SYNTHESIS, CHARACTERIZATION AND ACTIVITY OF MIXED METAL OXIDE (Mg, Zn, Al) CATALYSTS FOR TRANSESTERIFICATION OF WASTE COOKING PALM OIL, EDIBLE AND NON-EDIBLE OILS

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by

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
A	Pre-exponential factor	L mol^{-1} min^{-1}
C, C_t	Concentration at any time, t	mg/L
C_0, C_{A0}	Initial concentration	mg/L
E_a	Activation energy	J/mol
H	Hysteresis type	
k	Rate constant	(1/min)
k_r	True rate constant	mg/(L.min)
K	Dimensionless constant	
K_A	Adsorption equilibrium constant	L/mg
$^{\bullet}OH$	Hydroxyl radical	
OH^-	Hydroxyl ion	
P	Pressure	bar
P_0	Initial pressure	bar
r_{A0}	Initial rate of reaction	mg/(L.min)
R^2	Correlation coefficient	
θ_{Ads}	Surface coverage of adsorbed species	

LIST OF ABBREVIATIONS

A_{Kpptd}	Ammonium hydroxide precipitated
ASTM	American Standards of Testing and Measurements
AGO	Automotive gas oil
Al	Aluminium
AC	Activated carbon
BET	Brunauer–Emmet–Teller
BJH	Barret–Joyner–Halenda
CCO	Coconut oil
CJO	Crude jatropha oil
CO_2	Carbon dioxide
DG	Diglyceride
DOE	Design of experiments
EDX	energy dispersive X-ray
EN	European Standard
FAME	Fatty acid methyl ester
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
H_2O	Water
K	Potassium
K_{pptd}	Potasium hydroxide precipitated
KNO_3/Al_2O_3	Potasium nitrate on alumina support
KOH	Potasium hydroxide
L-H	Langmuir-Hinshelwood

Mg	Magnesium
MG	Monoglyceride
PKO	Palm kernel oil
RSM	Response surface methodology
RPO	Refined pal oil
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TG	Triglyceride
WCPO	Waste cooking palm oil
wt %	Weight percent
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide
$ZnCl_2$	Zinc chloride

SINTESIS, PENCIRIAN DAN AKTIVITI MANGKIN CAMPURAN OKSIDA LOGAM (Mg, Zn, Al) BAGI TRANSESTERIFIKASI SISA MINYAK MASAK KELAPA SAWIT, MINYAK BOLEH DIMAKAN DAN TIDAK BOLEH DIMAKAN

ABSTRAK

Biodiesel, yang juga dikenali sebagai “fatty acid methyl esters” (FAME), merupakan alternatif bahan api yang boleh dihasilkan melalui proses pemangkinan homogen atau heterogen. Biodiesel adalah bahan api yang boleh diperbaharui dan pembakarannya yang mesra alam jika dibandingkan dengan fosil (petroleum mentah). Kajian ini memberi tumpuan kepada pembangunan dan sintesis mangkin pepejal melalui gabungan beberapa logam untuk menghasilkan mangkin komposit dengan formula $Mg_{1-x}Zn_{1+x}Al_{(2-y)/3}O_3$ (at $y = 0$ dan $0.1 \leq x \leq 0.9$) sesuai untuk menghasilkan FAME daripada pelbagai sumber minyak sayuran yang boleh dimakan dan tidak boleh dimakan (minyak kelapa sawit ditapis (RPO), sisa minyak masak sawit (WCPO), minyak kelapa (CCO), minyak isirung sawit (PKO) dan minyak jatropha (CJO)) terutamanya daripada minyak kelapa sawit kerana Malaysia adalah salah satu pengeluar terbesar di dunia dan ia boleh didapati dalam kuantiti komersil. Mangkin yang disintesis dengan aktiviti yang dipertingkatkan dalam transesterifikasi telah dibangunkan dan disediakan melalui kaedah pemendakan bersama campuran hidroksida logam-logam daripada sebatian nitrat masing-masing yang diperolehi dalam tiga peringkat mangkin 1 ($K_yMg_{1-x}Zn_{1+x}O_3$), mangkin 2 ($Mg_{1-x}Zn_{1+x}O_2$) dan mangkin 3 ($Mg_{1-x}Zn_{1+x}Al_{(2-y)/3}O_3$). Mangkin-mangkin tersebut tertakluk kepada suhu $460 \pm 1\ ^{o}C$ untuk 4.41 h. Prestasi mangkin diperolehi daripada pencirian sifat-sifat tekstur,“surface scanning electron microscopy”(SEM) untuk morfologi mikrostruktur dan permukaan dan “X-ray diffraction”(XRD) dan “Fourier Transformed Infra Red” (FTIR) untuk menganalisis struktur dan kumpulan berangkap masing-masing. Hasil analisis menunjukkan bahawa mangkin yang disediakan terbukti berkesan dalam transesterifikasi dengan 87% FAME telah dihasilkan bagi mangkin 1 menggunakan RPO, 87% dan 83% bagi mangkin 2 menggunakan WCPO dan RPO masing-masing. Walaubagaimanapun, nilai larut lesap yang tinggi bagi mangkin 1 iaitu 13%, hasil yang rendah dan luas permukaan yang rendah iaitu 9.67 m^2/g bagi mangkin 2 menyebabkan pengubahsuaian selanjutnya diperlukan. Mangkin 3 menunjukkan prestasi yang lebih baik apabila aluminium, dimasukkan dengan meningkatkan luas permukaan, larut lesap kurang dalam bentuk ion dalam lingkungan 1-2% dan 94% FAME dihasilkan untuk minyak tidak boleh makan, asid lemak dan kandungan kelembapan minyak mentah jatropha melalui cara sintesis satu kelompok. Sifat amfoterik mangkin 3 dengan kehadiran aluminium dalam komposit ini bertanggungjawab meningkatkan prestasi dan ia boleh diguna sebanyak lima kitaran. Pelbagai parameter antaranya nisbah metanol kepada molar minyak (9-18), jumlah mangkin (1.5-10.5 wt %), suhu (150-190 ^{o}C) dan masa tindakbalas (6 h) telah dikaji. Parameter-parameter ini telah dioptimumkan dengan penggunaan perisian reka eksperimen, bagi memperoleh keadaan optimum iaitu (88% FAME; nisbah metanol kepada minyak, 11:1; jumlah mangkin, 3.32 wt % pada suhu 182 ^{o}C) untuk mangkin 3 menggunakan minyak jatropha, tekanan autogenous dalam linkungan 12-22 bar dan suhu didapati menjadi salah satu parameter yang ketara. Analisis produk menunjukkan persamaan dengan piawaian American Standards for Testing and Measurements (ASTM) dan European Union Standards (EN) bagi biodiesel. Kajian kinetik juga dikaji untuk minyak jetropha pada keadaan optimum dan tindakbalas dijelaskan dengan kadar tertib pertama. Di samping itu, nilai-nilai tenaga bebas Gibb (ΔG, J/mol), tenaga pengaktifan (E_a, kJ/mol) dan pra-eksponen faktor A, L/mol/min) adalah -1285.6, 161.4 and 1.0 x 10^{-4}, masing-masing.

