producer. Its 1992 Common Agricultural Policy states that subsidy for plantations will be increased if the land is used to plant raw materials for the production of biodiesel. In 1994, 90% tax exemption was given for biodiesel compared to only 50% for diesel. In European countries, biodiesel is normally produced from rapeseed oil. European Union passed a directive requiring member nations to substitute 2% of its fossil fuel with biodiesel by 2005 and 5.75% by 2010 (Karinen & Krause, 2006). Current biodiesel blending stands at 5-10 vol.% as amended by Fuel Quality Directive. The total biodiesel demand in EU is expected to exceed 27 billion liters in 2020 with 47% of the demand met by imports (Pinto, 2011).

Japan in their national energy strategy, articulated the goal to decrease their dependency on fossil fuel to 80% of current usage by 2030. In order to achieve the goal, the government of Japan is set to introduce 500 thousand kL (oil basis) of biofuels by 2017 and to domestically produce next generation biofuel by 2015. It is worth mentioning here that the supply of biofuels in 2010 is roughly 175 thousand kL (oil basis) accounting for approximately 0.3% of domestic fuel consumption. The current government of Japan also aims at reducing Japan's GHG level by 25% than recorded in 1990 by the year 2020. A small-scale biodiesel feasibility project called the 'Rapeseed Project' where rapeseed is grown to produce cooking oil and the used cooking oil is collected to be converted to biodiesel are conducted by municipal governments and regional non-profit organizations. Another project collects used cooking oil from restaurants and individual household to be processed into biodiesel and used in government vehicles or municipal buses (Iijima, 2011).

According to India Biofuels Annual by Aradhey (2011), India is the fifth largest primary energy consumer (per international energy annual) and the fourth largest petroleum consumer in the world; making India the fourth largest global contributor to carbon emissions. Therefore, the National Policy on biofuel was approved in 2009 to encourage the use of renewable energy resources as an alternative fuel for transport and proposed to achieve the target of 20% blending of biofuel by 2017.

Malaysia joined the foray of production, utilization and exportation of palm biodiesel in 1982 when former Prime Minister of Malaysia, Tun Dr Mahathir Mohamad mooted the vision to use palm oil for fuel. He encouraged Petronas to jointly sponsor the research in 1982. In 1985 National Energy Policy was implemented. The policy stressed on the reliability and security of the biodiesel source. Financed by Petronas and in collaboration with Petronas, Universiti Malaya, Universiti Teknologi Malaysia and PORIM (now MPOB) started on Palm Oil Methyl Ester (POME) project. POME project was to evaluate development of new fuel, that can be used in existing engines without any major modifications (Salam, 1987). National Biofuel Policy was introduced in March 2006; highlighting the growing concern of the nation due to the depletion of fossil fuels, environmental issues such as GHG emissions and escalating petroleum prices. The policy encourages the use of biodiesel in line with the nation's Five Fuel Diversification Policy which is in accordance to the objectives of United Nation's Framework Convention on Climate Change (UNFCCC). The policy focuses on blending processed palm oil with petroleum diesel and converting palm oil into methyl esters (biodiesel) mainly for export. The National Biodiesel Policy is underpinned by five strategic thrusts:

- Biofuel for transport - B5 Diesel for land and sea.
- Biofuel for industry - B5 Diesel used in firing boilers in manufacturing, construction machinery and generators.
- Biofuel technology - Research, development and commercialization of biofuel technology, funded by the government and private sector.
- Biofuel for export - Malaysia have an edge because it is the major palm oil producer and exporter in the world.
- Biofuel for cleaner environment - Minimize emissions of CO_2, CO, SO_2 and particulates.

In spite of the policy that was in place since 2006, biodiesel production was at a standstill even up to 2011. The ever rising price of crude palm oil made it practically impossible for the players of the industry to maintain the operating costs. The B5 mandate was implemented in only a few states in the central region of the Peninsula which explains the lack of momentum in the increase in domestic usage of biodiesel (Hoh, 2011).

