DEVELOPMENT OF LIMESTONE BASED CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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ABSTRACT

Recent developments in biodiesel production have heightened the need for feasible feedstock as this biofuel has high demands because of its advantages. Besides, catalysts play a significant role in improving production of biodiesel fuel. In addition, the determination catalyst is main important for designing a transesterification system. Industrial production of biodiesel employs homogeneous catalysts such as NaOH or KOH which are cannot be recovered and tolerate to soap formation. Thus, the purpose of this research is to develop and characterize the catalyst derived from limestone based. The effect of various condition i.e. different activation catalysts, temperature, WCO to methanol ratio, catalyst loading, reaction time and recyclability on biodiesel production will be studied. Besides, this research also attempts to utilize waste cooking oil as viable feedstock for biodiesel production. A catalyst produced from cement clinker (limestone based) with particle size of 250µm was prepared via wet impregnation method using aqueous solution of potassium hydroxide (KOH) and calcination. The characterizations of catalysts were done using Hammett indicators, X-Ray Fluorescence, SEM, BET and BJH and the product of biodiesel were determined using GC and HPLC. From this research, it was found that KOH activated limestone based catalyst shows a good potential as an alternate for one-step transesterification of low FFA waste cooking oil. Conventional transesterification of WCO using this activated catalyst was found to give the highest WCO conversion to FAME at 96.8% and FAME yield of 60.4% within 60 min of reaction. The end-product from this research also complies with ASTM Standards D6751. The results suggest that the catalyst employed in this work might be useful as a new low cost catalyst for biodiesel production.

ABSTRAK

Perkembangan semasa dalam industri penghasilan biodiesel telah meningkatkan keperluan untuk mendapatkan bahan mentah apabila bahan api berasaskan sumber bio ini mendapat permintaan yang tinggi. Selain itu, pemangkin memainkan peranan yang penting dalam meningkatkan lagi penghasilan biodiesel. Tambahan lagi, penentuan pemangkin adalah faktor terpenting dalam membina sistem untuk proses transesterifikasi. Pada masa kini, industri penghasilan biodiesel menggunakan pemangkin bersifat homogen seperti NaOH atau KOH yang tidak dapat diguna semula dan juga menyebabkan penghasilan sabun yang merencatkan penghasilan biodiesel. Oleh itu, tujuan penyelidikan ini adalah untuk mencipta dan mengkaji ciri-ciri pemangkin yang berasaskan batu kapur. Kesan pemangkin dalam keadaan tindakbalas yang berbeza seperti perbezaan proses pemangkin diaktifkan, suhu, nisbah penggunaan minyak masak terpakai (WCO) kepada metanol, kepekatan pemangkin, masa tindakbalas dan keupayaan untuk diguna semula juga dikaji. Penghasilan pemangkin daripada simen klinker (berasakan batu kapur) dengan saiz partikel 250μm dihasilkan melalui kaedah ‘wet impregnation’ menggunakan larutan kalium hidroksida dan dibakar pada suhu yang tinggi. Pengesanan ciri-ciri pemangkin dijalankan dengan menggunakan penunjuk Hammett, X-Ray Fluorescence, SEM, BET dan BJH. Produk biodiesel yang dihasilkan ditentukan menggunakan GC dan HPLC. Daripada penyelidikan ini, pemangkin berasaskan batu kapur yang diaktifkan menggunakan KOH mempunyai potensi yang baik sebagai alternatif untuk proses transesterifikasi. Proses transesterifikasi secara konvensional menggunakan pemangkin ini telah menghasilkan penukaran sebanyak 96.8% dan penghasilan biodiesel sebanyak 60.4% dalam masa 60 minit tindakbalas. Biodiesel yang dihasilkan juga telah memenuhi piawaian ASTM D6751. Penemuan ini mencadangkan penghasilan pemangkin ini dapat digunapakai sebagai pemangkin yang mempunyai kos yang lebih rendah dalam penghasilan biodiesel.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
B100	100% biodiesel from vegetable oils
BET	Braunar-Ennett-Teller
BJH	Barrect-Joyner-Halenda
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatography
SEM	Scanning Electron Microscopy
WCO	Waste cooking oil
XRF	X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Most of the global primary energy production derives from fossil energy. Fossil-fuel resources are decreasing daily and due to environmental concern, biodiesel comes as a renewable energy to overcome this issue. Biodiesel as a biofuel is getting attention around the world as the suitable solution due to shortage of petroleum resources and earth pollution. Several biofuel were proposed to displace fossil fuels in order to eliminate the vulnerability of the energy sector (Singh *et al*., 2011). Biodiesel fuel is a mixture of mono-alkyl esters of long chain fatty acids (FAMEs) derived from plants oil or animal fats (Abdullah *et al*., 2009). Biodiesel has received high attention since the fossil-fuel resources are depleting due to development of various kinds of petrochemical industries. Biodiesel was used as an alternative fuel to compete with rising price of crude oil. Biodiesel or fatty acid methyl ester (FAME) is a renewable, biodegradable and alternative fuel for diesel engines obtained from transesterification of vegetable oils or animal fats with alcohols. As a renewable energy from plant, biodiesel can contribute to a reduction of greenhouse-gas emissions if it sustainable managed.