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ABSTRACT

Biodiesel, also known as fatty acid methyl esters (FAME), is an alternative fuel that could be obtained by homogeneous or heterogeneous catalytic processes. It is renewable and its combustion is environment friendly compared to fossil (crude petroleum). This research focused on the development and synthesis of solid catalyst from combination of some metals to produce composite catalyst with $K_yMg_{1-x}Zn_{1+x}Al_{(2-y)/3}O_3$ (at $y = 0$ and $0.1 \leq x \leq 0.9$) suitable to produce FAME from different vegetable oils-edible and non-edible sources (refined palm oil (RPO), waste cooking palm oil (WCPO), coconut oil (CCO), palm kernel oil (PKO) and crude jatropha oil (CJO)) most specifically from palm oil since Malaysia is one of the world's largest producer and it's available in commercial quantity. The synthesized catalyst with an enhanced activity in transesterification was developed and prepared by co-precipitation of the mixed metal hydroxides from their nitrates compounds achieved in three stages named as catalyst 1 ($K_yMg_{1-x}Zn_{1+x}O_3$), catalyst 2 ($Mg_{1-x}Zn_{1+x}O_2$) and catalyst 3 ($Mg_{1-x}Zn_{1+x}Al_{(2-y)/3}O_3$). All the catalysts were subjected to heat treatment at 460 ± 1 ^{o}C for 4.41 h. Insights to the catalyst performance was obtained from characterization for its textural properties, surface scanning electron microscopy (SEM) for microstructure and surface morphology and, X-ray diffraction (XRD) and Fourier Transformed Infra Red (FTIR) for structural and functional groups analysis, respectively. The analysis revealed that the developed catalysts proved to be effective in transesterification with FAME yields of 87 % for catalyst 1 using RPO, 87 % and 83 % for catalyst 2 using WCPO and RPO, respectively. However, high value of leaching for catalyst 1(13 %), low yield and low surface area (9.67 m^2/g) for catalyst 2 make further modification imperative. Catalyst 3 performed better when Al was incorporated with improved surface area, tolerable leaching of 1-2 % and FAME yield of 94 % for non-edible, high fatty acid and moisture content CJO in one-batch synthesis. The amphoteric nature of catalyst 3 with inclusion of Al in the composite is responsible for its high performance and it is reusable over five cycles. Various parameters such as methanol to oil molar ratio (9-18), catalyst loading (1.5-10.5 wt. %), temperature (150-190 ^{o}C) and reaction time (6 h) were investigated. These parameters were optimized with the used of design of experiment software, to obtain optimum conditions (88 % FAME; methanol to oil ratio, 11:1; catalyst loading, 3.32 wt. % at temperature 182 ^{o}C) for catalyst 3 using CJO, autogenous pressure range of 12-22 bar and temperature was found to be one of the most significant parameters. Analysis of the product showed agreement with American Standards for Testing and Measurements (ASTM) and European Union Standards (EN) for biodiesel. Kinetic study was investigated using CJO at the optimum conditions and the reaction was described by first order rate. In addition, values of Gibb's free energy (ΔG, J/mole), activation energy (E_a, kJ/mole) and pre-exponential factor (A, L/mol/min) are -1285.6, 161.4 and 1.0 x 10^{-4}, respectively.

CHAPTER 1

INTRODUCTION

1.0 Global demand for alternative energy source

Recent research showed that there is increased global awareness in the utilization of alternative (renewable) sources of energy (Adelman and Watkins, 2008). The reason for this has been the increase in the cost of energy produced from fossil fuels coupled with the fact that it is a finite resource; it grossly affects the environment (Phan and Phan, 2008). There is the need to evolve new measures, in terms of appropriate technology and resources, to promote a shift from fossil fuels. Due to astronomical growth in world population and rapid industrialization which are direct consequence of increased technological breakthrough in almost all spheres of life, it is believed that the global energy demand will definitely increase. Thus, the search for the renewable resources such as solar, wind, water, biomass and other clean energy sources will surge in demand and eventually account for the vast majority of overall energy usage in the near future.

The increasing decline in crude oil reserves has made alternative energy sources inevitable and of great importance. This is in the light of increasing campaign for cleaner burning fuels in order to safeguard the environment and protect man from inhalation of toxic substances. The exhaust from petroleum diesel is known to be carcinogenic in nature, since they contain polycyclic aromatic hydrocarbons and nitrated polycyclic aromatic hydrocarbons (PAHs and NPAHs), carbon monoxide, sulphates, and particulate matter (Canakci and Gerpen, 1999).