The 'food-for-fuel' and 'orang utan' habitat conservation controversies caused a great impact on the usage of palm oil in biodiesel production. In order to resolve these problems, the Roundtable on Sustainable Palm Oil (RSPO) was formed to promote the growth as well as the use of sustainable palm oil. The Malaysia Palm Oil Wildlife Conservation Fund (MPOWCF) was set up to conserve the forest of Malaysia (Malaysian Palm Oil Board, 2012; Malaysian Palm Oil Council, 2012). Moreover, the government of Malaysia has started to look at *Jatropha* as the next promising alternative feedstock for biodiesel. The Malaysia Rubber Board is engaged in seed breeding, while the Malaysian Palm Oil Board was tasked on carrying out performance tests on the *Jatropha*-biodiesel. Although a few private companies are willing to invest in *Jatropha* cultivation, the impact on the biofuel industry can only be seen in the next two years (Hoh, 2011).

1.4 Advantages of biodiesel as fuel

In view of the spiraling and volatile oil prices, the uncertainties and risks of oil geopolitics and the necessity of phasing out fossil fuel to mitigate the GHG effects, biofuel was found to be the best substitute for petroleum diesel (Griffin, 1993). Reduced emissions profile, renewable and environmental friendly properties make biofuel more desirable compared to conventional fossil fuel (Ayhan, 2006). Biofuels are fuels that are derived from biomass, that are recently living organisms or their metabolic by-product. Biofuel can be divided into biodiesel, bioethanol and biogas. The feedstock for the production of this alternative energy differentiates the three types of biofuel. As the world starts to accept the winds of change towards green energy, biofuel stands at the forefront of this ideology.

Biodiesel, a component of biofuel is rapidly emerging as a source of sustainable alternative to fossil fuel due to its renewable and green properties. Biodiesel is fast becoming nature's answer to mankind for the depletion of fossil fuel because of its comparable calorific value, low toxic emission, as well as being carbon neutral and environment-friendly. The closed carbon cycle of biodiesel with clean tail pipe emissions reduces hydrocarbons, carbon monoxides and particulate matter emissions when blended with fossil fuel; making this alternative fuel more attractive for gradually replacing fossil fuel in the near future (Knothe, 2005). In addition, the exhaust emissions of sulphur dioxides and sulphates (major components of acid rain) from biodiesel are basically eliminated in comparison to diesel fuel. Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog forming precursors. Pure biodiesel emissions have decreased levels of polycyclic aromatic hydrocarbons (PAH) and nitrited PAH compounds that are potentially cancer causing. Also, particulate matter, an emission linked to asthma and other diseases, is reduced by about 10%, carbon monoxide, a poisonous gas was reduced by 11%, unburned hydrocarbons was reduced by 21% and carbon dioxide emission was reduced by 15% when B20 blends of biodiesel was used. It was also shown that production and use of B100, led to more than 75% reduction in carbon dioxide emissions compared to petroleum diesel (National Renewable Energy Laboratory, 2008; The National Biodiesel Board, 2012).

Biodiesel has superior cetane number and lubricity characteristics compared to petroleum middle distillates, with comparable heat of combustion and kinematics' viscosity values, and is also non-flammable, making it safer to store and handle (Meher *et al.*, 2006). As an alternative fuel it is technically feasible, economically competitive, environmentally acceptable, and readily available. Biodiesel is also biodegradable, non-toxic and has low emission profiles as compared to petroleum diesel (Ma & Hanna, 1999).

Biodiesel has other general benefits; such as promoting the use of agricultural surplus which helps to improve rural economies. It is an alternative to petroleum-based fuel, which implies a lower dependence on crude oil foreign imports. The usage of biodiesel promotes reduction in GHG emissions in line with the Kyoto

Protocol agreement (Sven *et al.*, 2007; Vicente *et al.*, 2004). When 20% of biodiesel blend was used, peak thermal efficiency was improved by 2.5% and the smoke opacity values were reduced considerably (Agarwal & Das, 2001). Based on engine testing, using the most rigorous emissions testing protocols required by EPA for certification of fuels or fuel additives in the U.S., the overall potential of hydrocarbon exhaust emissions from biodiesel to form ozone (smog) is nearly 50% less than that measured for diesel fuel (The National Biodiesel Board, 2012).

