UNIVERSITI PUTRA MALAYSIA

MODIFICATION OF DOLOMITES USING TIN AND ZINC AS EFFICIENT SOLID CATALYSTS FOR METHYL ESTERS PRODUCTION

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By

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Thesis Submitted to the School Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master Science

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master Science

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July 2014

Chairman : Professor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

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Rapid energy consumption nowadays has led to the development of renewable resources of energy such as biodiesel. However, high cost of biodiesel production retards further development of this industry. Dolomite is a naturally occurring source of CaO and MgO which promotes a high potential heterogeneous base catalyst for biodiesel production. Transesterification of palm oil via calcined dolomite (AD8) catalyst exhibited 98.3 % conversion of fatty acid methyl ester (FAME). Selective metal oxides, Sn and Zn were as dopants since they have amphoteric properties which can improve the basicity of the parent material (dolomite). In order to obtain modified dolomite catalyst, 1, 3 and 5 % of metal oxides (Sn and Zn) were doped separately on the AD8 via wet impregnation method and exposed for calcination in air at 773 K for 3 h. These catalysts were denoted as 1DSN, 3DSN and 5DSN for Sn-dopant, whereas 1DZN, 3DZN and 5DZN for Zn-dopant. The catalysts were characterized by using X-ray Diffractometer (XRD), Brunauer-Emmet-Teller (BET) surface area, Scanning Electron Microscopy (SEM) and Temperature Programmed Desorption (TPD) of CO_2. The catalysts were then employed for transesterification reaction under different conditions (time of reaction, methanol to oil molar ratio and amount of catalyst) to investigate the catalytic activities of the catalysts. From the result, calcined dolomite (AD8) which has been doped with 3 % of SnO_2 (3DSN) showed optimum conversion of 99.98 % at the least conditions i.e. 1 wt.% of catalyst amount, in 15:1 methanol to oil molar ratio reacted in 4 h compared to 3DZN and AD8. The catalytic activities of these catalysts were found depending on the basicity and the surface area of the catalyst used. Several tests were conducted to study the physicochemical properties such as pour point, flash point, kinematic viscosity, sulphur content and cloud point of biodiesel produced. Based on the results, the synthesized biodiesel is comparable with conventional diesel in the market since it meets the international standards of biodiesel (ASTM, EN) and MS for diesel fuel specifications as well.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENGUBAHSUAIAN KE ATAS DOLOMIT MENGGUNAKAN TIMAH DAN ZINK SEBAGAI MANGKIN PEPEJAL YANG EFISIEN UNTUK PENGHASILAN ESTER METIL

Oleh

SHAJARATUN NUR BINTI ZDAINAL ABIDIN

Julai 2014

Pengerusi : Profesor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

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Penggunaan tenaga yang pesat pada masa kini telah membawa kepada perlunya pembangunan sumber tenaga alternatif yang boleh diperbaharui seperti biodiesel. Walau bagaimanapun, kos pengeluaran biodiesel yang tinggi melambatkan perkembangan industri ini. Dolomit adalah sumber semula jadi CaO dan MgO yang boleh dijadikan mangkin heterogen alkali yang berpotensi tinggi untuk pengeluaran biodiesel. Trans-pengesteran minyak sawit daripada asid lemak metil ester (FAME) menggunakan mangkin dolomit yang telah dikalsin (AD8) menunjukkan penukaran sebanyak 98.3 %. Logam oksida terpilih iaitu Sn dan Zn telah digunakan sebagai dopan-dopan memandangkan kedua-duanya memiliki sifat-sifat amfoterik yang mana dapat meningkatkan sifat bes katalis asalnya (dolomit). Untuk mengubah suai mangkin dolomit ini, sebanyak 1, 3 dan 5% logam oksida (Sn dan Zn) telah didopkan secara berasingan pada AD8 melalui kaedah pengisitepuan basah kemudian dikalsin di dalam pengaliran udara pada suhu 773 K selama 3 jam. Mangkin-mangkin ini telah dilabelkan sebagai 1DSN , 3DSN dan 5DSN untuk Sn-dopan , manakala 1DZN , 3DZN dan 5DZN untuk Zn-dopan. Pemangkin telah dicirikan dengan menggunakan instrumen pembelauan sinar-X (XRD), pengukuran luas permukaan Brunauer - Emmet - Teller (BET), pengimbas microscopi elektron (SEM) dan penyahjerapan karbon dioksida pada suhu terkawal (CO_2-TPD). Pemangkin kemudiannya digunakan untuk tindak balas trans-pengesteran pada beberapa keadaan (masa tindakbalas, nisbah molar metanol terhadap minyak dan jumlah pemangkin) untuk mengkaji aktiviti kesemua mangkin. Kajian menunjukkan, dolomit yang telah dikalsin (AD8) dan didopkan dengan 3% SnO_2 (3SD) dapat melakukan penukaran optimum sebanyak 99.98 % pada keadaan yang paling rendah berbanding 3ZD dan AD8 iaitu dengan menggunakan 1 wt. % jumlah mangkin, 15:1 nisbah molar metanol kepada minyak dan bertindak balas dalam masa 4 jam. Aktiviti-aktiviti mangkin ini didapati bergantung kepada kealkalian dan keluasan permukaan mangkin tersebut. Mangkin 3DSN telah digunakan semula sehingga 4 kali dan menghasilkan penukaran ester metil yang tinggi (lebih dari 80 %). Beberapa ujian