Direct blending, micro-emulsification, pyrolysis and transesterification have been used to produce biodiesel from vegetable oils. The most favoured process for biodiesel production is transesterification which involves alcohol and oil in the presence of catalyst to produce FAME and glycerol. Many research has been done to produce biodiesel from various vegetable oils such as palm oil, corn oil, peanut oil, soybean oil, sunflower oil and, etc. However, this edible type oil has been plunged by controversy because it competes with food demands. Besides, all these crops also require land for the production of biodiesel. Comparing to other source such as inedible oils, waste cooking oil (WCO) is the most attractive option to overcome this issue. Utilisation of lower cost vegetable oil such as waste cooking oil (WCO) may be able to reduce the overall cost of biodiesel production (Noshadi *et al*., 2012). Furthermore, utilization of waste cooking oil circumvents the oil vs. food issue, which has become a hotly debated issue during past few years. The consumption of cooking oil is increasing and its consistent supply makes waste cooking oils as commercial viable feedstock. Approximately, there are about 3 billion litres of cooking oil consumed in Malaysia annually, for which about 30% of WCO available for biodiesel production translating to about 10% of diesel demand in Malaysia (Kumaran *et al*., 2011). This project attempt is to utilize waste cooking oil as viable feedstock for biodiesel production.

Catalysts play a significant role in improving production of biodiesel fuel. The choice of catalyst is mostly controlled by the nature of raw material to be used. The performance of acid and alkaline catalysts is usually affected by free fatty acids (FFAs) and water contents of the raw materials. In the case of heterogeneous (solid and enzymes) catalysts, the effects of water and FFAs contents are less noticed during transesterification process (Atadashi *et al*., 2012).The type of catalysts, oil to methanol ratio, reaction temperature and impurity contents in crude oil give effects to biodiesel synthesis in laboratory scale. Among that, the selection of catalyst is main important for designing a transesterification system (Lee *et al*., 2009). Catalyst has significant effect on improving the biodiesel production. At this time, industrial production of biodiesel employs homogeneous catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) which cannot be recovered and tolerate to soap formation if the FFA value in oil greater than 1 wt.% which lead to lower production yield (Wan Omar & Saidina Amin, 2011; Azcan & Yilmaz, 2012).

Transesterification of WCO to biodiesel present a greater challenges due to its high FFA value and water content which may cause soap formation instead of biodiesel thus an efficient catalyst is needed to solve this problem. Heterogeneous catalysts have advantages of being reusable, noncorrosive, show greater tolerance to water and FFAs in feedstock, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product (Ilgen & Akin, 2009;Jairam *et al*., 2012;Xie *et al*., 2006). Therefore, this work aims to prepare a heterogeneous catalyst from cement clinker that is easy to recover apart from providing an efficient conversion of vegetable oil to biodiesel.

As mentioned earlier, several factors give effect to biodiesel production such as the choice of alcohol, alcohol to oil ratio, catalysts type and its loading etc. The reaction temperature is a crucial factor as the reaction can reach its optimum condition to generate high yield. There are many research on development of catalyst for biodiesel production such as from alumina based (Ilgen & Akin, 2009), waste oyster shell (Jairam et al., 2012) and calcined Mg-Al hydrotalcites (Xie et al., 2006). However, the implement of heterogeneous catalyst in industry are still deliberate due the costs of catalyst synthesis and the possible way to reduce the costs of catalyst is to utilize agriculture waste as catalytic materials (Jairam et al., 2012). Apart from that, heterogeneous catalyst offer several advantages as easy to separate by-products, catalyst reusability and low energy as low water consumption (Atadashi et al., 2012;Kaur & Ali, 2011). Moreover, the catalyst selection of heterogeneous catalytic process is most crucial as appropriate catalyst preparation will affect transesterification efficiently.

1.2 Objectives

a) To develop and characterize the catalyst derived from cement clinker.

b) To study effect of various conditions i.e. different activated catalyst using KOH, temperature, WCO to methanol ratio, catalyst loading, reaction time and recyclability on biodiesel production by using the cement clinker-based catalyst.

1.3 Scope of this research

a) To study the surface morphology, pore size and surface area, basic strength, and chemical composition of the cement clinker-based catalyst.

b) To study effect of different activation (calcination at 500 and 700 °C for 2, 5 and 7 hours), temperature at 45 to 70 °C, WCO to methanol ratio from 2:1 to 6:1, catalyst loading from 2 to 6 wt.%, reaction time from 30 min to 5 hours and recyclability up to 3 times in batch mode.

c) To study the recyclability of catalysts on producing biodiesel.

d) To achieve high quality biodiesel that comply with ASTM D 6751 Standards.