Today, biodiesel is the most sought after greenhouse gas mitigation strategy for medium and heavy duty vehicles. A 1998 biodiesel lifecycle study, jointly sponsored by the U.S. Department of Energy and the U.S. Department of Agriculture, concluded that 78% carbon dioxide emissions are reduced when biodiesel is used in the place of petroleum diesel due to the closed carbon cycle of biodiesel. Plants that are growing recycle the CO_2 released into the atmosphere when biodiesel is burned and the cycle continues.

Neat (B100) biodiesel has been designated as an alternative fuel by the Department of Energy (DOE) and the U.S. Department of Transportation (DOT) (The National Biodiesel Board, 2012). Recently, the European regulations have restricted sulfur content in diesel fuel to no more than 50 weight ppm (Bournay *et al.*, 2005). World biofuel production in 2009 was believed to have reduced the global GHGs by 57% compared to equivalent petroleum fuels (Scotia Capital, 2010).

1.5 Feedstocks of biodiesel

Global biodiesel production hit 4.16 billion gallons in 2009. The usage of biodiesel is expected to double from 2009 to 2015 with United States leading the demand growth. Indonesia and Malaysia are to double their production of palm oil biodiesel, while Germany is projected to continue being the largest biodiesel producer in Europe. Biofuel is basically driven by four main factors; energy independence, climate change remediation, sustainable green economic development and the search for fuels that are lower in costs or in price volatility (Scotia Capital, 2010). Biodiesel feedstock can be divided into three main groups, namely;

- Plant-derived oils (soybean, rapeseed, oil palm), which is the most expensive.
- Animal-derived oils (includes tallow, poultry fat, white and yellow grease).
- Recycled oils and grease mainly from restaurants and food processing plants.

Biodiesel feedstock can be sourced from edible oils, non-edible oils, waste oils or animal fats. Feedstock accounts for more than 70% of the total biodiesel costs. Biodiesel feedstock makes up a major portion of the biodiesel production cost (Marchetti, 2011); mainly because, primary biodiesel feedstock are sourced from edible oils that compete with food industries. In order to reduce the cost of biodiesel production, interest looms in the direction of waste oils/fats to be used as biodiesel feedstock. The food-for-fuel controversy plaguing the biodiesel industry has shifted the interest of stakeholders and scientists alike to non-edible, waste oils and animal fats to be used as biodiesel feedstock (Chin *et al.*, 2009; Kumaran *et al.*, 2011; Ma *et al.*, 1998; Özbay *et al.*, 2008).

While United States shows interest primarily on soybean oil as a biodiesel source, many European countries focuses on rapeseed oil and countries with tropical climates preferring to utilize coconut oil or palm oil. Other vegetable oils, including sunflower and safflower have also been widely investigated. Sunflower oil (Kotwal *et al.*, 2009; Sun *et al.*, 2010), soybean oil (Batistella *et al.*, 2012; Tang *et al.*, 2008), rapeseed oil (Ivanova *et al.*, 2012; Shin *et al.*, 2012b) and palm oil (Jegannathan *et al.*, 2010; Kansedo *et al.*, 2009) are just some of the most sought after edible oils as feedstock for biodiesel production. However, the use of these feedstocks for biodiesel production is at the expense of the poor as it inevitably increases the price of the commodities. Ultimately, the price of biodiesel produced from these edible sources sky-rockets.

In an estimate made by Scotia Capital (2010), canola oil biodiesel was found to be the most expensive, followed by soybean oil and palm oil. Tallow based biodiesel was found to have the lowest price. Over the years, extensive research have been carried out in converting various types of oil such as okra seed oil (Anwar *et al.*, 2010), opium poppy oil (Laçine, 2011) and Iranian bitter almond oil (Atapour & Kariminia, 2011) into biodiesel. The International Grains Council estimates that 9% of all world vegetable oil consumption will be used for biodiesel, with rapeseed oil accounting for 50%, soy oil for 25% and palm oil for 12% of biodiesel feedstock. Although only 7.2% of world's grains and oilseeds were used for alternative and renewable fuel, uproar erupted over the usage of food source for fuel (Scotia Capital, 2010). As those who were negatively affected by soaring food price claimed the practice of using food source for fuel production is a crime against humanity.