telah dijalankan untuk menganalisa sifat-sifat fizikokimia biodiesel yang dihasilkan seperti takat tuang, takat kilat, kelikatan, kandungan sulfur dan takat awan. Berdasarkan keputusan tersebut, biodiesel yang dihasilkan didapati setanding dengan diesel konvensional di pasaran memandangkan ianya dapat memenuhi piawaian biodiesel antarabangsa (ASTM, EN) dan juga spesifikasi untuk bahan api diesel di Malaysia (MS).

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I certify that a Thesis Examination Committee has met on 4 July 2014 to conduct the final examination of Shajaratun Nur bt Zdainal Abidin on her thesis entitled "Modification of Dolomites using Zinc and Tin as Efficient Solid Catalysts for Methyl Esters Production" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the Degree of Master Science. The members of the Supervisory Committee were as follows:

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This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
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Signature: ______________________
Taufiq Yap Yun Hin, PhD

Signature: ______________________
Mohd Zobir Hussein, PhD

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ASTM	American Society for Testing and Materials
BET	Brunauer Emmett Teller
EN	European Standard
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
JCPDS	Joint Committee on Powder Diffraction Standards
MS	Malaysian Standard
MPOB	Malaysian Palm Oil Board
SEM	Scanning Electron Microscopy
SV	Saponification Value
TPD	Temperature Desorption Programmed
WD	Wave Dispersive
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Energy

Energy has become global attention today because of high consumption of it, leading towards exhaustion of non-renewable energy sources such as coal, nuclear, natural gas and fossil fuel. Industrial, residential, transportation and commercial buildings sectors entail high energy supplies to retain their activities. Due to severely rely on these finite sources, thus, world is looking for a renewable energy to sustain the energy supplies from several sources of energy for example, solar, hydropower, wind, geothermal, biomass and biofuel energies (Ma and Hanna, 1999; Huber *et al.*, 2006).

