TRANSESTERIFICATION/ESTERIFICATION OF NON-EDIBLE AND WASTE COOKING OILS TO FAME AND GLYCEROL FREE FAME USING CARBON AND SILICA-BASED CATALYSTS

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by

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LIST OF SYMBOLS

		Unit
Å	Angstrom	-
cSt	centistokes	mm^2s^{-1}

LIST OF ABBREVIATIONS

AC	Activated Carbon
B5	5% Biodiesel
BET	Brunauer-Emmett-Teller
CPKO	Crude Palm Kernel Oil
DG	Diglyceride
DMC	Dimethyl Carbonate
EDS	Energy Dispersive Spectroscopy
EPA	Environmental Protection Agency
EU	European Union
FAGC	Fatty Acid Glycerol Carbonate
FAME	Fatty Acid Methyl Esters
FFAs	Free Fatty Acids
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared
GC	Glycerol Carbonate
GDC	Glycerol Dicarbonate
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
JO	Jatropha Oil
KO	Karanj Oil
MeOH	Methanol
MG	Monoglyceride
MSDS	Material Safety Data Sheet
PFAD	Palm Fatty Acid Distillate
PORIM	Palm Oil Research Institute of Malaysia
PTFE	Polytetrafluoroethylene
Rpm	Revolutions per Minute
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TG	Triglyceride
TGA	Thermogravimetric Analysis
WCO	Waste Cooking Oil

TRANSESTIFIKASI/ESTERIFIKASI MINYAK TIDAK BOLEH DIMAKAN DAN SISA MINYAK MASAK KEPADA "FAME" DAN "FAME" BEBAS GLISEROL MENGGUNAKAN MANGKIN BERASASKAN KARBON DAN SILIKA

ABSTRAK

Biodiesel, juga dikenali sebagai asid lemak metil ester (FAME), adalah bahan api pengganti untuk enjin diesel yang sedang mendapat perhatian di seluruh dunia. Walau bagaimanapun, tanggungan daripada produk hasil sampingan gliserol bernilai rendah yang dihasilkan berlebihan dalam transesterifikasi lama boleh menggagalkan perkembangan industri biodiesel. Oleh itu, kajian ini bertujuan untuk mengkaji keberkesanan dua proses (dua-langkah dan langkah-tunggal) untuk menghasilkan "FAME" bebas gliserol. Proses pertama melibatkan dua langkah tindak balas kimia yang menukarkan sulingan asid lemak sawit (PFAD) dan sisa minyak masak (WCO) kepada FAME dan produk hasil sampingan gliserol dengan mangkin hampas tebu (SCB) dan ZrSi-2 dan diikuti dengan penukaran gliserol kepada gliserol karbonat dengan dimetil karbonat (DMC) dalam langkah kedua dengan mangkin Na/AC. Proses kedua hanya melibatkan satu langkah tindak balas kimia yang menukarkan WCO dan minyak tidak boleh dimakan (minyak jatropha (JO), minyak karanj (KO) dan minyak isirong sawit mentah (CPKO)) dengan DMC untuk menghasilkan "FAME" bebas gliserol dan asid lemak gliserol karbonat (FAGC) dengan mangkin Na/AC. Semua tindak balas kimia dikaji dalam proses kelompok dan telah dijalankan pada tekanan autogenus. Mangkin berasaskan karbon dan silika yang dihasilkan telah dicirikan dengan mikroskopi elektron imbasan, tenaga serakan X-ray, luas permukaan dan spektrometri inframerah jelmaan Fourier. Luas permukaan BET mangkin SCB, ZrSi-2 dan Na/AC didapati masing-masing sebagai 55 m^2g^{-1}, 303 m^2g^{-1} dan (495 – 897) m^2g^{-1}. Pelbagai parameter seperti nisbah

molar metanol/DMC kepada minyak/gliserol (1 – 18), muatan mangkin (1 – 30) berat%, suhu (100 – 200) °C dan masa (0.5 – 6) jam tindak balas telah disiasat. Keadaan optimum diperolehi untuk dua-langkah pertama adalah 0.5 – 5 jam , 2 – 9, 150 – 175 °C, 9 – 11.5 berat%, masing-masing untuk masa tindak balas, nisbah molar metanol kepada minyak, suhu dan jumlah mangkin transesterifikasi/esterifikasi PFAD dan WCO. Selain itu, syarat-syarat optimum diperolehi adalah 1 jam masa tindak balas kimia, dua nisbah molar DMC/gliserol, 5 berat% mangkin dan 100 °C suhu tindak balas bagi proses dua-langkah kedua. Kandungan FAME optimum sebanyak 80% dan penukaran gliserol sebanyak 90% telah didapati untuk dua-langkah pertama dan kedua masing-masing. Walau bagaimanapun, keadaan optimum langkah-tunggal diperolehi adalah 150 °C suhu tindak balas, 2 jam masa tindak balas, 3 – 9 nisbah molar DMC kepada minyak dan 3 – 15 berat% muatan mangkin. Penukaran minyak sebanyak 95%, hasil FAME sebanyak 85% dan hasil FAGC sebanyak 40% telah diperolehi. Keputusan menunjukkan bahawa mangkin berasaskan karbon dan silika yang dihasilkan boleh digunakan dalam pengeluaran FAME bebas gliserol sebagai mangkin pepejal. Walau bagaimanapun, mangkin Na/AC didapati lebih hebat dari segi aktiviti dan gunapakai semula apabila menggunakan DMC sebagai sumber anion methoxide berbanding dengan metanol. Kesimpulanya, kajian ini jelas menunjukkan bahawa hasil FAME yang tinggi lebih 90% dapat diperolehi dalam proses langkah-tunggal tindak balas berbanding dengan proses dua-langkah. Kajian kinetik menunjukkan proses transesterifikasi menggunakan jatropha sebagai minyak rujukan dengan DMC boleh dihuraikan melalui kadar tertib pertama pseudo dalam julat had pengkajian dengan tenaga pengaktifan sebanyak 30.2 kJ mol^{-1} dan pemalar tindak balas kimia sebanyak 0.0354 min^{-1}.