Waste animal fat collected from slaughter house was transesterified to biodiesel with 89% methyl esters yield. A two-step, esterification (with H_2SO_4) and transesterification (with NaOH) reaction was carried out to convert the animal fats into biodiesel (Gürü *et al.*, 2009). The same group of researchers also reported the usage of waste chicken fat for biodiesel production (Gürü *et al.*, 2010). Other than chicken fat, mutton tallow (Bhatti *et al.*, 2008) and waste lard (Dias *et al.*, 2009) were also used as feedstocks for biodiesel production. The similarity between these few published works is the imperative for the two-step method to overcome the high free fatty acids (FFA) content of the oil. Animal fat from the leather industry has also been collected as feedstock for biodiesel production (Alptekin *et al.*, 2012).

However, the major problems in using these types of feedstock are the presence of high water and FFA content. Water and FFA lead to saponification and subsequent reduction in the methyl esters produced. Separation of methyl esters becomes a major problem and the conventional homogeneous base catalysts will be consumed in the reaction (Liu *et al.*, 2008). Homogeneous base catalysts can only tolerate less than 0.06 % w/w of FFA and 0.5 % w/w of water (Ma *et al.*, 1998). This promptly paved the way for heterogeneous catalysts that could tolerate water and FFA better than the homogeneous catalysts (Ebiura *et al.*, 2005; Liu *et al.*, 2008). Although continuous researches are being done on these alternatives, not many have been able to go past the lab scale production of biodiesel. Few that were able to break through have been put under very strict public scrutiny as people are becoming more knowledgeable and do not accept ideas fed to them without proof that it actually works and is here to stay.

1.6 History of biodiesel production

Many techniques had been used to convert the alternative raw sources into biodiesel. Dating back to 1980's, direct use and blending of vegetable oils was practiced by a company in South Africa. Caterpillar Brazil used pre-combustion chamber engines with a mixture of 10% vegetable oils with diesel fuel without alterations to the engine (Narayan, 2002). However, problems occurred in the engines after operating on vegetable oils for elongated period of time. The problems include:

- Coking and trumpet formation on the injectors.
- Carbon deposits.
- Oil ring sticking.
- Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

Over the years, many other techniques have been used to produce biodiesel. Some of them are microemulsion techniques, thermal cracking (pyrolysis) and currently the technique of choice, transesterification (Ma & Hanna 1999). Research has shown that the use of crude (raw) vegetable oils or blending with diesel is only suitable for short-term engine operation. Even then, the high viscosity of vegetable oils and low volatility are the major problems compared to diesel fuel (Goering *et al.*, 1987). These drawbacks may be alleviated if vegetable oils are subjected to transesterification.

1.7 Biodiesel production by transesterification

In the oleochemical industry, methyl esters are produced by transesterification of triglycerides with methanol in the presence of catalysts. Methanolysis of naturally-occurring vegetable oils and fats takes place quite readily at temperatures between 50-70 °C and at atmospheric pressure, with excess methanol in the presence of an alkaline catalyst such as sodium hydroxide or potassium hydroxide (Freedman *et al.*, 1984; Kreutzer, 1984; Sonntag, 1982). Stoichiometrically, one mole of triglycerides reacts with three moles of methanol to produce three moles of methyl esters and one mole of glycerol (Figure 1.1). Transesterification reaction lowers the viscosity while increasing the volatility of the oil. The conversion of oils to methyl esters, with suitable catalysts, reduces the molecular weight up to 66 % (Pryde, 1983). Neat biodiesel has viscosity 10 to 20 times higher than that of diesel fuel (Rakopoulos *et al.*, 2006). Transesterification can be base catalyzed, acid catalyzed, lipase catalyzed or can be non-catalytic.