1.4 Main contribution of this work

This research aims to develop low cost and effective catalyst and to convert waste cooking oils to biodiesel. The idea on developing catalyst from cement clinker may reduce the biodiesel production cost by replacing the higher cost metal based or non-recyclable homogeneous catalyst that being currently used. The concept of 'from waste to wealth' also being applied by utilization of low cost waste cooking oils instead of using crude palm oils to avoid the rising price of this edible oils in the near future. The collection of waste cooking oil from local household also promote awareness to people that usage of recycled cooking oil for cooking is not advised because it is toxic to human.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a review on catalyst and its applications on biodiesel production. A detailed review on the previous work for synthesis of catalyst and the established methods for solid catalyst are presented. This chapter also provides a brief discussion of catalytic transesterification process using batch reactor conventionally or assisted both by microwave and ultrasonic. A brief discussion on potential feedstock for biodiesel production despite of waste cooking oil is also provided.

Chapter 3 presents the materials and methods used in this work. The methods related to the catalyst development and all equipment (SEM, BET, Basic Strength, XRF, FTIR) that used for its characterization was discussed. The characterization of WCO using CGMS and FAME using HPLC are also discussed. WCO transesterification and biodiesel purification are also discussed. The last section of this chapter discuss about the ASTM 6751 test for biodiesel.

Chapter 4 is divided into two sections to discuss the results from catalyst characterization and the second section was on WCO transesterification. The characterization of catalysts using the equipment such SEM, BET etc. was discussed. The second section of this chapter provides a detailed discussion on every factor for transesterification process (different catalysts, methanol to oil ratio, etc.) on its conversion and yield of FAME. At the end, the properties of FAME produced were compared to ASTM Standards to classify FAME as Biodiesel B100. The properties of FAME are also compared with the properties of petro diesel.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be useful for further work in this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Recent developments in biodiesel production have heightened the need for feasible feedstock as this biofuel has high demands because of its advantages. This chapter will review the biodiesel business in Malaysia, possible feedstock, catalysts used in biodiesel production and the emerging technology which had through the process to produce high quality biodiesel.

2.2 Introduction

Biodiesel has been embarked as a substitute to diesel due to its similarities in properties with petroleum based diesel. As a renewable biofuel, biodiesel has some advantages as it is biodegradable and non-toxic because it is made from biological sources such as vegetable oils and animal fats. Biodiesel also has low emission profiles and it is environmentally favourable. Biodiesel is widely produced by transesterification process which involves the reaction of a lipid with an alcohol to form esters and glycerol. The principle of this process is the action of one alcohol displacing another from an ester, also known by the term alcoholysis.

The current energy used in the world is depending on non-renewable sources through petrochemical sources, coal and natural gas. The majority of world energy needs are finite and at current usage rates, it will be consumed by the end of the next century with the exception of hydroelectricity and nuclear energy. The depletion of world petroleum reserves and increased environmental concerns have stimulated recent interest in alternative sources for petroleum-based fuels (Khan, 2002). Atadashi *et al*. (2012) estimated that the rate of global primary energy demand will increase about

1.7% to reach a value of 16,487 Mtoe from 2002 to 2030 annually. The energy availability was expected to be improved as the utilization of renewable energy was widened. In addition, renewable energy was the most efficient routes to achieve sustainable development. The environmental transesterification process using various type of catalyst also being studied to eliminate the release of abundant wastewater.

2.3 Biodiesel in Malaysia

Biodiesel is considered as a promising alternative fuel because of its reduction of exhaust emissions, improved lubricant, higher flash point, improved biodegradability and reduced toxicity over conventional diesel fuel (Yang *et al*., 2011). Biodiesel does not contain any petroleum products; however, it is compatible with conventional diesel. It can be blended with diesel or used directly with no major modification in ignition combustion engines (Jose *et al*., 2011).

The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used for its production (Abdullah *et al*., 2009). In Malaysia, biodiesel is included in the list of products/activities that are encouraged under the Promotion of Investment Act 1986. Biodiesel projects are therefore, eligible to be considered for the Pioneer Status or Investment Tax Allowance under the act.

Malaysia is considering as world producer for palm oil and produces 15 million tonnes annually. There are many company invested in palm oil industries and its product. With big areas of palm oil plantation, producing biodiesel from palm oil is applicable in Malaysia. Recently, Malaysia through Ministry of Plantation Industries and Commodities has launched the opening ceremony on commercialization of biodiesel from palm oil blended diesel namely B5. The used of B5 diesel has been mandated over the countries involving the government diesel engines vehicles (Ministry of Plantation Industries and Commodities, Malaysia).

After National Biofuel Policy has been endorsed in 2006, Malaysia Palm Oil Board (MPOB) initializes to commercialize biodiesel production from palm oil. Biodiesel become a part of business that making new growth for Malaysia economy through it export. The development of biodiesel production in Malaysia was showing an increasing trend from 2006 to 2010.

In addition, biodiesel production in Malaysia has been growth positively with government support and extension of production technologies. Research for development in biodiesel production also gets into local universities with collaboration from government agencies. This growing trend will give advantages as alternative fuel can be renewable, better quality of exhaust gas emissions, its biodegradability and the carbon present in biodiesel is photosynthetic in origin, it would not contribute to a net rise in the level of carbon dioxide which cause to the greenhouse effect (Azcan & Yilmaz, 2012).