A renewable resource is a natural resource that can be replaced or replenished by natural processes at a higher or equal rate to its rate of consumption. The renewable resources are part of the natural environment and constitute what is known as the eco-system. The world-wide energy demand is quite huge and more than 80% of this energy is currently supplied by fossil fuels, coal, oil or gas (Chapman, 1974; Cleveland *et al.*, 2000; Farrell and Brandt, 2006). Fossil fuels are non-renewable finite resource. The shrinking supply of this resource globally will not make it possible for continued dependence on it for a longer time because they will be used up within the next decades. Besides, the drastic increase in the emission of carbon dioxide into the environment, when fossil fuels (oil, gas, petrol, kerosene, etc.) are combusted in engines and automobiles has been identified as the major cause for the change of temperature in the atmosphere generally referred to as global warming. Thus, the search for an alternative that could replace fossil fuels in the short or medium term has become imperative.

The future potential of renewable energy for the mitigation of global warming is intended to focus on six most important energy technologies viz: - bioenergy, direct solar energy, geothermal energy, hydropower, ocean energy and wind energy. This research will mainly focused on the potential of one of these energy sources (bioenergy) taking into account its environmental, social, financial and technological benefits derivable from its clean technologies. The emphasis under this category (bioenergy) will be centered on the production of fatty acid methyl esters (FAMEs), also called biodiesel, a clean burning alternative fuel from renewable resources such as vegetable oils, animal fats and waste cooking oils. It is a nonpetroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, obtained by the process of transesterification of the oil (triglyceride) with primary alcohol (methanol) in the presence of a suitable catalyst (Shu *et al.*, 2009). The biodiesel (fuel) produced from this process can be used alone or blended with conventional petro-diesel in unmodified diesel engine vehicles (Sharma *et al.*, 2008).

The renewable sources or feedstock for biodiesel production are derived from different vegetable oils which are available as fresh plant oils such as palm oil (*Elaeis guineensis*), used (waste) vegetable cooking oil, palm kernel oil, coconut oil (*Cocos nucifera*), jatropha oil (*Jatropha curcas*), soybean oil (*Glycine max*), rape seed oil (*Brassica napus*), peanut oil (*Arachis hypogaea*), canola oil (*Brassica napus*), sunflower oil (*Helianthus annuus*) as well as animals fats with a high content in free fatty acids. In the most recent review, Europe stands out as the largest producer and user of biodiesel obtained from rapeseed (canola) oil while the United States closely followed as the second largest producer and user of biodiesel which is obtained from soybean oil or recycled restaurant grease. The type of starting feedstock for biodiesel production absolutely depends on availability and the suitability of the climate to cultivate vast hectares of land for the crop. For example, in other regions of the world (Asia for example), Malaysia, Indonesia and Thailand based their feedstock on the abundant supply of edible palm oil. India is known for the non-edible jatropha oil (Banapurmath *et al.*, 2008).

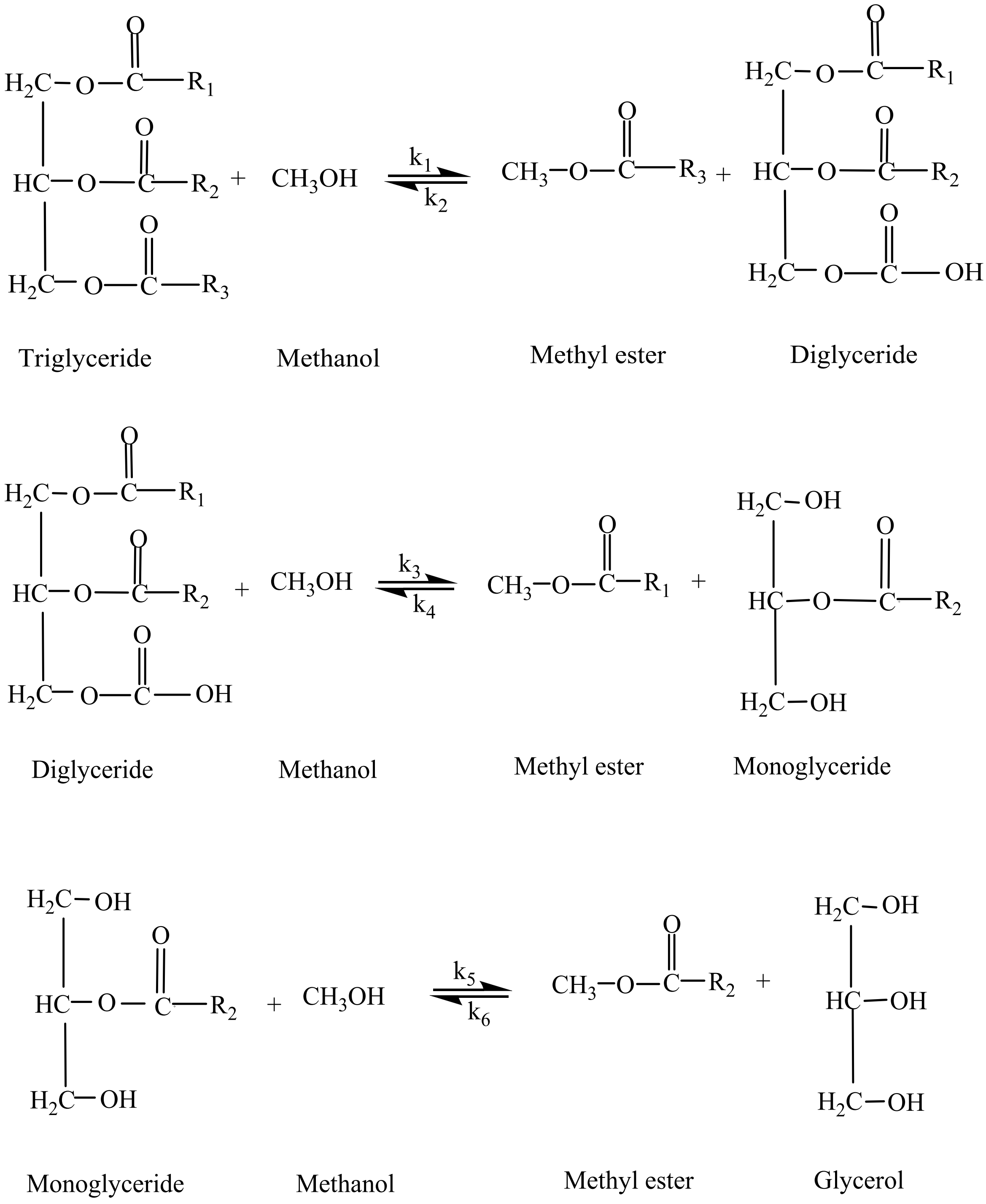
The immediate and longtime benefits derivable from renewable energy are numerous. These include environmental benefits in which case the renewable energy technologies are from clean sources of energy and have much lower environmental impact than conventional energy technologies. On the long time basis, it will provide energy for our children's children because the renewable energy will not “run out” forever. It will provide jobs and create a robust economy, and above all energy security will be guaranteed.

