METHYL ESTER PRODUCTION USING FEEDSTOCK AND CATALYSTS FROM WASTE SOURCES

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for the award of the degree of
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DEDICATION

Dedicated to my parents, my brothers, my sister and friends, who gave me everlasting inspiration, never- ending encouragements and priceless support towards the success of this study.

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ABSTRACT

In the present work, waste sources, namely boiler ash, baby clam (*Paphia undulata*) shell and capiz (*Placuna placenta*) shell have been successfully utilized as solid catalysts in the transesterification of palm olein (RBD-PO) and waste palm cooking oil (WPCO) to produce methyl esters (biodiesel). In order to enhance the catalytic activity, the boiler ash had been calcined at 500 ˚C for 5 h (was labelled as BA-500), while waste shells of baby clam and capiz have been calcined at 900 ˚C for 2 h (labelled as BC-CaO-900 and C-CaO-900, respectively). The optimal reaction conditions found to be: for transesterification of RBD-PO and WPCO using BA-500 as a catalyst were 3 wt.% catalyst amount (based on oil weight) and 9:1 methanol to oil molar ratio for 1 h reaction period, while BC-CaO-900 and C-CaO-900 with 5 wt.% catalyst amount, 12:1 methanol to oil molar ratio for 3 h reaction period. All catalysts achieved over 96.5% methyl ester content at the reflux temperature of methanol (65 ˚C). Furthermore, the mixed-shell catalyst of BC-CaO and C-CaO (labelled as BC-C-Mixed-900) at a 1:1 weight ratio showed similar activity as the individual catalysts. The regenerated of the catalytic activity was investigated, and found that the BA-500 could be reused up to two times, while BC-C-Mixed-900 catalyst reused up to seven times when maintaining methyl esters content above 90%. In addition, the BA and BC-C-Mixed-900 catalysts exhibit tolerance towards the presence of water at 1.75% and 2.0% and free fatty acid at 1.75% and 1.75%, respectively, with over 80% of methyl esters content. Oil extracted from decanter cake (DC) was also investigated in this study, via *in situ* transesterification with ultrasonic irradiation and mechanical stirring method. The catalyst amount of 20 wt.% (based on oil weight), 150:1 methanol to oil molar ratio, co-solvent:DC (1:1) weight were found as the optimal conditions, yielding 86% and 45% methyl ester content in an hour reaction period for ultrasound irradiation and mechanical stirring, respectively. The emissions performance of WPCO B10 blend using BA-500 as a catalyst was investigated on horizontal single cylinder 4-stroke diesel engine (YANMAR NF19-SK). The results indicated that the WPCO B10 blend biodiesel gives lower CO_2 and CO emission compared to commercial diesel, thus contributed to the reduction of greenhouse gases.