TRANSESTERIFICATION/ESTERIFICATION OF NON-EDIBLE AND WASTE COOKING OILS TO FAME AND GLYCEROL FREE FAME USING CARBON AND SILICA-BASED CATALYSTS

ABSTRACT

Biodiesel, also known as fatty acid methyl esters (FAME), is an alternative fuel for diesel engines that is gathering attention worldwide. However, the burden of excess low-value glycerol by-product that is produced in traditional transesterification may thwart the growth of the biodiesel industry. Therefore, this study aims to investigate the feasibility of two processes (two-step and single-step) to produce glycerol-free FAME. First process involved two-step of reaction, which converted palm fatty acid distillate (PFAD) and waste cooking oil (WCO) to FAME and glycerol by-product with sugar cane bagasse (SCB) and ZrSi-2 catalysts and followed by converting glycerol to glycerol carbonate with dimethyl carbonate (DMC) in the second step with Na/AC catalyst. Second process involved only single-step reaction, which converted WCO and non-edible oils (jatropha oil (JO), karanj oil (KO) and crude palm kernel oil (CPKO)) with DMC to produce glycerol-free FAME and fatty acid glycerol carbonates (FAGC) with Na/AC catalysts. All the reactions were studied in a batch process and the reaction was carried out at autogenous pressure. Developed carbon and silica-based catalysts were characterized by scanning electron microscopy, energy dispersive X-ray, surface area and Fourier transform infrared spectrometry. The BET surface area of the SCB, ZrSi-2 and Na/AC catalysts were found to be 55 m^2g^{-1}, 303 m^2g^{-1} and (495 – 897) m^2g^{-1}, respectively. Various parameters such as methanol/DMC to oil/glycerol molar ratio (1 – 18), catalyst loading (1 – 30) wt%, temperature (100 – 200) °C and reaction time (0.5 – 6) h were investigated. The optimum conditions obtained for first two-step

were 0.5 – 5 h, 2 – 9, 150 – 175 $^{\circ}$C, 9 – 11.5 wt%, respectively, for reaction time, methanol to oil molar ratio, temperature and amount of catalyst for transesterification/esterification of PFAD and WCO. Moreover, the optimum conditions obtained were 1 h reaction time, DMC/glycerol molar ratio of 2, 5 wt% catalyst loading and 100 °C reaction temperature for the second two-step process. The optimum FAME content of 80% and glycerol conversion of 90% were found for the first and second two-step, respectively. However, the single-step optimum conditions obtained were 150 °C reaction temperature, 2 hours reaction time, 3 – 9 DMC to oil molar ratio and 3 – 15 wt% catalyst loading. The oil conversion of 95%, the FAME yield of 85% and FAGC yield of 40% were obtained. The results indicate that the developed carbon and silica-based catalysts can be used in glycerol-free FAME production as solid catalysts. However, Na/AC catalyst was found to be greater in terms of activity and reusability when using DMC as a source of methoxide anion compare to methanol. In summation, it was clearly shown from these studies that high yield of FAME over 90% could be obtained in single-step process reaction compared to two-step process. The kinetic study showed that transesterification process using jatropha as reference oil with DMC could be described by pseudo first order within the limits of the experimental date range considered with an activation energy of 30.2 kJ mol^{-1} and reaction constant of 0.0354 min^{-1}.

CHAPTER ONE

INTRODUCTION

1.1   Environmental Issue

The depletion of fossil fuels, coupled with the increasing awareness of environmental protection, has led to concerted and escalating efforts in search for a renewable and environmentally friendly alternative energy source. It is well known that, many initiatives have been taken lately to address issues and problems pertaining to global warming and the greenhouse gas effects (Rotmans and Swart, 1990; McNeff *et al.*, 2008). The main agenda of deliberation was on the need to reduce the amount of atmospheric CO_2, a cause of global warming, emitted from the automobiles and industries (Singh *et al.*, 2008). In view of the fact that much of this greenhouse gas effect is caused by the combustion of fossil fuel, many countries particularly the more advance ones are making a switch to exploit and utilize other alternative source of energy supply that are renewable and greatly contribute toward the improvement of the environment. Although economically, the utilization of these renewable energy such as biofuel may not appear to be as attractive as the conventional energy, that should not prevent its widespread use in the future as the concern towards depletion of the fossil fuel and significantly rising of fuel price and environmental factors becomes more and more pressing (Figure 1.1) (NRC, 2013).

1.2   World Biodiesel Production

In the global scene, especially on the European front, the use of methyl esters as diesel fuel has achieved widespread acceptance. Germany is the world champion in the production of ecofuels. The factory Horen Industries, in the city of Freiburg will soon begin production of biodiesel (Tolmac *et al.*, 2014). In Germany, Oil World expects global biodiesel production up 6.3% in 2013, due to more soybean oil in the US and Brazil used as feedstock. Soy oil demand for biodiesel seen up 2.9% in 2013 at just over 7 million tons while palm oil and canola oil will supply feedstock for 6.3 and 6 million tons respectively (Sapp, 2013). Hence, global biodiesel supply will have to double over the 2010-2020 timeframe to accommodate demand requirements that governments around the world are aiming to implement (Pinto, 2013).
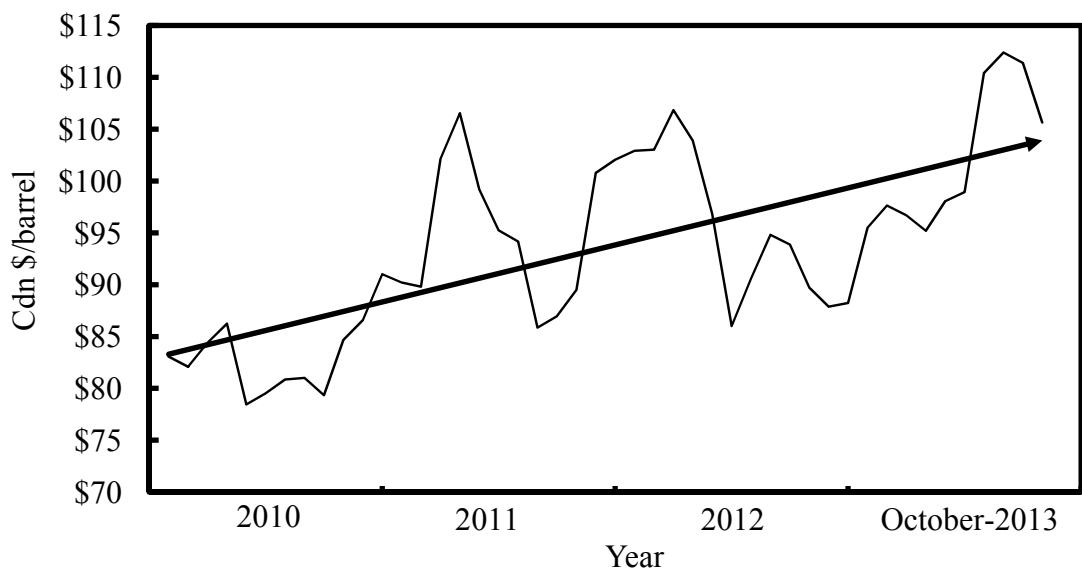
Figure 1.1   WTI NYMEX Chicago crude oil prices per barrel (2010-2013) (NRC, 2013).