1.1 Transesterification process

Transesterification is the term used to describe a class of organic reactions in which an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, for example, transesterification process is called alcoholysis and in particular methanolysis if lowest molecular weight methanol is used. Transesterification is a reversible reaction and the tendency to attain equilibrium depends on the operating variables. The presence of excess alcohol in the reaction mixture and a catalyst (acid or base) could accelerate and control the equilibrium to achieve a high yield of the ester.

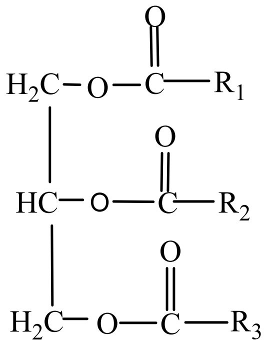
The stoichiometry of transesterification reaction requires 1 mol of a triglyceride (TG) and 3 mols of the alcohol to form di- and mono-glycerides (partial glycerides) and the final products methyl esters and glycerol. Usually, an excess of the alcohol is used to increase the yield of the methyl esters and to allow its physical separation from the glycerol formed. Investigations have shown that transesterification reaction depends on some number of parameters which enhances the product conversion.

In other words, the extent of the reaction will depend on the type of catalyst (acid or base), alcohol to vegetable oil molar ratio, temperature, purity of the reactants and free fatty acid content. Methyl esters of fatty acids are produced by alcoholysis (transesterification) of triglyceride with methanol in the presence of an acid or base catalyst as illustrated by the reaction Scheme 1.1. Complete conversion of the triglyceride involves three consecutive reactions with monoglyceride and diglyceride intermediates.



Scheme 1.1: 3-step reversible reactions of triglyceride where R_1, R_2, and R_3 are long chains of carbons and hydrogen atoms (fatty acid chains) (Fukuda *et al.*, 2001)

Triglycerides are simple lipid and are fatty acid triesters of the trihydroxy alcohol glycerol which are present in plant and animal tissues. In particular, they are found in the food storage depots (the triglycerides in the food storage depots represent a concentrated energy source, since oxidation provides more energy than an equivalent weight of protein or carbohydrate) either as simple esters in which all the fatty acids are the same or as mixed esters in which the fatty acids are different. Similarly, triglycerides constitute the main component of natural fats and oils. The typical molecular structure of a triglyceride is given as Scheme 1.2.



Scheme 1.2: A mole triglyceride

where R_1CO_2H, R_2CO_2H, and R_3CO_2H represent molecules of either the same or different fatty acids, such as butyric or caproic (short chain), palmitic or stearic (long chain), oleic, linoleic, or linolenic (unsaturated).

1.1.1 Homogeneous transesterification process

Transesterification reaction as mentioned earlier requires a suitable catalyst for the conversion of the triglyceride (vegetable oil) to fatty acid methyl esters (FAME). The use of homogeneous catalyst where the catalyst and the reactants are in same liquid-liquid phase for the production of FAME is among the various technologies that emerged over decades and has gained increased acceptability because it is widely known to give higher conversion to methyl esters but not without some shortcomings. These include free fatty acid in feedstock which formed saponified products, water in raw materials interferes with the reaction, glycerol separation is usually difficult, and purification of methyl esters require repeated washing with water which when discharged make the environment unsafe (Ma *et al*., 1999; Fukuda *et al*., 2001; Apostolakou *et al*., 2009).

The current industrial production of FAME basically employed homogeneous alkali-catalyzed transesterification of vegetable oils with methanol. This is because of the fast kinetics of the reaction that is involved by the use of homogeneous catalysts. For example, NaOH, KOH, $(K^+ \text{ or } Na^+)^-OCH_3$ are most often used. It is also a known fact that, though the reaction involving these catalysts is fast, saponification (a side reaction) in the system considerably reduced FAME yield, the product requires repeated washing with water to remove glycerol. Also, in homogeneously catalyzed process, fats and alcohols are not totally miscible and vigorous mixing is required to increase the area of contact between the two immiscible phases and a kind of emulsion is produced which reduce the yield of fatty acid methyl ester (FAME) product. Moreover, the catalyst is not reusable and soap is formed. The glycerin by-product that is contaminated with the alkaline catalyst also has little market worth and disposal problem becomes aggravated. The conventional production of FAME relies on soluble sodium and potassium hydroxide catalysts; however, removal of these catalysts is technically difficult and brings extra cost to the final product.