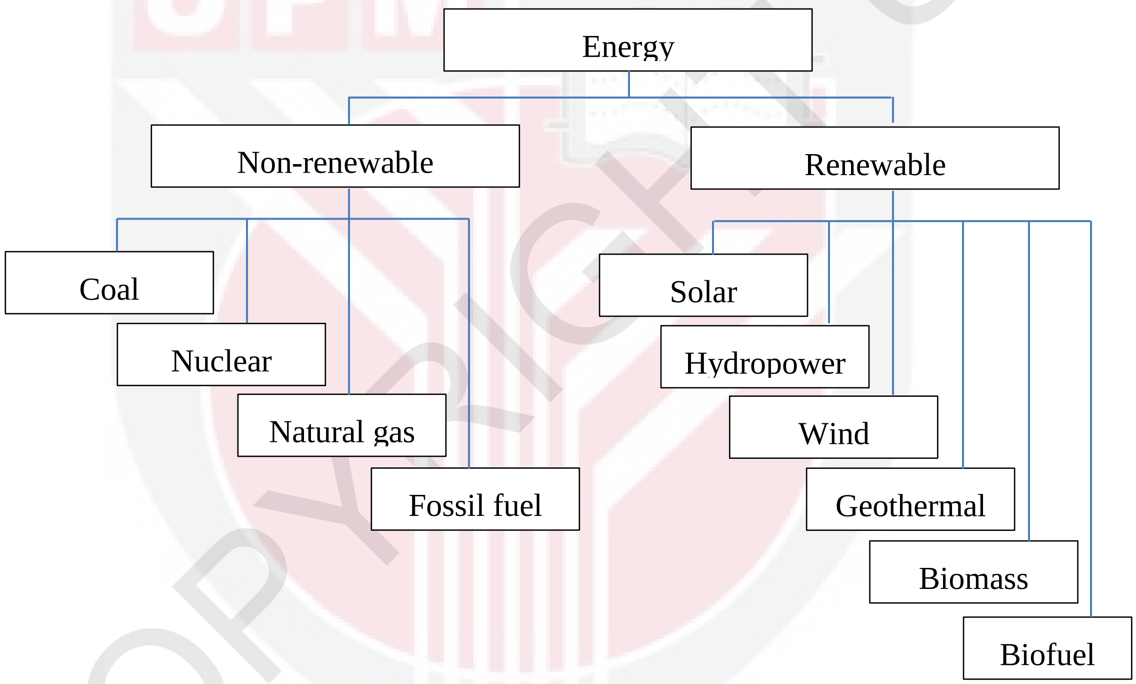
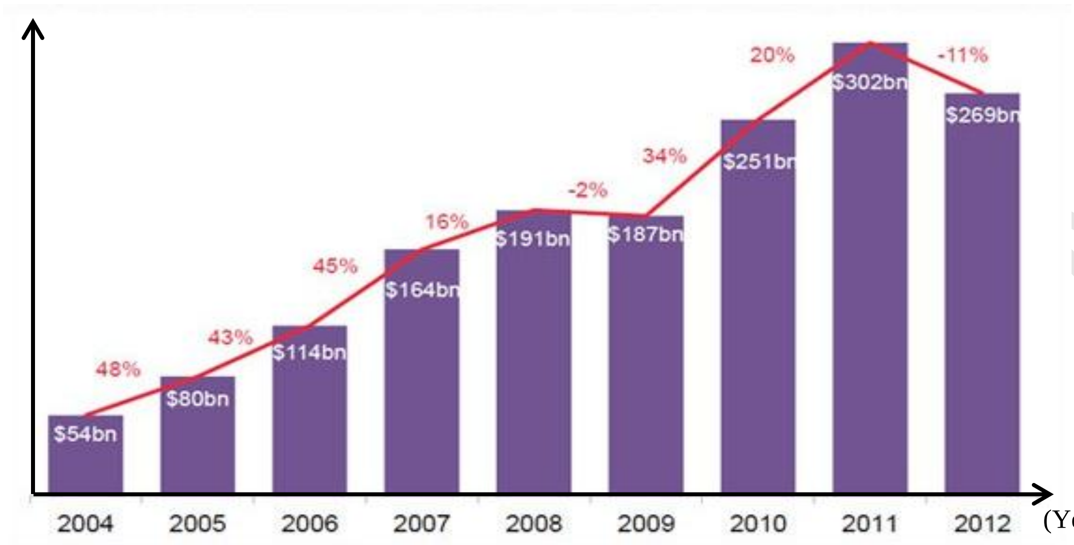


Figure 1.1. Non-renewable energy and renewable energy sources.

As reported in Global Trends in Renewable Energy Investment, (2013), there is a rapid growth of global investment in renewable energy sources until year 2012, mainly supported by corporate and government research and development (R&D). Efforts have been taken since year 2000, realizing that fossil fuel caused the climate change and it is running out sooner or later. Therefore, response from researches to this phenomenon has increased with the same purpose which to preserve the environment and searching for a sustainable energy for the future.

(Investment, %)



(Year)

Figure 1.2. Global total investment in clean energy 2004 – 2012 (USD Billion). (Source: *Global Trends in Renewable Energy Investment 2013*; Bloomberg New Energy Finance, 2013).