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In any case, biodiesel offers the environmental advantage of reducing greenhouse gas emissions compared with the use of fossil fuels, especially in resort areas, marine parks and highly polluting cities in terms of air quality. New legislation and government incentives strongly support the use of biofuel particularly biodiesels that have been introduced (UFOP, 2005). As shown in Figure 1.2, global biodiesel production grew exponentially from less than 20 thousand barrel per day in 2000 to over 250 thousand in 2010. The EU has dominated world production. It's continuous production growth though can only be partly attributed to its extensions in the number of its Member States since the core EU biodiesel production centers are Germany and France; followed by Spain, Italy, and Poland. Many governments around the world have implemented national biodiesel production and consumption targets over the past years (Lamers, 2011). In Malaysia, the government had approved 60 biodiesel manufacturing licenses with a total annual capacity of 6.5 million tons as at end of September 2013. Of the total, 21 biodiesel plants have been commissioned since 2006 with production capacity of 2.96 million tons per year. From January to September 2013, there were 12 biodiesel plants in operation with total yearly production capability of 1.22 million tons for local consumption. The biodiesel program has contributed to 44% increase in palm biodiesel production to 249,213 tons in 2012 compare with 173,220 tons in 2011 (Adnan, 2013). Brazil has developed a new diesel combined with vegetable oil, which will drastically reduce the need for the country to import diesel. The government of biggest populated country, Indonesia, predicted the construction of 11 factories for the production of biodiesel (Tolmac *et al.*, 2014).

On the other hand, the United States has increased its production from 35 million gallons in January 2011 to 128 million gallons in August 2013 (EIA, 2013b).

While 128 million gallons is smaller than the EU production but it represent significant growth. In US, biodiesel is registered as a fuel and fuel additive with the Environmental Protection Agency (EPA) and meets clean diesel standards established by the California Air Resources Board. The Department of Energy and the US Department of Transportation have designated neat biodiesel as an alternative fuel. In the Far East, Japan, Korea, China and Thailand have also expressed interest in biodiesel in the last few years. All of these developments underscore the environmental benefits in terms of lesser green house gas emission, reduced dependence on the fossil fuel imports and positive impact on agriculture.
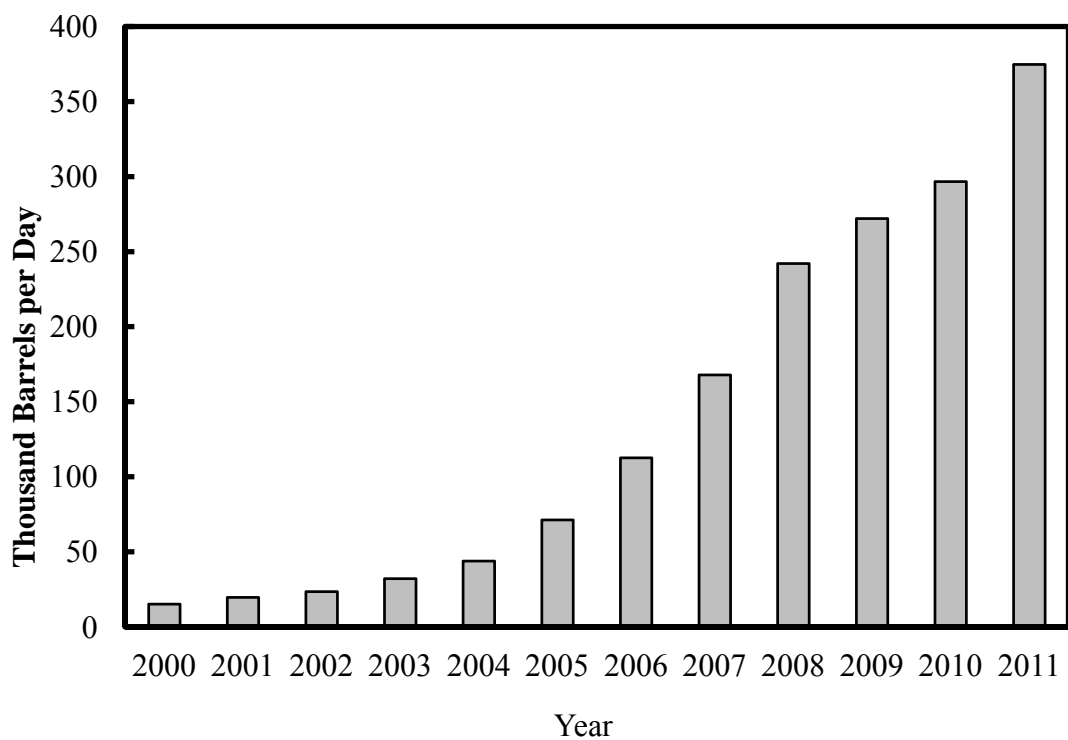
Figure 1.2   World biodiesel production by year (EIA, 2013a).