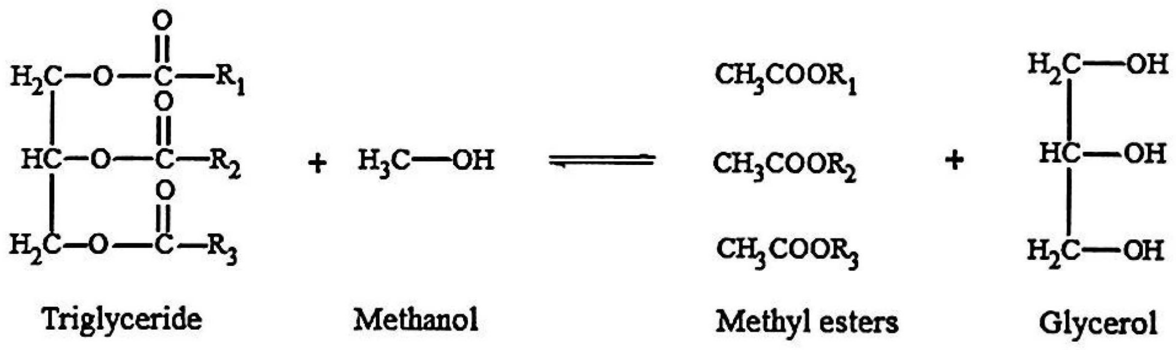

Figure 1.1:Transesterification of triglyceride with methanol

Basically, transesterification is affected by the amount of alcohol to oil molar ratio, reaction time, reaction temperature and catalyst concentration (Leung & Guo, 2006; Zhang *et al.*, 2003b). The use of excess methanol increases the yield of methyl esters and allows the phase separation from glycerol formed (Schuchardt *et al.*, 1998). However, further increase in methanol beyond the optimal amount will not cause any further increase in methyl esters yield (Agarwal *et al.*, 2012).

The effect of reaction time on transesterification also follows the same pattern as methanol amount; where the rate of conversion increases until a certain period of time and reaches a plateau. This observation is due to the reversible nature of the transesterification reaction and further increase in reaction time will eventually lead to decrease in the methyl esters yield (Eevera *et al.*, 2009). An increase in catalyst concentration also increases the methyl esters yield to certain extend. When an optimum concentration is reached, no increase in yield will be observed. Further increase will cause soap formation for homogeneously catalyzed transesterification and difficulty in stirring as far as heterogeneous catalysts are concerned, both of which will decrease the methyl esters yield (Agarwal *et al.*, 2012; Eevera *et al.*, 2009; Leung & Guo, 2006).

1.7.1 Homogeneous catalysis

Biodiesel (monoalkyl esters) are commonly produced through transesterification of triglycerides with low molecular alcohol (ethanol or methanol) in the presence of homogeneous basic catalysts such as sodium or potassium hydroxides, carbonates, sodium and potassium alkoxides such as sodium methoxides, sodium ethoxide, sodium propoxide and sodium butoxide (Ma & Hanna, 1999; Marchetti *et al.*, 2007). These catalysts are basic in nature, therefore can only be used for transesterifying low FFA oil (Ma & Hanna, 1999). Generally, homogeneous base catalysts are of interest to the biodiesel industry due to the high conversion to methyl esters in short period of time and lesser corrosive nature of the catalysts compared to homogeneous acid catalysts (Schuchardt *et al.*, 1998). Table 1.1 lists the various homogeneous catalysts available for transesterification reaction.