In the same vain, acid transesterification allows formation of ester without by-products. The main disadvantage of this process lies in the fact that the acid homogeneous transesterification involve the application of corrosive catalyst such as H_2SO_4, H_3PO_4, HNO_3, and HCl. In addition, the reaction rate is generally slow. However, at high operating temperatures and pressures, the rate and yield could be improved but this will add extra cost to the final product Macario *et al.*, (2010). All the limitations mentioned here make the homogeneous process cumbersome and uneconomical. Thus, this makes investigation into suitable acid or basic heterogeneous catalysts, or heterogeneous catalyst with dual sites, that is, with both acid and basic functions for the process imperative.

1.1.2 Heterogeneous transesterification process

Heterogeneous catalysts (where the catalyst and the reactants are in different phase, that is, solid-liquid phase) could be employed in the transesterification process to improve the yield of fatty acid methyl ester (FAME) at lower cost. There is significant demand in energy consumption worldwide and to meet this challenge, a new and efficient catalyst for fatty acid methyl ester (FAME) production which possesses criteria such as good activity and selectivity, low cost, ease of separation and environmental friendliness is required.

Heterogeneous catalysts have been used in various processes, for example, alkali metal (Li, Na, and K) promoted alkali earth oxides (CaO, BaO, and MgO), as well as K_2CO_3 supported on $Al_2O_3(K_2CO_3/Al_2O_3)$, has been used for transesterification of different vegetable oils (D'Cruz *et al.*, 2007). However, there was potassium leaching into the product during the reaction and require catalyst modification to obtain higher yield and eliminate or reduce leaching.

The utilization of heterogeneous catalyst in transesterification reactions appeared very promising because they could become cheaper materials in substitution of noble metal supported on alumina, silica and other inert solids in addition to the ease of separation of the products. Heterogeneous CaO has been used in transesterification of soybean oil (Kouzu *et al.*, 2009). Soybean and poultry fat using nano crystalline CaO (Reddy *et al.*, 2006) have also been reported. For example, activated CaO on rapeseed oil using 0.10 g catalyst with 3.90 g methanol and 15 g oil at 60 ^{o}C in 3 h, gave 90 % and CaO pretreatment was carried out by activation with methanol at 25 ^{o}C in 1.5 h before contacting with oil (Kawashima *et al.*, 2009).

In a similar work, Nakatani *et al.*, (2009) reported transesterification of soybean oil over combusted oyster shell with 25 wt % catalyst, 65-70 ^{o}C in 5 h and obtained 73.8 % conversion. Mg-Al hydrotalcites was used for transesterification of rape oil at 1.5 wt % catalyst loading, alcohol to oil ratio of 6:1 and 65 ^{o}C in 4 h and the yield obtained was 90.5 % (Zeng *et al.*, 2008). Silica-supported solid acid catalyst has also been used for the esterification of free fatty acids in sunflower oils (SO) for the production of diesel fuel (Ni and Meunier, 2007). Basic solid Mg/Zr catalysts have been applied on edible and non-edible oil with ratio Mg/Zr of 2:1 (wt/wt %), when 0.1 g catalyst was mixed with 1 g oil and 2.5 mL methanol at 65 ^{o}C for 2 h for transesterification and the results indicated over 90% methyl ester conversion.

1.2 General uses and properties of biodiesel

Biodiesel, a renewable alternative fuel to diesel from fossil, will be extensively used in the near future due to its many benefits. Biodiesel can be used in the blended form-B20 (20 % of biodiesel with 80 % petroleum diesel) or in the pure form (B100) depending on the feedstock from which it is derived or the quality of the finished fuel (Sharma *et al.*, 2008). In the blended form, it can be used in unmodified diesel engines. The flow and combustion properties of biodiesel are similar to petroleum-based diesel and thus, it can act as a substitute for diesel fuel and justify its suitability as blends with fuels. Higher blends, or even pure biodiesel (100 % biodiesel or B100), can be used in some other engines, for example as in aviation with little or no modification.

In terms of efficiency, biodiesel has positive performance attributes such as increased cetane, high fuel lubricity, and high oxygen content, which may make it a preferred blending stock with future ultra-clean diesel. It is a performance enhancer in terms of operations to conventional diesel. There is an increase in engine life span because biodiesel is more lubricating than diesel fuel. The increased lubricity will enhance engine performance and reduce the frequency of engine parts replacement. Thus, it can serve as a replacement to sulphur (a lubricating agent) in blends. Sulphur dioxide is produced during combustion of sulphur containing diesel fuel which is a primary component in acid rain (Gerpen *et al.*, 1997). Pure biodiesel carries about 90 % of the energy content of the normal diesel and hence it can be expected that the engine performance can be nearly the same.

Emissions of nitrogen oxides increase with the concentration of biodiesel in the fuel and the increase is roughly 2 % for B20 (Ban-Weiss *et al.*, 2007; Demirbas, 2007). Some biodiesel produces more nitrogen oxides than others, and some additives have shown promise in reducing the increase production of these oxides in the fuel. In the case of biodiesel, NOx emissions are a function of combustion temperature. The higher the heat of combustion the greater is the NOx emissions. Also, because biodiesel contains more oxygen than diesel fuel, the heat of combustion is slightly higher.

Biodiesel is biodegradable and this feature makes it ideal for use in fragile areas such as natured reserves, water reserve, forestry estates, bodies of water, inland waterways and coastal waters, and in urban agglomerations. Production and use of biodiesel are environmentally friendly because of their proximity to the feedstock. Besides, biodiesel is safe to transport because it has a high ignition temperature (higher flash point than normal diesel). No danger of explosion is associated with this fuel.

The production of biodiesel is relevant for most industrialized nations where energy demand is quite huge. For example, the demand for transport fuels is going to increase to a great extent as the world population increases. Biodiesel will enable the development and the support for sustainable society projects that are of strategic importance. Similarly, the economic and social aspects of development which aims at greater energy self-sufficiency, a more secured environment (by decreasing the air pollution from transportation and mitigating greenhouse gas emissions) and socio-economic benefits of the bottom billion will be promoted.