1.3   Economic Feasibility

Technically palm biodiesel project has been proven viable but it is not viable to use palm biodiesel in Malaysia, as our petroleum is still cheap. Now diesel price is RM2.00 per liter after subsidized with RM0.74 from the government (Malek, 2013) while crude palm oil prices range from RM2225 to RM2545 per ton in the next 12 to 18 months 2014 (Fitch, 2014). It is very feasible for the oversea market where the petroleum diesel is very expensive. For example, In Germany, the petroleum diesel is sold at about one US dollar per liter excluding taxes (EIA, 2013c). Nevertheless, biodiesel price depends primarily on the cost of feedstocks, the price of which makes 70 – 95 % of the total biodiesel cost (Balat, 2011; Gui *et al.*, 2008; Leung *et al.*, 2010). The use of cheap non-edible oils can be a way to develop the economy of biodiesel production and its viable production at the industry scale. For the reason that of different climate conditions, different countries have been looking for different types of non-edible vegetable oils for potential use in biodiesel production (Banković-Ilić *et al.*, 2012).

1.4   Non-edible Feedstocks

Lately, non-edible oils have been considered as prospective raw materials for fatty acid methyl ester production. This is mostly credited to their capability to surmount the dilemma of fuel versus food predicament associated to fatty acid methyl ester production from edible oils. Furthermore, they are simply obtainable in any areas particularly that are not fortunate for food cultivation; reduce rate of deforestation, more environmentally amicable, more competent, and economical

comparable to edible oils (Silitonga *et al.*, 2011; Atabani *et al.*, 2012; Mofijur *et al.*, 2012).

Several instances of non-edible oils that are obtainable globally are *Jatropha curcas* L. (available in Thailand and Indonesia), *Millettia pinnata* L. (available in India), kernel of the oil palm *Elaeis guineensis* Jacq., and palm fatty acid distillate (available in Malaysia and Indonesia) (Wu *et al.*, 2014; Halder *et al.*, 2014; Cho *et al.*, 2012b; Jitputti *et al.*, 2006). Other feedstock for fatty acid methyl ester is waste cooking oil readily available at any restaurant or café locally, which have been considered a promising alternative with a relative cheap price for fatty acid methyl ester production in comparison with fresh vegetable oil. Fatty acid methyl ester from waste cooking oil is one of the options for economical sources of fatty acid methyl ester production (Tanawannapong *et al.*, 2013; Talebian-Kiakalaieh *et al.*, 2013; Shah *et al.*, 2013a). However, it must be mentioned that global fatty acid methyl ester feed stocks should not depend on certain sources. Hence, fatty acid methyl ester feedstock should be as diversified as possible, depending on geographical locations in the world (Atabani *et al.*, 2013).

1.5   Two Processes for Glycerol-Free FAME Production

Currently, triglycerides are seen as good potential raw materials for biodiesel production, due to their effortless availability from non-edible and waste cooking oils. Nevertheless, in the preparation of biodiesel from triglycerides, 10 wt% of glycerol has been always co-produced, which without doubt reduces the finances of the process (Simanjuntak *et al.*, 2011). In this situation, conversion of glycerol

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into high value added chemicals and produce glycerol free FAME is highly important.

There are two processes to produce glycerol-free FAME which is shown in Figure 1.3. The first process is a two-step process which produces glycerol and FAME in the first step reaction. After that, the glycerol by-product which produced in the first two-step can be used to convert to more valuable chemical commodity in the second step of the reaction. Hence, with this two-step process, the production cost of FAME will be reduced indirectly with the trade of more valuable chemicals from glycerol by-product. Alternatively, the second process is a single-step process which directly producing glycerol-free FAME in one step chemical reaction. This single-step process will bypass the separation and purification process of glycerol by-production for the second two-step process. In conclusion, these two-step and single-step processes will easily overcome the dilemma from excess of glycerol by-product and significantly reduce the FAME production cost.

1.6   Problem Statement

Currently, fatty acid methyl esters are generally underwent transesterification/esterification of triglyceride/free fatty acid with short chain alcohols. Homogeneous acid or base catalysts are normally used in this reaction. Nevertheless, in the homogeneous reaction, it is difficult to remove the base catalysts after reaction, saponification and emulsion are formed by aqueous quenching, resulting in difficulty of the FAME separation, and a substantial amount of wastewater was generated to divide and scavenge the products and the catalyst. For that reason, ecologically cordial heterogeneous catalysts are likely to take the place

of homogeneous catalysts in the future as a result of reduced complexity in the existing processes and environmental restraints.