Table 1.1: Transesterification reaction catalyzed by homogeneous catalysts

Catalysts	References
	Base catalysts
Potassium hydroxide	Agarwal *et al.* (2012); Stavarache *et al.* (2005); Vicente *et al.* (2004)
Sodium hydroxide	Jain and Sharma (2010); Stavarache *et al.* (2005); Vicente *et al.* (1998)
Potassium methoxides	Alptekin and Canakci (2011); Mendow *et al.* (2011); Vicente *et al.* (2004)
Sodium methoxides	Chen *et al.* (2012b); Freedman *et al.* (1986); Mendow *et al.* (2011); Vicente *et al.* (2004)
	Acid catalysts
Sulphuric acid	Jain and Sharma (2010); Kildiran *et al.* (1996); Siler-Marinkovic and Tomasevic (1998)
Hydrochloric acid	Ayhan (2008)

The main drawbacks of using homogeneous base catalysts are the low tolerance towards FFA and water content. Water hydrolyses triglycerides and methyl esters to FFA, meanwhile FFA react with base catalysts to form soap which complicates the separation of methyl esters. Free fatty acids (FFA) consume base catalyst during the reaction thereby creating the need for additional catalyst to be added to the reaction system. Massive amounts of water is required to remove the catalyst and soap from the product which results in production of large amount of waste water (Liu *et al.*, 2008). Conventional base catalysts such as hydroxides and methoxides of sodium can only tolerate less than 0.06 % w/w of FFA and 0.5 % w/w of water (Ma *et al.*, 1998). Therefore, drying of feedstocks to get rid of water is important when conventional base catalysts are used (Boey *et al.*, 2011d).

However, the production cost to synthesize biodiesel through this way is higher compared to petroleum-based diesel fuel due to the use of high quality refined oils as feedstocks (Lotero *et al.*, 2005). Therefore, conventional homogeneous base catalysts are no longer feasible when it involves transesterification of low quality oils as the base catalyst reacts with FFA to form soap that eventually leads to difficulty in product separation and decrease in biodiesel yield. Figure 1.2 highlights the adverse effects of FFA and water in a homogeneous base catalyzed transesterification process.