2.4 Potential feedstock for biodiesel production

2.4.1 WCO

Waste cooking oil (WCO) is an alternative feedstock for biodiesel production as it can be collected from restaurants and houses freely. The public awareness campaign was recommended to precede the collection process using special bin. Non-government organisation (NGO) in Malaysia has conducted an awareness campaign to give the knowledge to people that direct discharge of WCO into drainage system can cause the environmental impact. The direct disposal will cause water and soil pollution consequently disturbs the aquatic ecosystem. In addition, the usage of recycled WCO as cooking media in meal preparation give negative effects to human health. Recycled WCO was believed to cause cancer as the toxic contents are produced when the oil is oxidised. The generated WCO was increased rapidly due to tremendous human population which directly related to increment of food consumption (Yaakob *et al*., 2013).

Waste cooking oil sources are different around the world because it referred to plant-based lipids such as corn oil, sunflower oil, palm oil or animal-based lipids such as butter and fish oil. The most common cooking oil in Malaysia was made from palm oil because of its availability and lower cost compared to other sources such soybean oil etc. The employment of edible oil to produce biofuel has received bad criticism from several NGOs worldwide because the millions of people facing hunger and starvation. In addition, the demand for edible oil would increase the market price and tends to unnecessary clearing of forests for plantation. This deforestation will disturb the ecosystems of both animal and plant.

Zhang *et al*., 2012 recommended that utilize waste cooking oil into biodiesel could be three-win alternative as dealing with food security, environmental pollution and energy security. Some countries which are world energy producing and consuming such as US, Japan, Brazil and Germany have enacted the policies to support this plan. The policies that supported biofuel such as subsidies, financial support and waste disposal etc were critical to be carrying out. The indirect incentives in environmental-typed policies as target planning, legal regulation, tax preference and intellectual property protection also provided by government to facilitate the conversion of biofuel from waste cooking oil. The policy from the perspective of value chain is extremely important as under circumstances, the waste cooking oil supply was shortage as it was bring flow back to the dining table. The value chain for producing bio-fuel from waste cooking oil included four stages which are research and development, recycling and disposal of waste cooking oil, production and marketing and the most important is waste cooking oil detecting technique. Therefore, the characteristics of value chain at different stages are important in formulating biofuel policies.

2.4.2 Edible Oil

The first generation of biodiesel was obtained using edible oils as feedstock. In Turkey, biodiesel can be produced from sesame seed oil as it is produced about 43,000 ha in Turkey. Sesame oil has high stability to oxidation compared with other vegetable oils. Biodiesel obtained is about 58wt/wt.% from experiment is well comparison with fuel properties and showing viscosity and density value is close to commercial diesel (Saydut *et al*., 2008). In Malaysia, palm oil is the most suitable feedstock for biodiesel production because it have high production yield and only require low of water, pesticide and fertilizer (Mekhilef *et al*., 2011). Crude palm oil and refined palm oil are at tops list in the vegetable oils market in the world. Because of its nutrient fact, demands for palm oil used in daily life are increasing. Even though there are arising issue of competitions needs between food and biofuel, Malaysia through Malaysian Palm Oil Board (MPOB) already commercializing biodiesel for export market. Whereas, the coconut oil has been discovered to be an alternative oils that can be utilized in the production of biodiesel. Coconut oil is available at low price and it has been produced on a large scale in Thailand (Nakpong & Wootthikanokkhan, 2010). However, coconut oil contains high value of free fatty acid. The minimum 95% conversion of oil to fatty acid methyl ester (FAME) achieved when the reaction time pass about an hour.

2.4.3 Non-edible Oil

Apart from using edible oils, researches on using non-edible oil were done using rubber seed oil. Due to the increasing demand for natural rubber with the development of rubber industry, the cultivated area of rubber tree increases remarkably (Yang *et al.*, 2011). The main yield of rubber plantation is latex. However, the rubber tree also produces large volumes of seed, which is underutilized (Jose *et al.*, 2011). Rubber seed oil is considered as an attractive candidate for development to supplement current supply of vegetable oils. The oil has found little or no economic importance except for inadequate reports on its possible uses in soap, alkyd resin, and lubricating oil industries (Yang *et al.*, 2011).In India, Neem seed oil was used as feedstock in biodiesel production. Free fatty acid in neem seed oil was removed using phosphoric acid modified mordenite (PMOR) catalyst (SathyaSelvabala *et al.*, 2010). Besides, Sarin *et al.* (2010) explored T. belerica seed as a potential biodiesel feedstock. T. belerica fruits contains a small kernel, it nut contain 3.9% seed kernels and 91.1% of seed shell. The oil content was found about 31% by weight of dry crushed seeds. Extraction of oil from T. belerica seed was studied by Soxhlet method with average yield of 98%.