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│  Two Processes for Glycerol-Free │
│       FAME Production        │
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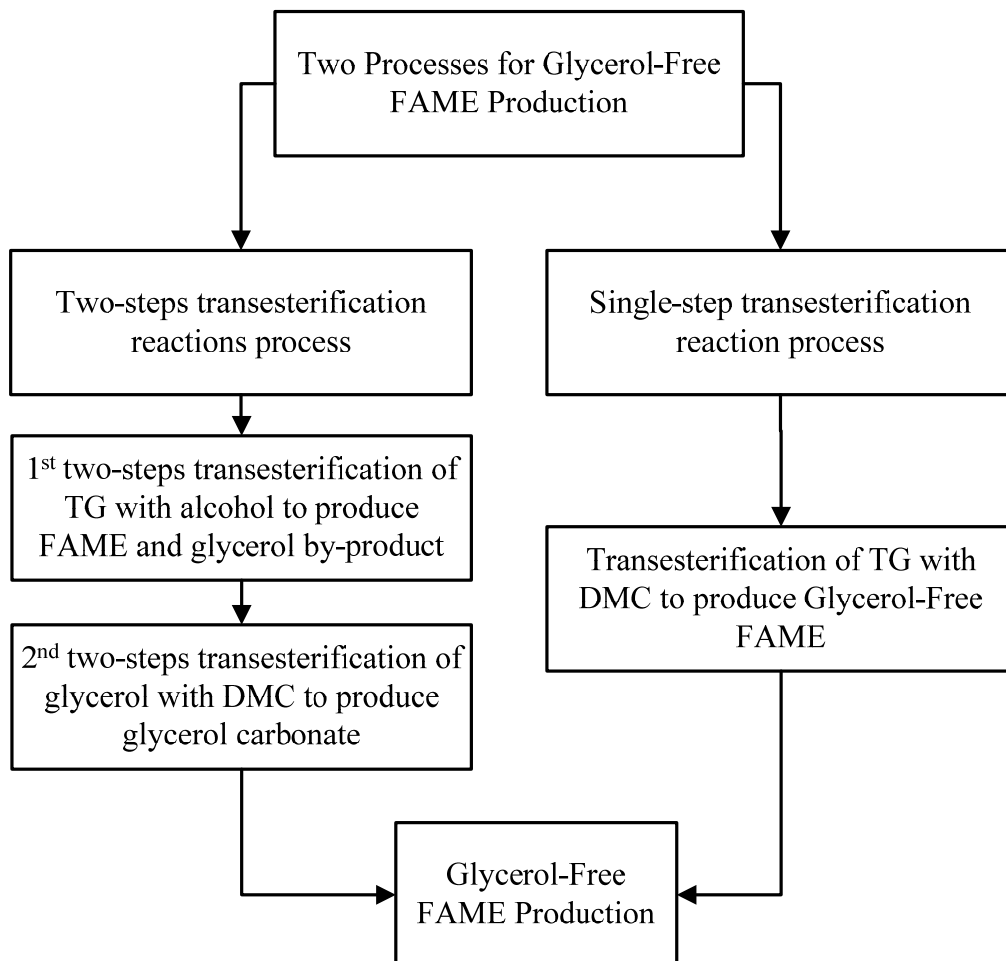
Figure 1.3   Two processes for glycerol-free FAME production.

This research considers the development of carbon and silica-based catalysts that will meet the criteria such as catalyst stability (leaching and reusability), availability and simplicity in method of preparation. Hence, sugar cane baggase was selected for catalyst support due to low cost and readily available, while, Na/AC and ZrSi were selected as heterogeneous catalysts due to its high surface area and simplicity in preparation for Na/AC catalyst.

Furthermore, the transesterification/esterification process converts triglycerides or FFA into FAME, but glycerol is discarded as undesired by-product. Then again, 10 to 20% of the total amount of product formed is composed of glycerol. Increasing FAME production will direct to huge surpluses of glycerol. In addition, the incrementing development in FAME production may create difficulty for the market distribution of glycerol, reducing its price. As a result, new utilizations of glycerol plus alternatives plan to convert it into glycerol derivatives are now under research. This has become one of the key justifications that the present research is fixated on developing expertise to utilize the glycerol with the aim of amending the biodiesel financially viable and significantly amend its business.

Hence, this study aims to investigate the feasibility of different synthesized carbon and silica-based catalysts as heterogeneous catalysts for transesterification/esterification of non-edible (palm fatty acid distillate, jatropha, karanj and crude palm kernel) and waste cooking oils to glycerol-free fatty acid methyl esters in two-step or single-step processes.

1.7   Research Objectives

The purpose of this research was to develop efficient heterogeneous catalysts for the production of fatty acid methyl esters (FAME) and glycerol-free FAME from non-edible and waste cooking oils. The specific objectives were focused to:

i)   Develop heterogeneous (sugar cane bagasse as catalyst support, ZrSi and Na/AC) catalysts for the transesterification/esterification of non-edible

(palm fatty acid distillate, jatropha, karanj and crude palm kernel) and waste cooking oils.

ii) Characterize the developed catalysts in terms of surface morphology, energy dispersive spectroscopy, surface area, pore volume, pore size and Fourier transform infrared spectrometry.

iii) Study the activity of the developed (sugar cane bagasse, ZrSi and Na/AC) catalysts and variation in reaction parameters (reaction temperature, the amount of catalyst, reaction time and methanol to oil molar ratio) and obtain optimum value for the parameters to produce glycerol and FAME from non-edible (palm fatty acid distillate) and waste cooking oils for the first two-step process.

iv) Study the activity of the developed Na/AC catalysts and variation in reaction parameters (reaction temperature, amount of catalyst, reaction time and DMC to glycerol molar ratio) and obtain optimum value for the parameters to produce glycerol carbonate from glycerol for the second two-step process.

v) Study the activity of the developed Na/AC catalysts and variation in reaction parameters (reaction temperature, amount of catalyst, reaction time and DMC to oil molar ratio) and obtain optimum value for the parameters to produce glycerol-free FAME from non-edible (jatropha, karanj and crude palm kernel) and waste cooking oils for single-step process.

vi) Evaluate kinetic parameters for the transesterification of Jatropha oil with DMC over Na/AC catalyst.

1.8   Scope of Research

The scope of the present study covered the development, characterization, and the test of activity of the developed heterogeneous catalysts in transesterification/esterification of non-edible and waste cooking oils with methanol or DMC to produce FAME and glycerol-free FAME. The catalysts were developed on carbon and silica based. Sugar cane bagasse catalyst was prepared by sulphonation of partially carbonized sugar cane bagasse with excess of concentrated H_2SO_4 (96%) in an autoclave. ZrSi was synthesized by hydrothermal method with $ZrOCl_2 \cdot 8H_2O$ and TEOS as Zr and Si sources, respectively. The catalysts preparations were studied to establish optimum preparation parameters such as Na loading on activated carbon and calcinations temperature to give the best results. A particular amount of pellet NaOH between 5 to 40 wt% of AC was dissolved in distilled water and mixed together with activated carbon. On the other hand, calcinations of the sodium supported on activated carbon catalyst were conducted between 250 to 650 °C. Synthesized catalysts are characterized using scanning electron microscope (SEM), transmission electron microscopy (TEM), surface area and pore size distribution analyzer, Fourier transform infrared (FTIR) and X-ray diffractometer (XRD).