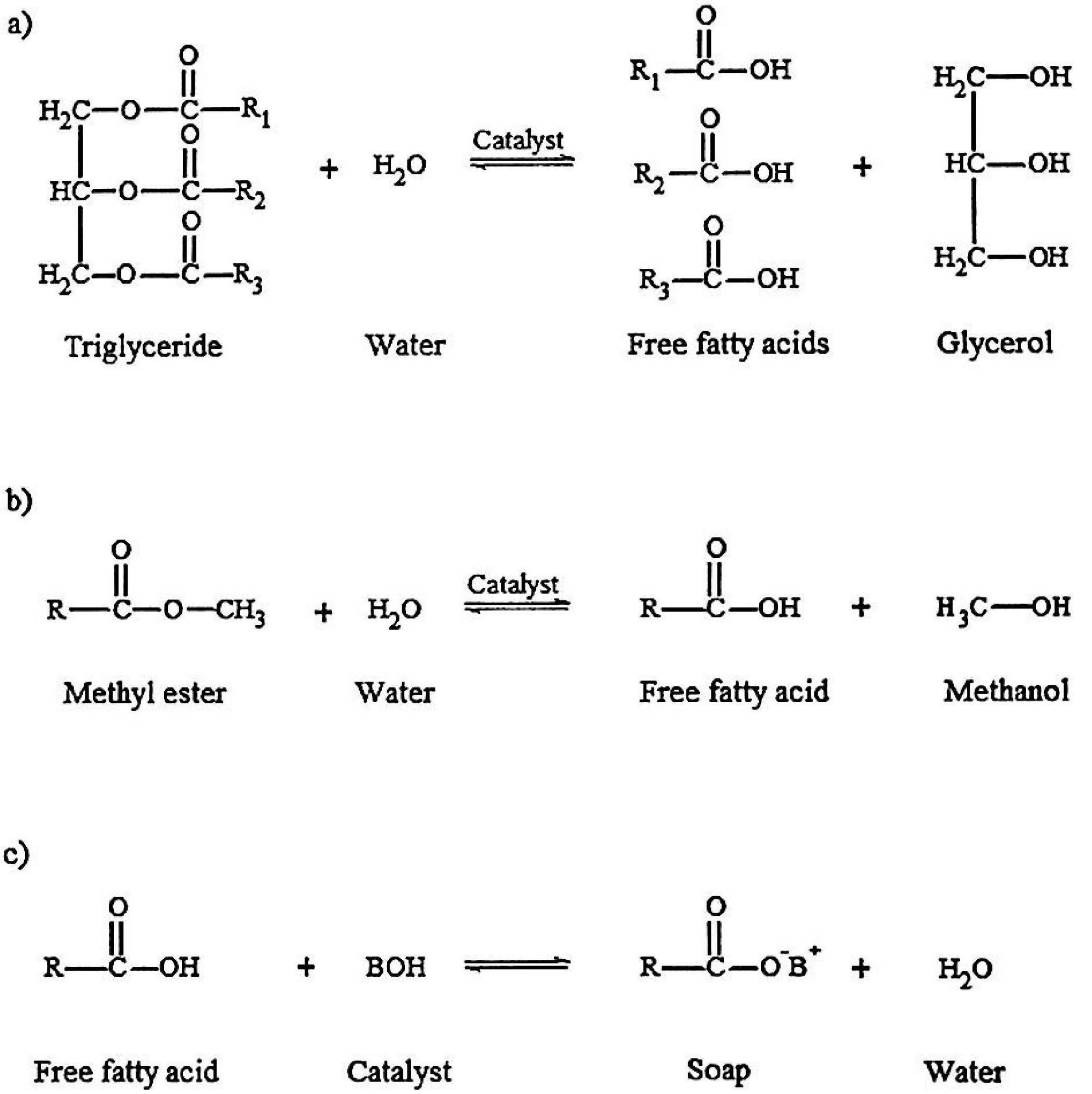

Figure 1.2: The effects of (a) water on triglycerides, (b) water on methyl esters and (c) FFA on homogeneous base catalyst

Acid catalyzed transesterification, although gives higher yield and not affected by saponification, takes a longer time and higher temperatures to be completed (Choo, 2004; Crabbe *et al.*, 2001). The fact that homogeneous acid-catalyzed reaction is 4000 times slower than homogeneous base-catalyzed reaction makes this catalyst undesirable for transesterification (Srivastava & Prasad, 2000). However, acid catalyzed transesterification is useful for transesterification of waste frying oil, which has high FFA and water content as reported by Zheng *et al.* (2006). They concluded that at 70 °C and methanol to oil molar ratio of 245:1, completion was 99±1% at 4 hours. Study has shown that the one-step acid-catalyzed procedure is more economical than the two-step alkali-catalyzed process, where an extra step is required to convert FFA to methyl esters, thus avoiding soap formation (Zhang *et al.*, 2003a; Zhang *et al.*, 2003b).

1.7.2 Heterogeneous catalysis

As discussed in Section 1.5, the use of edible oils for biodiesel production not only increases the price of the commodity but it also increases the cost of biodiesel production. Therefore, interest looms in the direction of heterogeneous base catalyzed transesterification for biodiesel production. Homogeneous catalysts are fast being pushed into extinction with the emergence of current technologies such as ionic liquid catalysts (Elsheikh *et al.*, 2011), supercritical methanol (Wang *et al.*, 2011) and heterogeneous catalysts. Heterogeneous transesterification is preferred as the process is more cost-effective and, as such, large scale production becomes comparatively easy. Various types of heterogeneous catalysts such as alkaline-earth metal oxides and solid acid catalysts have been explored for transesterification as well as esterification reactions (Albuquerque *et al.*, 2008). The main advantages of heterogeneous basic catalysts in transesterification are lower production cost due to catalyst reusability (Boey *et al.*, 2009a; García-Sancho *et al.*, 2011; Granados *et al.*, 2007) and the higher tolerance towards water and FFA (Boey *et al.*, 2009a; Lotero *et al.*, 2005). The use of heterogeneous base catalyst also paved the way for the use of waste oils and fats of higher FFA and water content for biodiesel production (Boey *et al.*, 2012b; Jacobson *et al.*, 2008). Russbueldt and Hoelderich (2010) investigated a range of rare earth oxides for transesterification of triglycerides and found that lanthanum oxide showed exceptionally high activity compared to the rest of the rare earth oxides. This observation was supported by Sun *et al.* (2010) where they reported successful usage of La_2O_3/ZrO_2 for transesterification of sunflower oil.