The increased utilization of biodiesel will help to develop the economy and provides significant results in microeconomic growth for both the urban and rural sectors. In addition, it is hoped that the research will generate employment opportunities, thereby providing livelihood support (economic empowerment). It is expected that more plantations of oil yielding plants such as palm tree (cash crop) and others for the production of biodiesel will help to create eco-restoration and environment sanity vis-à-vis environment security and reduce drought. The long term benefits derivable from using biodiesel are improvement in national security, environmental protection, guarantees public health cum safety, and a source of income to farmers.

1.3 Problem Statement

The surge in industrialization and the unprecedented rise in world population have necessitated some few questions being asked by both developed and developing nations pertaining to human survival. The aspects of energy generation and consumption, safe environment and food are areas that have direct impact on the population. How can energy be produced from a source to meet increasing industrial demand and its consumption will pose lesser danger on the environment? How many more years shall we wait to nurse the fear of exhaustion and depleting crude petroleum reserves? How could the human race survive starvation? The answer to the above posers lies in massive investment in renewable resources (water, agriculture, wind and solar) to generate sustainable energy, ensure safe environment and improve food supply.

The increase in transportation system in most urban centers of the world has grown rapidly in the past decades with the new emerging technologies in the automobile industry. Fuel from fossil source is the main energy that is being used to operate these vehicles whether on land, rail, sea or air. The fuel consumption from the automobile industry generates huge amount of carcinogenic substances consisting of polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, carbon monoxide, sulphates and particulate matter. The release of these substances into the environment is hazardous to man and could cause disruption to ecosystem through global warming.

Thus, huge environmental burden evolved due to the present utilization of energy derived from fossil fuel requires the elaboration of alternative solutions. The number of automobiles in Malaysia and fuel demand has increased in recent years and emission from exhaust of these vehicles makes the environment unsafe.

From the available possibilities which depending on the locality, current research focuses on the utilization of biotechnology to produce fuel from edible and non-edible sources of vegetable oils (refined palm oil, waste cooking palm oil, palm kernel oil, coconut oil and jatropha oil) to provide alternative sources of energy using simple yet actively selective heterogeneous catalyst. More importantly, the industry needs an effective catalyst that could be employed to produce FAME from different oil sources to minimize their operation cost. This will require the synthesis of heterogeneous catalyst from a combination of metals (Mg, Zn, Al and K used as fluxing material) having empirical formulae $K_yMg_{1-x}Zn_{1+x}O_3$ and

$Mg_{1-x}Zn_{1+x}Al_{(2-y)/3}O_3$. This is due to the fact that their independent structures and properties have been investigated and were chosen for this study because they are of interest in a large field of application and possess desirable properties such as basicity, catalytic properties, surface area and good porosity.

Heterogeneous catalysts (solid catalysts) are more flexible in handling than homogeneously catalyzed process which is characterized by cumbersome purification steps rendering the environment unsafe and it is not reusable. However, heterogeneous catalyzed process is accompanied with fewer complications because it is easily separable from product mixture of glycerin and FAME. Thus, the catalyst is reusable after cleaning/treatment/regeneration. In heterogeneous catalyzed reaction, the refining steps in the purification process is less demanding (simple centrifuge and in few cases require less amount of water washing to remove solid catalyst fines in the FAME product. In heterogeneous process, application of solid catalyst in continuous packed bed reactors is feasible.

The use of heterogeneous catalysts makes the reaction mixture a three-phase (Liquid-Vapour-Solid) system comprising of the vegetable oil, alcohol (methanol), and solid catalyst. Though, heterogeneous catalysis requires relatively higher reaction conditions in terms of pressures and temperatures, the selectivity towards the product yield is excellent. For example, few researches have been conducted at as low temperature as 65 ^{o}C (approximately at the reflux temperature of methanol) while some at elevated temperatures of above 250 ^{o}C. In some cases however, higher temperatures and pressures favours the conversion to products.

The activity of the catalyst will be tested on five oil types namely:- refined palm oil, waste cooking palm oil, palm kernel oil, coconut oil and jatropha oil. All these oils except jatropha are found to be abundant in Malaysia and its usage for biodiesel production could make the country another great exporter of biodiesel in addition to palm oil. Malaysia is one of the world's leading producers of palm oil. Local palm oil refineries are flourishing because of large hectares of land cultivated to grow the commodity. Both refined edible oil and waste are being produced and export of the refined product constitutes huge income generation for the economy

In order to diversify the income generation, this research considers the development of a suitable catalyst as stated above that will meet the criteria such as catalyst stability (leaching, reusability and regeneration), availability and simplicity in method of preparation and inexpensive to produce FAME from the abundant oil source. The performance of the catalyst towards the production of FAME from these oils coupled with characteristics that meet the stability criteria will promote the biofuel industry. Similarly, investment in the industry will in no doubt put Malaysia as one of the economically developed nations with less dependence on fossil fuels for her energy generation. However, future attempts could be made to further invest in oil from other sources (apart from oil palm) to produce biodiesel from non-edible sources (jatropha). This will put to rest the food for oil debate.

In conclusion the novel idea of the present research are summarized as: (1) No catalyst has been developed to produce biodiesel with application to more than two types of vegetable oil in one batch process, (2) Heterogeneous catalysts have been widely reported but information on leaching, reusability and stability is limited, and (3) No study has been carried out to investigate the synergistic effect and application of synthesized heterogeneous catalyst from three metals (Mg, Zn and Al) to transesterified five types of feedstock.