2.4.4 Algae

Alga or microalgae which is normally found on the surface of water area have gain high attentions to be a potential feedstock in biodiesel production because of high photosynthetic efficiency and the capacity to produce lipids (Singh *et al.*, 2011). By its advantages such as require small area; uncompetitive to food demands as well as greenhouse gas absorber so it becomes a significance discovery to biofuel energy. In addition, recent problem for crops in biodiesel production is limited because of unavailability land for cultivation area. Several activities in preparing the cultivation area lead to emit CO_2 gases. Nevertheless, algae are not only as for biodiesel feedstock but also used to keep a better environment because large amount of CO_2 gases is utilized during its cultivation. Besides, there are too many species either from freshwater alga species and marine alga species which is not yet studied.

2.5 Catalyst

Catalysts are function to speed up chemical reactions and can be recovered unchanged at the end of reaction. There are two kinds of catalysts which is homogeneous and heterogeneous. **Table 2.1** shows the comparison of these catalysts by some of the properties itself.

Table 2.1: Comparison between homogeneous and heterogeneous catalyst.

Properties	**Homogeneous**	**Heterogeneous**
Catalyst form	Metal complex	Solid, often metal or metal oxide
Mode of use	Dissolved in reaction medium	Fixed bed or slurry
Solvent	Usually required - can be product or by-product	Usually not required
Selectivity	Can be tuned	Usually poor
Stability	Often decompose <100°C	Stable to high temperature
Recyclability	Can be very difficult	Can be recycled

Chiusoli & Maitlis (2006) identified homogeneous catalysis as the metal complex catalysts and promoters, the reagents and products are all soluble in the reaction medium which is easier to understand. Lee *et al*. (2009) also supported that homogeneous acid-catalyzed reaction provide high yields of FAME but suffers slow reaction rate compare with base-catalyzed which result in long process or high reaction temperature are required. In addition this reaction has low tolerance to water content that end up to soap formation. Besides, homogeneous catalyzed reaction also suffers some disadvantage such as corrosion of reactor and pipelines which affect the material cost for system construction, non-recyclability of catalysts that leads to environmental pollution by means catalyst separation only can be achieved by neutralization and the limitation to design a continuous biodiesel production. According to Yang *et al*. (2011), current studies are focus on solving problem from homogeneous and heterogeneous catalyzed process, supercritical process and enzymatic process.

2.5.1 Heterogeneous catalyst

Heterogeneous catalysts provide a green and recyclable catalytic system as it is fast and easy to separate from the reaction mixture without neutralization process. Several studies such as that conducted by Li *et al*. (2011) have prepared a solid base catalyst from neodymium oxide loaded with potassium hydroxide has longer lifetime and sustain the activity after five cycles with non-corrosive to reactor as well as environmentally benign. However, these catalysts require high temperature to achieve high conversion as need long time (more than 3 hours) to reach higher biodiesel yield. Implicationally, it will increase the production cost to meet these requirement. The process of synthesizing of catalyst from limestone based has been studied by Lin *et al*. (2011) using cement kiln dust (CKD) and lime kiln dust (LKD) without impregnation method and thermal treatment. The CKD and LKD is by-product of manufacture of cements.

Comparatively, heterogeneous catalyzed process have slow reaction rate that can be intensified by enhancing its rates using high reaction temperature, high catalyst loading and big methanol to oil ratio. Another problem discovered is the dissolutions of active species of heterogeneous catalyst into liquid can affect the biodiesel quality and limits the recyclability of catalyst itself. Catalyst deactivation or leaching of active species is very important due to its effect on recyclability, the purity of biodiesel and application of glycerol produced (Lee *et al*., 2009). Most crucial part for heterogeneous process are catalyst selection and appropriate catalyst preparation that efficiently affects the transesterification process (Refaat, 2011).

Most researchers (Liu *et al*., 2008; Kawashima *et al*., 2009; Hsiao *et al*., 2011, Refaat, 2011) prefer heterogeneous catalyst because of its advantages such as easier to separate the product. But this catalyst have several drawbacks such as weak catalytic activities besides it reaction requires high temperature and long reaction time. Heterogeneous catalysts are able to outcome the high energy consumption and high cost separation on overall biodiesel production. Within last decade, there are many types of heterogeneous catalyst being studied such as from alkaline earth metal oxides, boron group based, transition metal oxides, mixed metal oxides, carbon group based and waste material based. The low cost of heterogeneous catalysts with recyclability is most favourable to industries. Therefore, heterogeneous catalysis has dominated many commercial processes.

The heterogeneous catalyst is more favourable compare to homogeneous catalyst because of its advantages such as require mild reaction condition, easy to be separated from reaction mixture as well as can be recycled. The reagents whether as gases or liquids are led over through the catalyst, and it is relatively simple to separate out the products. Industrial heterogeneous catalyst widely applied are solid metals, oxides or halides, through some systems such as an ion-exchange and polymer supported metal complexes, supercritical fluids, ionic liquids and etc. Calcium oxide (CaO) is one of the most common used heterogeneous base catalysts for the transesterification of vegetable oil. Producing biodiesel using CaO as a solid base catalyst has many advantages, such as higher activity, mild reaction conditions, reusable and low cost (Liu *et al*., 2008; Kawashima *et al*., 2009; Hsiao *et al*., 2011).