Another mixed heterogeneous basic catalyst, Mg/Zr (2:1 wt./wt.%) was found to be able to transesterify triglycerides of sunflower oil to methyl esters in 30 min at 65 °C (Sree *et al.*, 2009). The basic Mg-Al hydrotalcite was reported to give more than 95% methyl esters yield in 5 h for transesterification of soybean frying oil using ultrasound (Georgogianni *et al.*, 2009). Hamad *et al.* (2010) employed a novel solid base catalyst, ZrOCs, that could transesterify rapeseed oil in 5 h with methanol to oil molar ratio of 18:1 to give 100% conversion at methanol refluxing temperature. Realising the importance of discovering the best heterogeneous catalyst for transesterification reaction, scientists around the world are clamouring to investigate various combination of existing and newly discovered catalyst.

Table 1.2 lists some of the diverse heterogeneous base catalysts that have been reported since the start of the year 2012. All heterogeneous base catalysts listed in the table was reported to give more than 90% methyl esters yield with good catalyst reusability. The water and FFA tolerance of the catalysts differ from one another while maintaining tolerance well above that of homogeneous base catalysts.

Table 1.2: Various heterogeneous base catalysts for transesterification

Catalysts	References
	Heterogeneous base catalysts
CaO/KF	Liu *et al.* (2012)
CaAl2-layered double hydroxide (Hydrocalumite)	Sankaranarayanan *et al.* (2012)
$CaMnO_x$	Dias *et al.* (2012)
KF/CaO-MgO	Fan *et al.* (2012)
$Ca(NO_3)_2/Al_2O_3$	Benjapornkulaphong *et al.* (2009)
CaO/ZnO	Alba-Rubio *et al.* (2012)
CaO/ZrO	Molaei Dehkordi and Ghasemi (2012)
K/Hydrotreated TiO_2	Salinas *et al.* (2012)
KOH/alumina	Agarwal *et al.* (2012)
MgO	Gombotz *et al.* (2012)
TiO	Gombotz *et al.* (2012)
SrO/SiO_2	Chen *et al.* (2012a)
CaO/Al_2O_3	Umdu and Seker (2012)
K_3PO_4	Yin *et al.* (2012)
$Ba_{0.04}La_{1.96}O_3$	Ivanova *et al.* (2012)
Ion exchange resin	Li *et al.* (2012)

However, heterogeneous acid catalyzed transesterification was found to require higher methanol to oil molar ratio and longer reaction time compared to homogeneously catalyzed transesterification. For example, linear polystyrene was sulphonated and used to transesterify beef tallow to more than 90% methyl esters yield in 18 h with 100:1 methanol to oil molar ratio (Soldi *et al.*, 2009). However, Jitputti *et al.* (2006) showed that 1 wt.% of acidic solid SO_4^{2-}/ZrO_2 is able to transesterify triglycerides in 4 h with methanol to oil molar ratio of 6:1 to give more than 95% methyl esters conversion. However, the reaction was conducted under nitrogen atmosphere at 50 bars and at 200 °C.

1.7.3 Other catalytic and non-catalytic methods

One of the popular catalytic methods that are being intensively studied for biodiesel production is enzymatic catalysis. In a recent work reported by Batistella *et al.* (2012), they carried out transesterification of soybean oil and esterification of lauric acid with two commercial immobilized lipases under ultrasound irradiation. Although they achieved more than 90% methyl esters yield, the catalyst activity decayed after two cycles. *Candida antartica B* lipase immobilised on foam carbon was used as a biocatalyst for transesterification of *Persea americana mill* oil (Aguacate) to methyl esters with 3-methyl-1-butanol to give 100% conversion. However, the catalyst activity and operational stability was greatly affected as the by-product of transesterification, glycerol was easily adsorbed onto the surface of the immobilised lipase (Giraldo & Moreno-Piraján, 2012).