Furthermore, the key idea of this study is to develop reusable heterogeneous catalysts for the syntheses glycerol-free FAME by two-step process and single-step process. The two-step process was at first converting PFAD/WCO to produce FAME and glycerol by-product. In this first two-step process, sugar cane bagasse, ZrSi and Na/AC catalysts are employed. Subsequently, upgrading glycerol to glycerol carbonate in the second step of reaction. In this second two-step process, commercial

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glycerol was used instead of glycerol by-product in order to stay away from the uncertainty of glycerol by-product concentration from the first two-step reaction. Besides, in the step, Na/AC was used as a catalyst for transesterification of glycerol to produce GC.

On the other hand, single-step process converting non-edible and waste cooking oils to glycerol-free FAME was also carried out with the developed Na/AC catalysts. The scope covered three non-edible oils, namely, Jatropha oil, Karanj oil and Crude Palm Kernel oil. This single-step process offers realistic and cost-saving benefits since it enables the production of FAME without requiring steps to remove or upgrading glycerol by-product.

The esterification/transesterification reaction were carried out in 100 mL stainless steel reactor. The reaction variables were methanol/DMC molar ratio (1 – 18), catalyst loading (0 – 30 wt%), reaction temperature (100 – 200 °C) and reaction time (0.5 – 6h). The reusability of the developed catalysts was also examined up to five consecutive reaction cycles at the optimum reaction conditions. Kinetic study was conducted for the transesterification of Jatropha oil with DMC using developed Na/AC catalyst.

1.9   Organization of the Thesis

There are five chapters in this thesis. An overview on biodiesel usage and viability of biodiesel production from non-edible and waste cooking oils are outlined in Chapter One. The problem statement, research objectives, scope of research and organization of the thesis are also provided in this chapter.

Chapter Two presents a review of the literature. It is divided into seven major sections. The first section gives a review about the properties of reactants and products. This is followed by detailed information on the transesterification and esterification reaction in section two. Then, review of different processes for glycerol-free biodiesel production is given in section three with two-step and single-step process. Comparison between homogeneous and heterogeneous catalysts is provided in section four. Section five focuses on the technical aspect of biodiesel production by transesterification/esterification using heterogeneous catalysts. Section six focuses on the kinetic study. Lastly, a short summary on the literature review is presented in section seven.

Chapter Three covers the methodology for the experimental work done in this research. This chapter is divided into three sections. The first section presents the materials such as fatty acids and oils, chemicals and gases used in the experiments. The second section gives a general description experimental set-up, analysis system and general description of the characterization of the solid catalysts. On the other hand, the third section provides explanation on the experimental procedure in this study.

Chapter Four presents all the acquired results and discusses on the findings. It is grouped into eight main sections. Section one introduction while section two presents the characterization of solid catalysts. Section three presents the transesterification/esterification of PFAD and WCO with methanol for FAME production. In section four presents the transesterification of glycerol to glycerol carbonate. Single-step transesterification reaction process for glycerol-free FAME production is presented in section five while section six presents the comparison

between two-step and single-step glycerol-free FAME production process. Lastly, section seven presents kinetic model of transesterification of JO with DMC and section eight presented the calculation of activation energy.

Finally, Chapter Five gives the conclusion and some recommendations for future research. The conclusions are written according to the finding found in Chapter Four. Based on the conclusion, recommendations for future work are suggested.

CHAPTER TWO

LITERATURE SURVEY

This chapter provides the literature review of the properties of reactants and products in section one. Section two provides an outline of transesterification and esterification reaction. After that, different process for glycerol-free biodiesel production is presented, followed by a comparison between homogeneous and heterogeneous catalysts. The technical aspect of biodiesel production by transesterification/esterification using heterogeneous catalyst is presented in section five. Kinetic study is presented in section six and lastly, a short summary on this chapter is provided in section seven.

2.1   Properties of Reactants and Products

2.1.1   Properties of Non-Edible and Waste Cooking Oils

Around the world, more than 350 plant oils known as prospective raw materials for FAME production (Balat M and H., 2008; Silitonga *et al.*, 2011; Atabani *et al.*, 2012; Mofijur *et al.*, 2012). However, vegetable oils have high viscosity (30 – 40 cSt at 38 °C) which is due to their bulky molecular mass (600 – 900) that is near 20 times higher than petroleum diesel (Goering *et al.*, 1982; SEA, 1996). Besides, vegetable oils have very high flash point (> 200 °C). Nevertheless, the volumetric heating values (39 – 40 MJ kg^{-1}) are insignificant difference compared to petroleum diesel ($\approx$ 45MJ kg^{-1}) due to the presences of chemically bound oxygen in vegetable oils (Barnwal and Sharma, 2005).

Vegetable oils, also known as triglycerides, have the chemical structure given in Figure 2.1 comprise of 98% triglycerides and small amounts of mono- and diglycerides. Triglycerides are esters of three molecules of fatty acids and one of glycerol and contain substantial amounts of oxygen in their structure. The fatty acids vary in their carbon chain length and in the number of double bonds (Barnwal and Sharma, 2005).
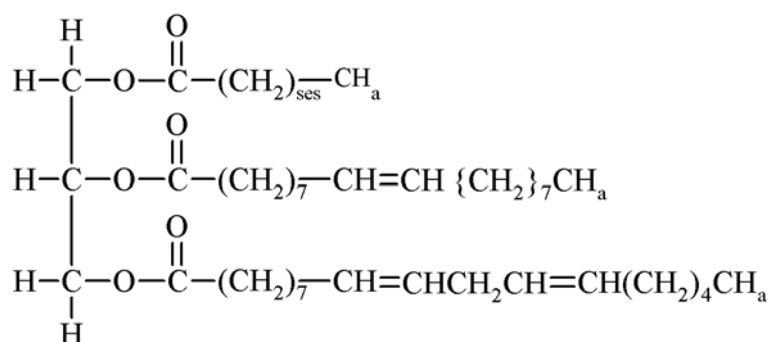
Figure 2.1   Structure of a typical triglyceride molecule (Barnwal and Sharma, 2005).