1.4 Research Objectives

This research is aimed at developing an efficient heterogeneous catalyst to produce fatty acid methyl ester from vegetable oils taking cognizance of the identifiable problems associated with the homogeneous catalysts in trans-esterification process. The objectives will be achieved through the outlined steps.

i. To develop heterogeneous mixed metal oxide (Mg, Zn, Al) catalyst for the transesterification of vegetable oils through screening to obtain different combination of metal oxides developed from their original nitrate compounds.
ii. To characterize the developed catalysts for its morphology, textural and surface functional properties.
iii. To study the activity of the developed metal oxides catalyst and variation in process parameters (such as reaction temperature and time, methanol/oil molar ratio, catalyst loading etc.) during transesterification of different oils from edible and non-edible sources with methanol. These includes: refined palm oil, waste cooking palm oil, palm kernel oil, coconut oil and jatropha oil and obtain optimum value for the parameters.
iv. To obtain a reaction mechanism for the transesterification using model oil (jatropha oil) and to use suitable mathematical techniques to evaluate kinetic parameters of the process for the purpose of design.

1.5 Scope of study

The scope of the present study covered the development, characterization, optimization and the test of activity of the developed heterogeneous catalyst in trans-esterification of vegetable oils from refined palm oil, waste cooking palm oil (WCPO) and non-edible oil with methanol. The catalyst was developed using combination of metallic compounds mixed and co-precipitated in solution in an alkali medium. The treatment conditions employed in the catalyst preparation was studied to establish a suitable method of precipitation, either hot or cold. The further treatment employed on the catalyst includes determination of optimum calcination temperature to synergize the combined metallic oxides, ratio of metal combination and calcination time to give the best product yield. Synthesized catalysts are characterized using surface area analyzer, scanning electron microscope (SEM), transmission electron microscope (TEM), thermogravimetric analyzer (TGA), X-ray diffractometer (XRD) and energy dispersive X-ray (EDX).

The main idea of this study is to develop a reusable heterogeneous catalyst for the synthesis of fatty acid methyl esters (FAME). This is an attempt to lower the current cost of biodiesel production and overcome the drawbacks of the homogeneous process. In this study, K, Mg, Zn and Al are considered for the catalyst development as they are cheap and available and are not corrosive. In few cases, K, Mg or Zn oxides alone had been employed for the synthesis of (FAME) using different types of oils, but it has not been reported where the performance of the combination of these metals was used for the synthesis of FAME. Moreover, the reaction takes place in homogeneous phase and with serious consequences. A quick reference in this regard is K which is commonly used in the form of homogeneous

KOH. The above mentioned important points calls for further study into the process of synthesizing FAME from vegetable oils using heterogeneous catalyst. The activity and the stability of the catalyst during transesterification were tested using chromatographic technique. The structures of the catalyst are characterized by TEM and SEM. The embedded metal particles in the composite catalyst are detected by EDX. The nature of metal oxides formed after heat treatment was studied by XRD technique.

A laboratory-scale PARR reactor with a turbine impeller was used to test the activity performance and selectivity of the catalyst. The activity of the catalyst was tested on vegetable oils with both low and high fatty acid content and high moisture content. Important process variables in the production of biodiesel were studied. The data obtained from this study were further developed and used for the derivation of kinetic model using mathematical concepts governing processes that involve solid-liquid-vapour phases. For example, mass transfer operations, thermodynamics and rate laws were used. All operations were conducted in closed batch reactor for the study of the catalyst activity and the kinetics of the system using model oil (jatropha oil). Interactive effects of four critical process parameters during transesterification were investigated using surface response methodology (RSM). The variables involved were methanol/oil ratio, catalyst loading (wt % of oil), reaction temperature (^{o}C) and reaction time (h).The reusability and regeneration of the developed catalyst was tested using appropriate techniques. The scope was expanded to cover on additional four types of vegetable oils among which include testing with non-edible oil of high fatty acid content.

1.6 Organization of the Thesis

This thesis is put together in six major chapters. Each chapter represents an integral part of the main work that is sequentially arranged. In order to assist the reader, this thesis is organized as follows.

Chapter 1 (Introduction)

Chapter one gives an overview on sustainable energy through a renewable source and the depleting resource of fossil fuels and the cost of energy derived from it. The global efforts to search for alternative through renewable technologies and more importantly, biofuels was presented. The problem statement, research objectives, scope and justification, and organization of the thesis are provided in this chapter.

Chapter 2 (Literature review)

This chapter presents a detailed review of literature. This chapter takes into cognizance where we are coming from (the past), where we are at present (current) and what are the challenges and benefits ahead (the future). The Chapter takes an in-depth look into the study that has been carried out prior to this work in order to identify shortcomings, areas of improvement and direction of this study. The chapter gives detailed background study of the process of transesterification, highlights the chemistry and suitable conditions for the process.

Chapter 3 (Materials and methods)

This chapter dwells on the materials used and the experimental procedure employed in this study. The experimental strategy used in this work as a result of these findings is well laid here. The materials are subdivided into two groups viz: - The consumables (comprising of all chemicals and reagents) and the hardware (which represents various units of equipment used in this study). The stage wise process involved in the catalyst development the test of activity of the developed catalyst was discussed.

Chapter 4 (Results and Discussions)

The outcome of the investigation made in chapter two which resulted into series of experimental work were presented and discussed. There are a total of three catalysts developed and synthesized. The characterization and the activity of each catalyst were presented. Discussions on the effect of various process parameters are explained. The results of optimization studies carried out work for this are explained and the relationships between the operating variables on the desired responses using Design of Experiments (DOE) method and the optimum conditions based Response Surface Methodology (RSM) are presented. Lastly, the chapter includes the results and discussion of regeneration and reusability (leaching) of the catalyst and concluded with what makes the as-synthesized catalyst in this work stand out.

Chapter 5 (Thermodynamics and kinetics of the process)

This chapter gave the detailed investigation of the kinetic study carried out on the transesterification process at the optimum conditions. The results obtained for the kinetics and thermodynamic study using jatropha oil as the reference oil were presented. Kinetic model was developed to obtain the equation that governs the catalyst deactivation and presents explanation on the thermodynamics of the process. The efficiency of the catalyst developed is evaluated in terms of the conversion of vegetable oil to methyl esters and other products (partial glycerides). Based on the investigation, a mechanism for the reaction is proposed.