ABSTRAK

Dalam kajian ini, bahan buangan abu tandan kosong, cengkerang batik dan cengkerang kapis telah digunakan sebagai mangkin pejal dalam proses transesterifikasi menggunakan minyak sawit tulen (RBD-PO) dan minyak masak sawit terpakai (WPCO) untuk menghasilkan metil ester. Dalam usaha untuk meningkatkan aktiviti mangkin, abu tandan kosong telah dikalsin pada suhu 500 ˚C selama 5 jam (dilabel sebagai BA-500), manakala cengkerang batik dan cengkerang kapis telah dikalsin pada suhu 900 ˚C selama 2 jam (masing-masing dilabel sebagai BC-CaO-900 dan C-CaO-900). Keadaan optimum tindak balas untuk transesterifikasi RBD-PO dan WPCO dengan menggunakan BA-500 sebagai mangkin adalah 3% (berdasarkan berat minyak) dan 9:1 nisbah molar metanol kepada minyak, selama 1 jam, manakala transesterifikasi dengan menggunakan mangkin daripada cengkerang menggunakan 5% (berdasarkan berat minyak), 12:1 selama 3 jam. Kesemua mangkin mencatat lebih 96.5 % metil ester pada suhu refluks metanol (65 ˚C). Campuran cengkerang (dilabel sebagai BC-C-mixed-900) pada nisbah berat 1:1 menunjukkan aktiviti yang sama seperti cengkerang individu. Keberkesanan penggunaan semula mangkin dikaji dan didapati bahawa BA-500 boleh digunapakai semula sebanyak 2 kali dan BC-C-mixed-900 sebanyak 7 kali dengan kandungan metil ester lebih dari 90%. Tambahan pula, BA-500 dan BC-C-mixed-900 masing-masing menunjukkan toleransi terhadap air pada 1.75% dan 2.0 % dan asid lemak bebas pada 1.75%. Pengekstrakan minyak daripada *decanter cake* (DC) juga dikaji melalui kaedah transesterifikasi *in situ* dengan kaedah sinaran ultrasonik serta kaedah adunan mekanikal dengan 20% mangkin (berdasarkan berat minyak), 150:1 nisbah molar metanol kepada minyak dan pelarut:DC (pada nisbah berat 1:1) telah didapati sebagai keadaan pelarut optimum, 86% dan 45% kandungan metil ester dalam satu jam untuk kaedah sinaran ultrasonik dan kaedah adunan mekanikal. Prestasi gas ekzos biodiesel B10 juga dikaji, hasil dari metil ester WPCO dan BA-500 menggunakan enjin diesel silinder tunggal melintang 4-lejang (YANMAR NF19-SK). Data menunjukkan bahawa B10 menghasilkan CO_2 dan CO yang lebih rendah berbanding dengan diesel komersial, sekaligus menyumbang kepada pengurangan gas rumah hijau.

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LIST OF ABBREVIATIONS

BA	Boiler ash
BA-500	Boiler ash calcined at 500 ˚C, 5h
BC-CaO	Baby clam shell calcium oxide
BC-CaO-900	Baby clam shell calcium oxide calcined at 900 ˚C, 2h
BC-C-Mixed-900	Baby clam and capiz shell mixed calcined at 900 ˚C, 2h
BET	Brunauer-Emmett-Teller
CPO	Crude palm oil
DC	Decanter cake
DOBI	Deterioration of bleachability index
EFB	Empty fruit bunch
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FFB	Fresh fruit bunches
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
GHG	Greenhouse gases
^{1}H-NMR	Proton nuclear magnetic resonance
ICP-MS	Inductively coupled plasma mass spectrometry
ME	Methyl esters
MeOH	Methanol
O-DC	Oil extracted from decanter cake
PE	Petroleum ether
RBD-PO	Refined, bleached and deodourized palm olein
SBC	Spent bleaching clay
SEM	Scanning electron microscopy
TGA/DTA	Thermogravimetry analysis/ differential thermal analysis
TLC	Thin layer chromatography
WPCO	Waste palm cooking oil
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The global population is estimated to increase up to 30% in the next 25 years, where 80-90% of the increase is predictable to be in developing countries (IEA, 2004). At the same time, global energy demand is increasing in worldwide. United State, Russia and China are the world's largest producers and consumers of world energy. In the World Energy Outlook 2004, it is estimated that huge investments in production capacity and infrastructure are needed in many countries to secure the necessary access to energy (IEA, 2004). For many decades, fossil fuel is the most important energy source, worldwide while the issues of pollution and fossil fuel reserve are high in current decades. The global warming due to carbon dioxide emission will have a great impact on the climate and the temperature of our earth where the increase is estimated between 2 to 6 ˚C year 2100.

The growing awareness concerning the environmental issues on energy supply and usage have recently been the topic of interest in research. Among various alternative energy discovered, biodiesel is one of the promising blended fuel to substitute petroleum derived diesel which offers friendly and sustainable environment. Commonly, biodiesel is produced from neat vegetable oil such as soybean, palm, rapeseed, and sunflower. The European Union (EU) uses rapeseed as a major biodiesel lipid feedstock; the United State (US) utilizes oil from soybean for this purpose.