In addition, heterogeneous catalysts are less corrosive and could reduce environmental pollution. As reported by Refaat (2011), the sustainability and reusability of heterogeneous catalyst almost threaten by leaching process as the extensive leaching will affects industrial application. Transesterification also affected by hydrolysis of esters and triglycerides as the feedstock contains high amount of water. Hydrolysis could lower yield of esters as it was an undesired side reaction that cost total production. The heterogeneous catalyst seemed favourable with low quality feedstock with water content. The presence of water was found to reduce biodiesel quality during storage and on application of diesel engines.

2.5.2 Adsorption isotherm of heterogeneous catalyst

An Adsorption Isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (typically liquid N^2, 77K). Conversely desorption Isotherms are achieved by measuring gas removed as pressure is reduced. According to the IUPAC classification, six types of isotherms can be distinguished as shown in Figure 2.1. Only four isotherms are usually found during catalyst characterization which are Type I, II, IV and VI;

a) Type I

Pores are typically microporous with the exposed surface residing almost exclusively inside the microspores, which once filled with adsorbate, leave little or no external surface for further adsorption.

b) Type II

Most frequently found when adsorption occurs on nonporous powders or powders with diameters exceeding micropores. Inflection point occurs near the completion of the first adsorbed monolayer.

c) Type III

Characterised by heats of adsorption less than the adsorbate heat of liquification, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface.

d) Type IV

Occur on porous adsorbents with pores in the range of 1.5 – 100nm. At higher pressures the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer.

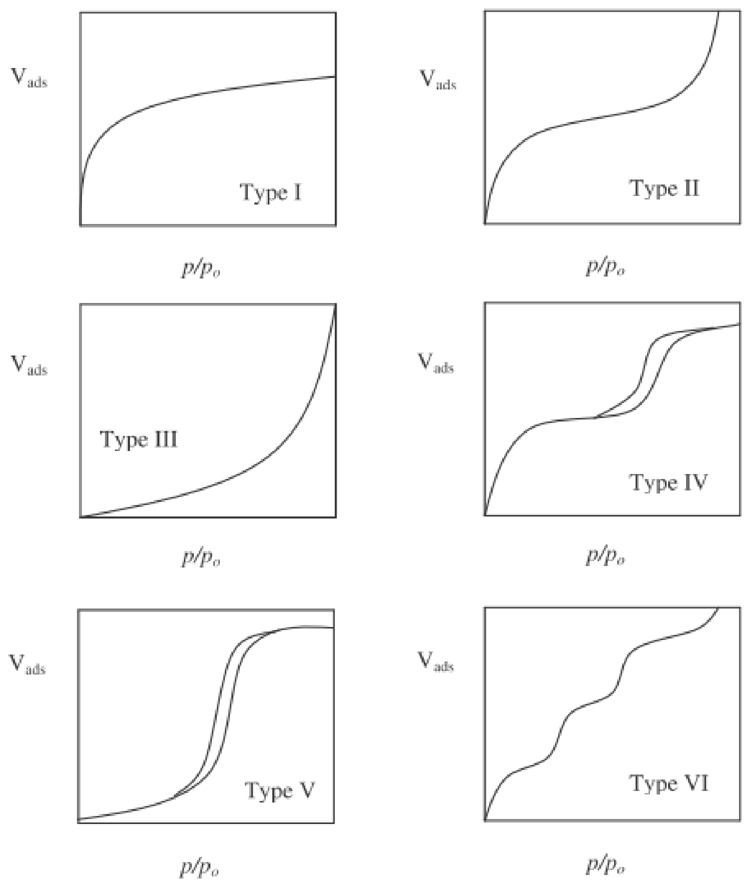

Figure 2.1: The IUPAC classification of adsorption isotherms for gas-adsorption equilibria. (Adapted fromSangwichien *et al*. (2002))

CHAPTER 1

INTRODUCTION

1.1 Background of Study

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Direct blending, micro-emulsification, pyrolysis and transesterification have been used to produce biodiesel from vegetable oils. The most favoured process for biodiesel production is transesterification which involves alcohol and oil in the presence of catalyst to produce FAME and glycerol. Many research has been done to produce biodiesel from various vegetable oils such as palm oil, corn oil, peanut oil, soybean oil, sunflower oil and, etc. However, this edible type oil has been plunged by controversy because it competes with food demands. Besides, all these crops also require land for the production of biodiesel. Comparing to other source such as inedible oils, waste cooking oil (WCO) is the most attractive option to overcome this issue. Utilisation of lower cost vegetable oil such as waste cooking oil (WCO) may be able to reduce the overall cost of biodiesel production (Noshadi *et al*., 2012). Furthermore, utilization of waste cooking oil circumvents the oil vs. food issue, which has become a hotly debated issue during past few years. The consumption of cooking oil is increasing and its consistent supply makes waste cooking oils as commercial viable feedstock. Approximately, there are about 3 billion litres of cooking oil consumed in Malaysia annually, for which about 30% of WCO available for biodiesel production translating to about 10% of diesel demand in Malaysia (Kumaran *et al*., 2011). This project attempt is to utilize waste cooking oil as viable feedstock for biodiesel production.