1.2 Conventional Diesel

Fossil fuel also known as petroleum has been used worldwide throughout these years as one of our source of energy, especially in transportation sector. Extracted from the core of earth, petroleum cannot be regenerated in a short time since it is naturally made from decaying ancient plants and animals over millions of years. Nowadays, demands on this fuel escalate rapidly for both industrial and living purposes, creating an economic crisis to the world. As predicted, intensive fuel consumption has resulted in rapid depletion of petroleum resources, thus, the price is getting higher, consequently (Lam *et al*., 2010). Since petroleum is not a renewable energy; amount of petroleum consumed is greater than amount of petroleum being generated; diminishing of this fuel becomes a great global concern on how it will be replaced.

Petroleum was claimed as one of the most prevailing causes of environmental devastations as regards toxicity, oil spillage, air pollution, acid rain and waste oil, resulting by burning of the fossil fuel. The emission of traceable amount of poisonous chemicals and gases such as plumbum, benzene, carbon monoxides (CO), nitrogen oxides (NO_x) and sulfur oxides (SO_x) into the surroundings are hazardous for humans and the ecosystems. Excessive amount of CO_2 emits from vehicles, generators and power plants cause the climate change and global warming. Meanwhile, the petroleum also contributes negative charge to water and land since it is not biodegradable and hydrophobic to water (Lim and Teong, 2010).

Petroleum diesel is called petrodiesel to distinguish from other alternatives diesel (synthetic biodiesel). It has been used in most and heavy duty engines (buses, trucks, trains, ships and barges) because of their greater energy and more power compared to gasoline (Kim *et al.*, 2004). In 2012, 19 % of petroleum products stated was petrodiesel production, second largest after gasoline as the main product (Global Trends in Renewable Energy Investment, 2013). However, due to the complications regarding petroleum products as mentioned before, the invention of biofuel such as biodiesel promotes a feasible solution to these matters (Silitonga *et al*., 2013),

1.3 Background of biodiesel

Biodiesel is one of renewable energy resources. It has been considered as an alternative oil or replacement for the conventional diesel. In 1893, Rudolf Diesel tried by using biodiesel for his invented diesel engine; after he failed to use pure vegetable oil for the same purpose (Lin *et al*., 2011). The vegetable oil is not suitable as fuel oil due to its high viscosity that blocked the engine, and then reduced the engine's performance. Similar characteristics of biodiesel with petrodiesel in some ways make it suitable for the replacement. Since then, production of biodiesel is boosted proportional to the world's demand. Furthermore, since the petroleum industries were mostly controlled by Middle-East regions, European and American countries were now struggled on the research and production of biofuels to cut demands on them later on.

Biodiesel comprised of fatty acid methyl ester (FAMEs) through the reaction involves triglycerides that hail from plant oils or animal fats, instead of petroleum based fuel (Meher *et al*., 2006). However, the animal fats are not commonly used due to high viscosity and readily solidify in room temperature. Therefore, biodiesel derived from plant oil offers solution to fossil fuel depletion and environmental degradation issues due to its ability to be renewed, sustained and biodegraded easily. Unlike petrodiesel, biodiesel does not contribute to excessive amount of carbon dioxide (CO_2) to the atmosphere since the CO_2 emission will be recycled for photosynthesis. Since there is no sulphur, plumbum and benzene contained in the biodiesel and it can lower the emission of carbon monoxide (CO) and nitrogen oxides (NO_x) to the atmosphere as well, therefore, biodiesel is not harmful to the environment and living things (Balat, 2011).

Despite the fact that biodiesel promotes the best answer to the issues related to petroleum based diesel, it was still not comparable with the conventional diesel since it is still expensive. This is due to higher cost of production and feedstocks hence increased the price of biodiesel. The cost of production is the cost of processes which includes the preparation, reaction, separation, and purification stages while the cost of feedstocks include the cost of vegetable oil, catalyst (for catalyzed reaction) and methanol (Atadashi *et al*., 2010).

1.4 Palm Oil as Malaysian Biodiesel Feedstock

There are various types of edible oil that have been studied as feedstock for biodiesel production worldwide for example rapeseed oil, soybean oil, peanut oil, coconut oil, sunflower oil and corn oil (Yusuf, 2011). However, the consumption of rapeseed and soy bean oil in US and EU countries to produce biodiesel resulting in high price of biodiesel, proposing that it derives from high quality vegetable oils. In Malaysia, high production of palm oil (*Elaeis guineensis*) annually gave some ideas on developing biodiesel production by using palm oil as the feedstock due to its availability and economic price rather than using other vegetable oils, suggesting that the production of the biodiesel using palm oil will be sustained (Abdullah, 2009).