Biodiesel also called as fatty acid methyl ester (FAME) is derived from vegetables oil or animal fats. Transesterification process is one of the methods to produce biodiesel. In light of the fact that it is non-harmful, biodegradable and non-combustible, biodiesel worldwide prevalence act as an elective vigour energy source. Biodiesel has alternate gain in term of ecological profits. Biodiesel has shown development environmental adaptation in comparison to conventional mineral diesel on its usage. Biodiesel does not contain sulphur or aromatics and can be used in conventional diesel engine which results in substantial reduction of carbon monoxide, particulate matter and unburned hydrocarbons. The use and production of biodiesel resulted in a 78.5% decrease in carbon dioxide emissions as reported by U.S Department of Energy (EIA, 2014). If biodiesel is widely used, it could decrease the carbon dioxide emissions in certain sector like in industry and transportation. There are number of research about the comparison of petroleum diesel with biodiesel in term of the performance of vehicle and the potential to reduce the emission of carbon. Biodiesel absolutely can decrease the emissions of carbon and increase the security of energy (Sheehan et al., 1998). With those reasons, we can prove that biodiesel has benefit in term of cleaner environment.

Other than that, to improve the economy of biodiesel production and its commercial production at the industry scale, the use of cheap feedstock is one of the ways. To ensure low biodiesel production cost, the best feedstock need to be selected. Feedstock alone accounted for 75% of the overall biodiesel production cost as shown in Figure 1.1. Feedstock should be available at low price in order for biodiesel to remain competitive compare to petroleum diesel. Others properties of feedstock includes low agriculture inputs, favourable fatty acid composition, increase oil content and potential market for agricultural by-products.

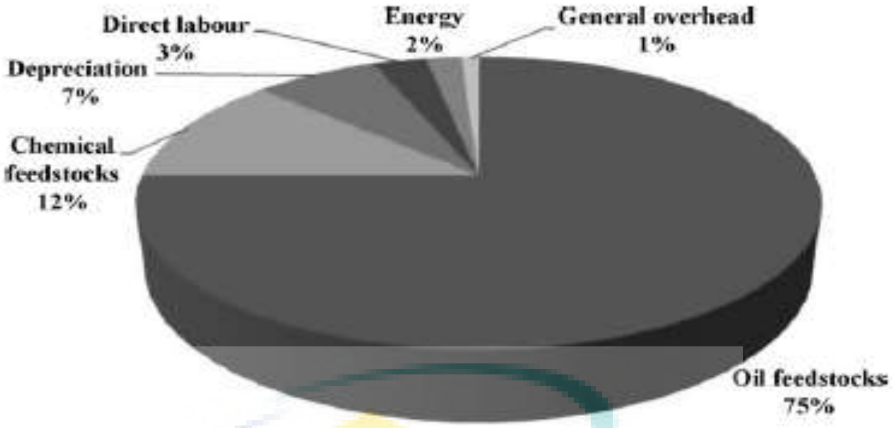


Figure 1.1: General cost breakdown for production of biodiesel

Source : Lim and Teong (2009)

In addition, the trend also indicates the need for large amounts of vegetable oil supply and if the major portion of the oil comes from neat edible oil then the question of food starvation arises. The concern in respect of food starvation or food for fuel already constitutes a heated argument. With the increasing need for oil in the near future, it will definitely complicate the situation, as globally there are 925 million people undernourished; reported by the Food and Agriculture Organization of the United Nations in 2011. Hence, the exploitation of raw materials waste source has been of recent interest. Researchers have effectively utilized waste cooking oil (WCO), chicken fat, beef tallow, spent bleaching clay (SBC), palm fatty acid distillate (PFAD), as a source of feedstock biodiesel (Ma et al., 1999; Chin et al., 2009; Lim et al., 2009; Malvade and Satpute, 2013, and Shi et al., 2013) .