Besides, different types of oils have different types of fatty acids. The empirical formula and structure of various fatty acids present in vegetable oils are given in Table 2.1. In addition, the plant oils generally contain free fatty acids, odorants, water, phospholipids, sterols and other impurities. For that reason, the oil cannot be utilized as fuel straightforwardly. To solve these problems the oil requires minor chemical alteration generally transesterification, esterification, pyrolysis or microemulsification. Among these, the transesterification and esterification is the solution and leading main step to produce cleaner and environmentally safe fuel from vegetable oils (Meher *et al.*, 2006b).

Table 2.1   Chemical structure of common fatty acids (Marckley, 1960).

Name of fatty acid	Chemical name of fatty acids	Structure (*xx:y*)	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9-,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucle	*cis*-13-Docosenoic	22:1	$C_{32}H_{42}O_2$

xx indicates number of carbons, and *y* number of double bonds in the fatty acid chain.

Meanwhile, a by-product, palm fatty acid distillate (PFAD), being unavoidably produced in the palm oil refinery purification process is used as feedstock in this research. It is low cost (US$ 814/ton) compared to other refined oils such as RBD palm oil (US$ 1117/ton) which are used in present biodiesel production (Cho *et al.*, 2012a).

In order to assess non-edible feedstock feasibility for biodiesel production, preliminary assessment of the chemical and physical properties is paramount. For that reason, this section reviews the properties of some non-edible feed stocks (palm fatty acid distillate (PFAD), jatropha oil (JO), karanj oil (KO), crude palm kernel oil (CPKO)) and compares with palm oil. Table 2.2 below shows the comparison among various feed stocks in terms of fatty acid composition.

Table 2.2   Comparison among various feed stocks in terms of fatty acid composition (%) (Bonnie and Mohtar, 2009)[a], (Henning, 2004)[b], (Halder *et al.*, 2014)[c]

Fatty acid	Palm fatty acid distillate[a]	Palm oil[b]	Jatropha oil[b]	Karanj oil[c]	Crude palm kernel oil[b]
Oleic	36.7	39.2	44.7	40.8	15.4
Linoleic	0.31	10.1	32.8	19.93	2.4
Palmitic	46.9	44.0	14.2	22.42	8.4
Stearic	4.3	4.5	7.0	7.4	2.4
Palmitoleic	0.15	-	0.7	-	-
Linolenic	9.03	0.4	0.2	-	-
Arachidic	0.28	-	0.2	1.32	0.1
Margaric	-	-	0.1	-	-
Myristic	1.2	1.1	0.1	-	16.3
Caproic	-	-	-	-	0.2
Caprylic	0.17	-	-	-	3.3
Lauric	0.46	0.2	-	-	47.8
Capric	0.2	-	-	-	3.5
Behenic	-	-	-	5.5	-
Lignoceric	-	-	-	2.63	-
Saturated	-	49.9	21.6	-	82.1
Monounsaturated	-	39.2	45.4	-	15.4
Polyunsaturated	-	10.5	33	-	2.4

2.1.2   Properties of Methanol and Dimethyl Carbonate

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are use most frequently, especially methanol because of its low cost and its

physical and chemical advantages (polar and shortest chain alcohol) (Ma and Hanna, 1999). However, after transesterification/esterification, several processes are used for biodiesel and glycerol by-product purification, and recover useful agents for recycling (Van Gerpen *et al.*, 2004). A paramount post-process of glycerol comprises of neutralization/acidification if homogeneous catalyst is used and distillation/evaporation to separate surplus of methanol for recycle and water. However, this is not always the case because utilizing fresh methanol is more cost effective than revitalization of excess methanol (Bohon *et al.*, 2011).

On the other hand, the specific advantages of DMC, and of alkyl carbonates in general, is that their building block is CO_2, an environmentally benign compound, which does not cause emissions of volatile organic compounds (VOCs) in the atmosphere (Tundo and Selva, 2002). Furthermore, DMC is a nontoxic compound contrast with methanol (Rivetti, 2000). Besides, it is an ignitable liquid, does not have mutagenic or exasperating effects either by inhalation or by contact and smell like methanol (Merck, 2014). Thus, it can be managed carefully lacking the particular protection necessary for the mutagenic and toxic chemicals. Moreover, DMC has a good blending octane ($R + M/2 = 105$), it does not phase separate in a water stream like some alcohols do, and quickly biodegradable (Pacheco and Marshall, 1997). In addition to its blending properties, DMC can be characterized as an outstanding oxygenate (due to its very high oxygen content, 53 wt.%) for environmental gasoline (Pacheco and Marshall, 1997). Table B1 in the Appendix B shows the information on basic physical and chemical properties for methanol and dimethyl carbonate.

2.1.3   Properties of FAME, Biodiesel

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel, which is seen as a probable replacement of usual diesel fuel is usually, composed of fatty acid methyl esters (FAME) that can be prepared from triglycerides in vegetable oil by transesterification with alcohol. The resulting biodiesel is quite comparable to usual diesel fuel in its major characteristics (Meher *et al.*, 2006b) (Table 2.3). Moreover, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability (Ma and Hanna, 1999).

As given in Table 2.3, the properties of diesel fuels and biodiesel show a number of conformity and as a result, biodiesel is an option to replace petroleum diesel. This is because the conversion of TG into fatty acid methyl ester decreases the viscosity, molecular weight, and increase slightly the volatility through the transesterification reaction. Furthermore, biodiesel can intensify the combustion process in compression ignition engine due to 10-11% oxygen (w/w) content (Barnwal and Sharma, 2005).