Chapter 6 (Conclusions and recommendations)

This chapter summarizes the findings of this research and gave recommendations for future studies in the field for synthesis of heterogeneous catalysts and improvement required in biodiesel production.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter focuses on what biodiesel synthesis entails and the application of various catalysts in the transesterification process. It detailed the discussion on homogeneously and heterogeneously catalyzed transesterification processes, its merits and demerits were reviewed. Basis for the method of preparation employed and selection of metal oxides (Mg, Zn, Al) used in catalyst synthesis for the process were discussed. A review of vegetable oils composition and properties were presented. Starting from its origin, brief information is provided about the cultivation of the types of vegetable oil feedstock used in this research and the in-depth discussion on the process parameters involved in transesterification (alcohol to oil molar ratio, reaction temperature, amount of catalyst and reaction time) among others also include the design of experiments and kinetics.

2.1 The origin and application of vegetable oil as diesel fuel

Vegetable oils have long been promoted as possible alternative for diesel fuel because it is derivable from a renewable natural resource and it is sustainable. On the other hand, diesel fuel is obtained from fossil and its combustion is known to be harmful to the environment (Correa and Arbilla, 2006). The idea for the application of vegetable oils in diesel engines dated back to decades ago by Gauthier, 1928 who was a French engineer and published a paper regarding the application of vegetable oils in diesel engines.

Particularly during the Second World War, there was an increase in the application of vegetable oils in various parts of the world. Shortly after the war, discovery of fossil fuels in substantial amounts, which is by far inexpensive and had superior engine performance over the vegetable oils, reduced the desire into the research for diesel alternatives.

In 1853, scientists E. Doffy and J. Patrick conducted an experiment on trans-esterification of vegetable oil many years before the first diesel engine became functional. Rudolf Diesel's prime model engine, a single 3 m iron cylinder with a flywheel at its base (which was built by the French Otto company), ran on its own power for the first time in Augsburg, Germany on August 10, 1893. This engine was powered by peanut oil, a biofuel, not a biodiesel (since it was not transesterified).

Rudolf Diesel believed that in the future, the engine will be run by biomass. Diesel in his speech in 1912 said “the use of vegetable oils for engine fuels may seem insignificant today but in the course of time, such oils may become as important as petroleum and coal tar of the present time” (Misra and Murthy, 2010). The manufacturers of the diesel engine altered their engines to utilize the lower viscosity of the petroleum based diesel instead of vegetable oil in the 1920’s making the petroleum industry capable to expand their markets, as most biodiesel engines then ran on petroleum based diesel.

Besides the lower viscosity of the petroleum diesel, it was also considerably cheaper, and also it is not a consumable commodity. Recently, due to environmental impact concerns and decreasing price differential; biomass fuels such as biodiesel has become a growing alternative.

On August 31, 1937, G. Chavanne of the university of Brussels (Belgium) was granted a patent for a “procedure for the transformation of vegetable oils for their uses as fuels”, Belgian patent 422,877. This was the patent for the alcoholysis (transesterification) of vegetable oils using methanol and ethanol in order to separate the fatty acids from the glycerol by short linear alcohols. This was the first account of the production of biodiesel (Chavanne, 1938). However, owing to oil embargoes in the late 1970’s, increase in the world crude oil price, oil politics and worldwide interest on environmentally friendly energy alternatives, there was a renewed vigour on alternative fuels research.

This occurrence made vegetable oils as an alternative to diesel fuel indispensable and as a result considerable work started recently in this field. Few examples of vegetable oils on which research has been carried out include sunflower oil, tobacco seed oil, corn oil and soybean, palm and palm kernel oils, coconut oil, animal fats, or other lipids. In order to lay to rest the intense debate on food for oil, several researchers have investigated other sources of feedstock to produce biodiesel which includes croton megalocarpus, karanj oil (*pongomia pinnata*), moringa oleifera and the non-edible oil used in this work, that is, jatropha oil (*Jatropha curcas* Linnaeus) (Karmee and Chadha, 2005; Meneghetti *et al.*, 2007; Shi and Bao, 2008; Benjapornkulaphong *et al.*, 2009; Gutiérrez *et al.*, 2009; Koberg *et al.*, 2010). Animal fats, although mentioned frequently, have not been studied to the same extent as the other vegetable oils because some methods of processing applicable to common vegetable oils are not suitable for it.

The differences in the physical property of animal fats when compared to other vegetable oils could be responsible for this trend. In further attempts to broaden the scope of biodiesel production from sustainable resources, investigation have been carried out on how to utilize oils from algae and microalgae, bacteria and fungi and, terpenes and latexes to produce biodiesel (Huber *et al.*, 2006; Chisti, 2008; Li *et al.*, 2008; Demirbas, 2009; Taravus *et al.*, 2009; Mata *et al.*, 2010). It is also necessary to balance the current argument and avoid the replacement of edible vegetable oils for the production of fuels which will lead to acute shortage of food worldwide. For this reason, renewable energy sources (wind, solar, hydro) other than alternatives from food sources could take the place of the nonrenewable resources. Equally non-edible oils stuffs could also be cultivated in large expanse of farmlands to boost the feedstock availability for production of diesel fuels and the vast plantation will serve to replenish the environment by maintaining eco-balance.

Combustion of fuel in ignition engines are capable of operating with a mixture of 10 % vegetable oil to maintain total power without any alterations or adjustments to the engine but it was later established that the engines could not run on 100 % vegetable oil for diesel fuel because of engine clogging, corrosion, poor ignition, to mention but few. However, a blend of 20 % vegetable oil and 80 % diesel fuel was found to be successful and excessive carbon deposits on combustion chamber parts do not occur.