Palm oil industry has been debated intensely regarding palm oil plantation that triggered deforestation and created global warming issues for over the past few years. However, palm oil has distinct advantages in biodiesel production industry including larger percentage of forest (60 %) in Malaysia was able to be reserved compared to many developing countries since less land was required for palm oil plantation than the other crops as tabulated in Table 1 (Pahl, 2005). Palm oil crop was also proclaimed to absorb a lot of CO_2 gas for production of biomass and release more oxygen during photosynthesis compared to the other crops such as rapeseed and soybean oil (Basiron, 2007). Still, the usage of oil palm to produce biodiesel turns out to be a massive concern worldwide because they have to compete with the food resources, thus non-edible oils such as jathropa and algae oils were introduced to replace them (Gui *et al*., 2008)

Table 1.1. Production of oil per area from different crops in the world.

Source	Yield (liters/hectare)	Comparison of yields
Palm	5,950	1.00
Coconut	2,689	0.45
Jatropha	1,818	0.31
Rapeseed	1,190	0.20
Soybean	446	0.07

(Source: Pahl, 2005).

Malaysia is the second world's largest palm oil producer after Indonesia (Palm Oil World, 2011). Despite the argument that oil palm is a food resource, it offers the most reasonable price among market vegetable oils and non-edible oils due to its efficient production (Table 1). In fact, land area devoted for oil palm plantation is the lowest compared to the other crops. High yields of palm oil per hectare only utilizes around 0.26 hectares of land to have a tonne of oil in return whereas low-yielding crops such as sunflower, soybean and rapeseed consume even more than a hectare to produce the same amount of oil (Malaysian Palm Oil Council, 2012). With the rapid development of technologies nowadays, the production of palm oil is believed to increase in future. Therefore, it is better to produce palm oil intensively which can guarantee a great return in the future.

Biodiesel implementation in Malaysia is still in its early age. In 2006, National Biofuel Policy announcement has been made by the government, thus many researches were done and numbers of biodiesel plants were established ever since. In order to reduce of dependence on petrodiesel, several petrol pumps in Selangor have started using B5 and B10 in 2010 followed by the other central region including Putrajaya, Kuala Lumpur, Melaka and Negeri Sembilan in 2011 (Wahab, 2012), where:

B5 comprised of 5 % of biodiesel blended with 95 % of petrodiesel,
B10 comprised of 10 % of biodiesel blended with 90 % of petrodiesel, and
B100 comprised of 100 % of biodiesel.
Unfortunately, due to uncertainty price of biodiesel feedstock and low in demand, some of the plants were forced to close down and there are only a few biodiesel plants that are under operation thus far. Malaysian government's decision to postpone the application of biodiesel nationally from 2011 to 2014 also retards the development of biodiesel industry in this country to date (Malaysia Debt Ventures Berhad, 2011).

Though the implementation of biodiesel is proposed to increase from B5 to B10 in 2014 by the government, the programme seems doubtful to be fulfilled and has been criticized by industry observers since the old programme (B5) still struggling in the market currently. Moreover, B5 programme is not nationwide implemented yet, signifying that the new programme (B10) is totally irrational. Significantly, decreasing in global biodiesel exports and investment from year 2011 to year 2012 are the reflections of this problem. Therefore, since B10 programme will be launched in this few months away, the implementation of biodiesel must be increasing nationwide from this point to make this programme possible.

1.5 What is dolomite?

Dolomite is a type of rock that occurs naturally all around the world. It appears in different colours (white, brown, yellow, pink, grey, etc.) and shapes like saddles or flakes. Chemically, it consists of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) as the main compounds with the presence of very small percentages of other compounds and has molecular weight around 184.4 g/mol. Dolomite comprises of alternating layers of Ca, Mg and CO_3 which CO_3 comes between Ca and Mg elements in a sequence (Wilson, 2008).