2.1.4   Glycerol Derivatives

Glycerol, a by-product obtainable in huge quantities at lower prices is due to increasing biodiesel production. A wide range of new useful derivatives can be made such as glycerol carbonate (GC) and fatty acid glycerol carbonate (FAGC) through the exploration of glycerol as a new applications platform chemical. The increasing

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industry interest for glycerol carbonate (GC) based on its reactivity and its physical properties. GC is a low evaporation rate thick liquid, not combustible, dissolved in water, non-hazardous and easily biodegradable. Alternatively, GC obtained from glycerol has a high renewable content (the mass % of the molecule coming from renewable sources), ranging between 76%, if obtained from glycerol and other raw material separately from CO_2, and 100%, if synthesized straight from glycerol and CO_2. (Ochoa-Gómez et al., 2012). GC becomes a green chemical because of all these characteristics and it can be utilized in many applications as shown in Table 2.4.

Table 2.3   Properties of biodiesel from different oils (Feuge and Gros, 1949; Rao and Gopalakrishnan, 1991; Ali et al., 1995; Dunn and Bagby, 1995; Chang et al., 1996).

Vegetable oil methyl esters (biodiesel)	Kinematic viscosity at 38°C $(mm^2 s^{-1})$	Cetane no. (°C)	Lower heating value $(MJ\ kg^{-1})$	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density $(kg\ L^{-1})$
Peanut	4.9	54	33.6	5	-	176	0.833
Soya bean	4.5	45	33.5	1	-7	178	0.885
Babassu	3.6	63	31.8	4	-	127	0.875
Palm	5.7	62	33.5	13	-	164	0.880
Sunflower	4.6	49	33.5	1	-	183	0.860
Tallow	-	-	-	12	9	96	-
Diesel	3.06	50	43.8	-	-16	76	0.855
20% biodiesel blend	3.2	51	43.2	-	-16	128	0.859

On the subject of GC reactivity, it has a pendant hydroxyl moiety and three carbon atoms of the dioxolane ring as reactive sites, which unlock various potential

for utilizing GC for manufacturing chemical intermediates in addition to other prospective valuable materials (Ochoa-Gómez *et al.*, 2012).

Table 2.4   Applications of glycerol carbonate

Applications	References
Solvents	(Kerton, 2009)
Carrier in lithium and lithium-ion batteries	(Abraham, 2011)
Solid laundry detergent compositions	(Brooker, 2011)
Building ecocomposites	(Magniont *et al.*, 2010)
Beauty and personal care	(Kahre *et al.*, 1999; Jeffsol GC, 2013)

Glycidol, which can be obtained from GC, is one of an appealing chemical used as a raw chemical for obtaining polyglycerol esters, glycidyl ethers, energetic matrices for solid propellants, pharmaceuticals, polyglycerols in addition to detergents, drugs, paints, UV curing agents for semiconductors, stabilizer for natural oils and vinyl polymers, demulsifier, dye-leveling agent, perfumes and cosmetics, etc (Ochoa-Gómez *et al.*, 2012). Presently, it is a valuable chemical and, therefore, wider scopes of utilizations are to be anticipated if a new cost-effective method for its production is worked. One of the methods could be the decarboxylation of GC shown in Equation 2.1. It is generally performed at temperature of 80−200 °C in the presence of catalysts such as anhydrous sodium sulphate (Uno and Okutsu, 2011), zeolite (Yoo *et al.*, 2001), ionic liquid (Gade *et al.*, 2012; Choi *et al.*, 2013), ZnO/CO_3O_4 and ZSM-5 (Bolívar-Diaz *et al.*, 2013) in 70 − 85% yields.

On the other hand, the transesterification among triglyceride and dimethyl carbonate prevents the generation of glycerol as well as yields a blend of fatty acid

glycerol carbonate (FAGC) as a substitute and FAME as shown in Figure 2.2(A) (Islam *et al.*, 2013).

Glycidol

Glycerol Carbonate
(GC)

(2.1)

(A)

TG   DMC   FAME   FAGC

(B)

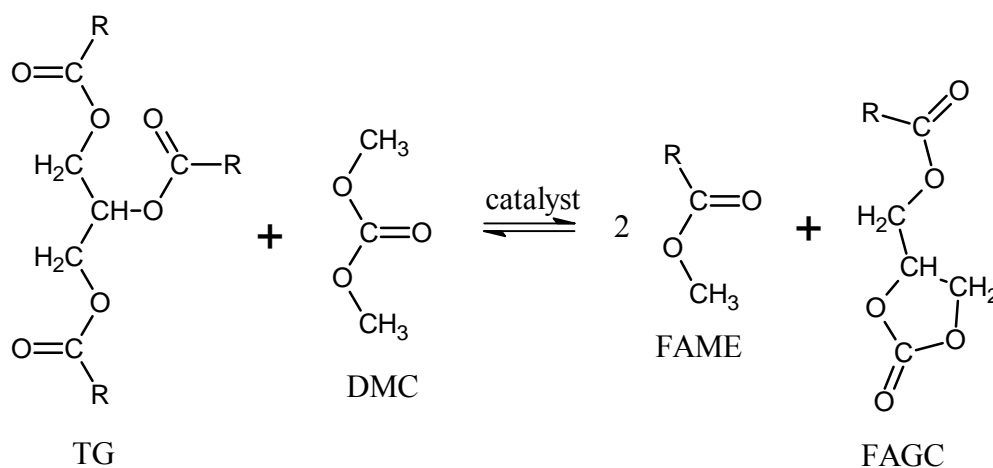FAGC   DMC   FAME   Glycerol dicarbonate

(C)

Glycerol dicarbonate

Glycerol carbonate

Figure 2.2   Transesterification of oil leading to (A) DMC biofuel, (B) series reaction for FAGC conversion, and (C) side reaction of glycerol dicarbonate (Zhang *et al.*, 2010).

2.2   Transesterification and Esterification Reactions

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The overall transesterification reaction (Otera, 1993) is given by three consecutive and reversible equations as below:

$$\text{Triglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Diglyceride} + \text{R}'\text{COOR} \qquad (2.2)$$

$$\text{Diglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Monoglyceride} + \text{R}''\text{COOR} \qquad (2.3)$$

$$\text{Monoglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Glycerol} + \text{R}''\text{COOR} \qquad (2.4)$$

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step (Freedman *et al.*, 1986; Noureddini and Zhu, 1997). The overall chemical reaction of the