Catalysts play a significant role in improving production of biodiesel fuel. The choice of catalyst is mostly controlled by the nature of raw material to be used. The performance of acid and alkaline catalysts is usually affected by free fatty acids (FFAs) and water contents of the raw materials. In the case of heterogeneous (solid and enzymes) catalysts, the effects of water and FFAs contents are less noticed during transesterification process (Atadashi *et al*., 2012).The type of catalysts, oil to methanol ratio, reaction temperature and impurity contents in crude oil give effects to biodiesel synthesis in laboratory scale. Among that, the selection of catalyst is main important for designing a transesterification system (Lee *et al*., 2009). Catalyst has significant effect on improving the biodiesel production. At this time, industrial production of biodiesel employs homogeneous catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) which cannot be recovered and tolerate to soap formation if the FFA value in oil greater than 1 wt.% which lead to lower production yield (Wan Omar & Saidina Amin, 2011; Azcan & Yilmaz, 2012).

Transesterification of WCO to biodiesel present a greater challenges due to its high FFA value and water content which may cause soap formation instead of biodiesel thus an efficient catalyst is needed to solve this problem. Heterogeneous catalysts have advantages of being reusable, noncorrosive, show greater tolerance to water and FFAs in feedstock, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product (Ilgen & Akin, 2009;Jairam *et al*., 2012;Xie *et al*., 2006). Therefore, this work aims to prepare a heterogeneous catalyst from cement clinker that is easy to recover apart from providing an efficient conversion of vegetable oil to biodiesel.

As mentioned earlier, several factors give effect to biodiesel production such as the choice of alcohol, alcohol to oil ratio, catalysts type and its loading etc. The reaction temperature is a crucial factor as the reaction can reach its optimum condition to generate high yield. There are many research on development of catalyst for biodiesel production such as from alumina based (Ilgen & Akin, 2009), waste oyster shell (Jairam et al., 2012) and calcined Mg-Al hydrotalcites (Xie et al., 2006). However, the implement of heterogeneous catalyst in industry are still deliberate due the costs of catalyst synthesis and the possible way to reduce the costs of catalyst is to utilize agriculture waste as catalytic materials (Jairam et al., 2012). Apart from that, heterogeneous catalyst offer several advantages as easy to separate by-products, catalyst reusability and low energy as low water consumption (Atadashi et al., 2012;Kaur & Ali, 2011). Moreover, the catalyst selection of heterogeneous catalytic process is most crucial as appropriate catalyst preparation will affect transesterification efficiently.

1.2 Objectives

a) To develop and characterize the catalyst derived from cement clinker.

b) To study effect of various conditions i.e. different activated catalyst using KOH, temperature, WCO to methanol ratio, catalyst loading, reaction time and recyclability on biodiesel production by using the cement clinker-based catalyst.

1.3 Scope of this research

a) To study the surface morphology, pore size and surface area, basic strength, and chemical composition of the cement clinker-based catalyst.

b) To study effect of different activation (calcination at 500 and 700 °C for 2, 5 and 7 hours), temperature at 45 to 70 °C, WCO to methanol ratio from 2:1 to 6:1, catalyst loading from 2 to 6 wt.%, reaction time from 30 min to 5 hours and recyclability up to 3 times in batch mode.

c) To study the recyclability of catalysts on producing biodiesel.

d) To achieve high quality biodiesel that comply with ASTM D 6751 Standards.

1.4 Main contribution of this work

This research aims to develop low cost and effective catalyst and to convert waste cooking oils to biodiesel. The idea on developing catalyst from cement clinker

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

This chapter presents the development of catalyst using cement clinker and transesterification process catalysed by developed catalyst to produce biodiesel. The characterization method of cement clinker and FAME also were discussed in this chapter. The biodiesel from this work are also tested for compliance to American Society for Testing and Materials (ASTM) D 6751.

3.2 Research methodology layout

The experimental work was done according to experimental flow chart as shown in Figure 3.1. These experimental work were included the collection of waste cooking oil and the development of activated catalyst.