In Malaysia, the price of dolomite is very cheap; US $20 - 40 per metric ton, since it is abundant and easy to get. Numbers of quarries for dolomite manufacturing can be found at Hulu Langat, Selangor and Chuping, Perlis. Due to these reasons, dolomite is mainly used in constructions as well as agricultural fields (Ngamcharussrivicahi *et al*., 2007). It is used in agricultural field as fertilizers which supplies Mg mineral to the plants that is necessary for their growth. In catalytic applications, dolomite is a promising heterogeneous catalyst since it promotes a non-toxic, basic catalyst which important for the reaction processes. Similar to other natural sources of $CaCO_3$ such as limestone and seashell, the active phases of the dolomite were obtained by thermal decomposition of dolomite into CaO and MgO as shown in Equation 1 below (Ilgen, 2011):

$$CaMg(CO_3)_2(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g) \quad (1)$$

In renewable energy's field, dolomites were commonly used in biomass and tar reforming areas. There were a few studies focusing on using activated dolomite as catalyst in biodiesel production. By using dolomite as catalyst for biodiesel production, the cost of chemical used in the reaction will be reduced.

1.6 Problem Statements

Global three-facet problems concerning energy are rising recently, they are:

1. Depletion of non-renewable energy resources
2. High cost of petroleum based fuel
3. Negative environmental impacts

To date, energy demands were increasing significantly since 1900s, resulting in the depletion of petroleum resources. The rate of this non-renewable energy has been consumed is greater than it has been produced or discovered. Consequently, the price of petroleum is getting higher. The consumption of fossil fuel also triggered environmental degradation which can be harmful to the ecosystems. These problems urge the findings of new resources especially renewable energy which can be sustained in the future.

Biodiesel is one of the renewable energy which able to solve this problem. However, biodiesel is not comparable with the petroleum based diesel due to its high production cost and feedstock price. Palm oil as feedstock can reduce the cost of feedstock to be compared to other edible and non-edible oils such as soybean and Jatropha oils.

It was claimed that catalytic transesterification reaction can promote an efficient way to reduce the cost of biodiesel production, yet the usage of homogeneous catalyst entails high cost of separation of the catalyst from the reaction medium. Invention of heterogeneous catalyst will reduce the cost of purification; however, it is usually higher in price and also requires higher reaction conditions. In order to overcome these problems, a cheap, heterogeneous catalyst which has good properties for transesterification reaction has been actively investigated.

Dolomite is a cheap, heterogeneous, basic catalyst which provides good properties for transesterification reaction. By incorporating Sn and Zn (amphoteric metal oxides) onto the dolomite, the properties of the catalyst was enhanced, hence the reaction conditions were reduced.

1.7 Scope of Research

Biodiesel production by using base-catalyzed transesterification method has been investigated in this study. The advantages of using palm oil as feedstock has been revised comprehensively and the influence of dolomites based catalysts with and without dopants in the biodiesel production were also discussed. Dolomite catalyst was modified by doping metal oxides with amphoteric properties (SnO_2 and ZnO), in order to increase the properties of the catalyst, thus improve the production of biodiesel. Furthermore, the effects of reaction conditions such as methanol to oil molar ratio, reaction time and catalyst amount were also investigated.

Chapter 1 introduces the energies which comprised of non-renewable and renewable energy sources. The biodiesel backgrounds, advantages and implementations in Malaysia were also reached. In Chapter 2, the previous studies related on studies and researched are reviewed. The experimental part is in Chapter 3, where the particular information of all materials, methods and instruments used in this study were presented. The preparation and the characterization of catalyst followed by transesterification reaction were described as well. The results and discussions part in Chapter 4 will discuss over all the results obtained. Finally, the conclusions and recommendations of this study will be made as whole in Chapter 5.

1.7 Objectives of Research

The objectives of this research are:

1. To modify dolomite catalyst by doping selective metal oxides which were SnO_2 and ZnO.
2. To characterize catalysts using various techniques:
    a. X-Ray diffraction (XRD) analysis
    b. Scanning electron microscopy (SEM) analysis
    c. Temperature programmed desorption of carbon dioxide (TPD-CO_2) analysis
    d. Brunauer-Emmett-Teller (BET) surface area analysis
    e. X-Ray fluorescence (XRF) analysis
3. To determine the reaction parameters in optimizing the production of biodiesel:
    a. reaction time
    b. catalyst amount
    c. methanol to oil molar ratio
    d. reusability of the catalyst

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