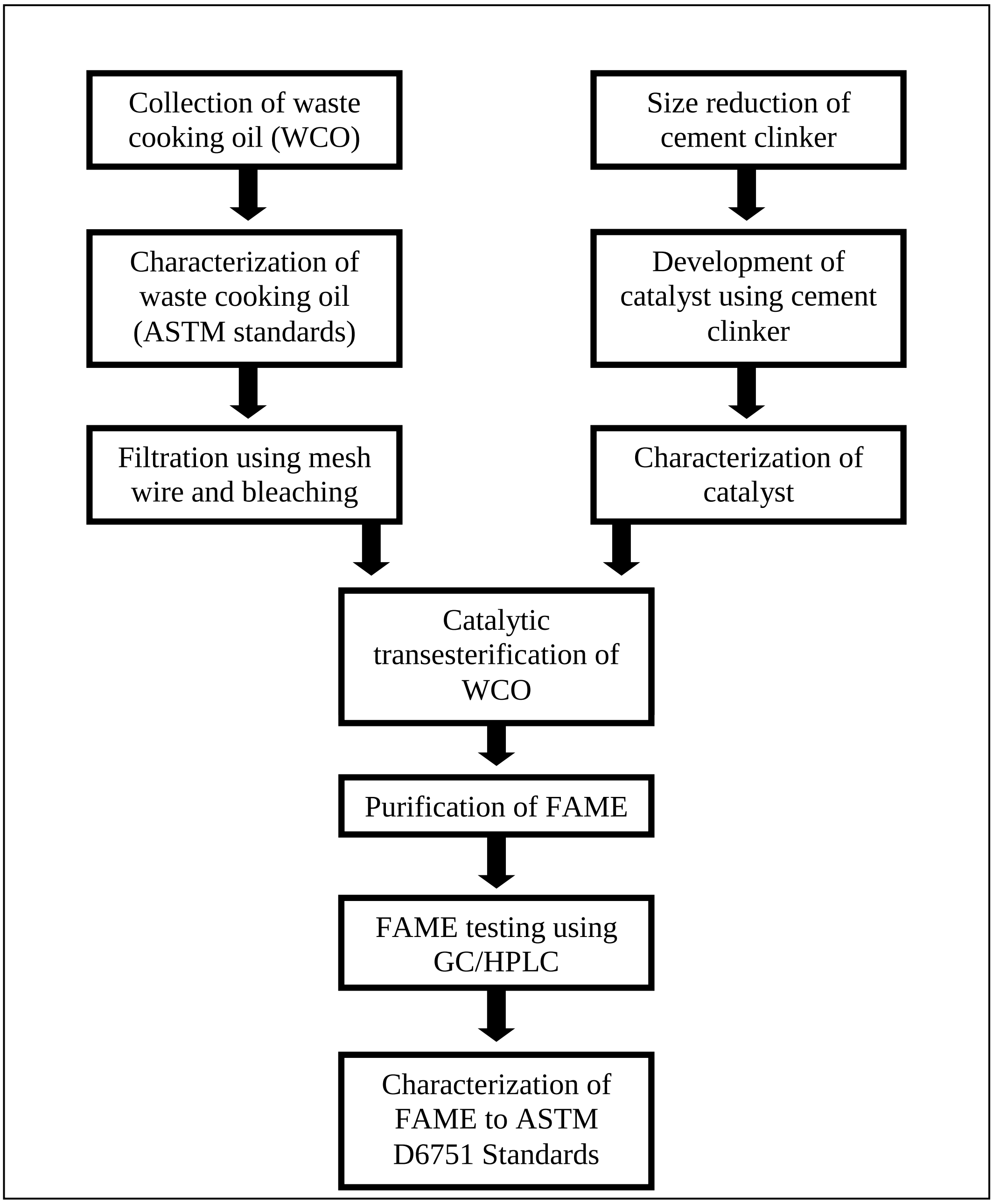

Figure 3.1: Experimental flow chart.

3.3 Materials and Methods

Chemicals for catalyst development and biodiesel synthesis were purchased from chemical laboratory suppliers. The raw material for catalyst development, cement clinker was collected from YTL-Pahang Cement (Malaysia) and feedstock used, waste cooking oil (WCO) was collected from local household. Chemical composition of cement clinker was characterized using XRF meanwhile free fatty acid (FFA) of WCO was determined according to ASTM.

The following chemicals were used:

a) methanol, sodium sulphate anhydrous, potassium hydroxide (KOH) pellets and Fuller's earth from Merck Germany

b) acetone analysis grade from Fisher Scientific US

Standards of fatty acid methyl esters (methyl oleate 99%, methyl palmitate 99% and methyl linoleate 99%), and methanol gradient grade for liquid chromatography were supplied by Sigma Aldrich US.

3.4 Preparation of catalyst

The preparation of catalyst from cement clinker (limestone based) with particle size of 250μm was prepared via wet impregnation method using aqueous solution of potassium hydroxide (KOH) in stirring process for 24 hours. The aqueous solution used is 10 wt.% solid (Ilgen & Akin, 2009). The catalyst dried in an oven at 105°C for 1 hour and calcined at 500°C or 700°C for 2,5, or 7 hours in muffle furnace Carbolite CWF 1200 (UK) with an increasing temperature rate of 10 °C/min as mention in Table 3.1. Calcination process is thermal treatment that applied to the ores or solid materials to get thermal decomposition or phase transition. Calcination process to catalyst as reported by Vujicic *et al*. (2010) gave high yield of biodiesel conversion compared to normal catalyst because calcined catalyst has high surface area that provides more reactions to take place in transesterification.