In Malaysia, the biodiesel initiatives started in 2006, 12 biodiesel plants are in operation, with a total annual production capacity of 1.22 million tonnes from January to September in 2013 (Adnan, 2013). In June 2011, B5 biodiesel can be found in the market, the B5 biodiesel is an addition of 5% biodiesel and 95% of regular petroleum-based diesel which is suitable for the normal diesel engine vehicle without any modifications. According to The Star Online, 2014, the biofuel option is often seen as a safety net project for the palm oil sector, especially when the price of crude palm oil (CPO) is about to hit rock bottom and the palm oil stockpile sits above the critical two million tonne mark. If the price of CPO falls especially below RM800 per tonne, it is best to go for biofuel or biodiesel and if the CPO price recovers, it will be switched back to food related production. Therefore, given the current dire situation whereby palm oil stocks are at a record high of 2.63 million tonnes and CPO price trading below RM2,500 per tonne, the Government has once again decided to revisit the biofuel option with focus on production and marketing of B10 biodiesel programme (Rittgers and Wahab, 2013).

The utilization of waste/used edible oils as raw material is a relevant idea, and there are many advantages for using waste feedstock for biodiesel production, namely (i) abundant supply, (ii) relatively inexpensive, and (iii) environmental benefits (Tashtoush et al., 2004; Boey et al., 2011c, and Wang et al., 2011). Waste oil in many countries is in abundance. It was reported that, annually, EU recorded 0.7–1.0 million tonnes of waste oil, Turkey 350,000 tonnes and Canada 120,000 tonnes, in addition to those uncollected oils, which goes to waste through sinks and garbage and eventually seeps into the soil and water sources (Balkanlioğlu, 2012). Furthermore, it is generally accepted that reusing used cooking oil for human consumption is harmful to health (See et al., 2006).

In addition, another waste oil source from decanter cake (DC) could be explored to be a feedstock for biodiesel production. DC is a solid waste produced when the crude palm oil is centrifuged for purification where the supernatant is the purer palm oil and the sediment is the decanter cake. DC contains water (about 76%, on wet basis), residual oil (about 12%, on dry basis) and nutrients, cellulose, lignin and ash. There are previous reports on the use of DC in the area of bio-fertilizer, biofuel and cellulose (Kandiah, 2012, and Razak et al., 2012). Oil adsorbed on DC is a minor by-product of palm oil purification process with appreciable magnitude that could be a potential feedstock for production of biodiesel (methyl ester).

A large range of industrial wastes, both natural and synthetic, are disposed without extracting the useful components from them. Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. Malaysia is the world’s second largest producer of palm oil and contributes 39% of the world's total palm oil production (GGS, 2013). The total crude palm oil (CPO) produced was 19.22 million metric tonnes in 2013, with of total 5.04 million hectares of land with oil palm trees (GGS, 2013, and MPOB, 2014), has an estimated total amount of processed fresh fruit bunches (FFB) of 7.8 tonnes/ha, 70% of which is removed as waste, such as palm press fiber (30%), empty fruit bunches (EFB, 28.5%), palm kernel shell (6%), decanter cake (DC, 3%) and others (2.5%) (Ramli et al., 2012, and Zafar, 2013). As such, in the processing of 39 million tonnes of FFB annually (7.8 tonnes/ha x 5 million ha), 1.17 million tonnes of waste DC (3% of 39 million tonnes FFB) is generated in Malaysia alone. Indeed, the boiler ash (BA) used as a catalyst in this work is also a waste by-product of palm oil mill. Generally, in palm oil mill, approximately 5% of BA is produced upon the burning of dry EFB, fiber and shell in boiler (Tangchirapat et al., 2007; Boey et al., 2011a, and 2012).

Currently, BA which is the by-products of oil processing is only used as boiler fuel and combustion ash is used as a substitute for fertilizer (Salètes et al., 2004) or animal feed (Zahari et al., 2012). Palm empty fruit bunches combustion ash has high potassium levels (45-50%) (Onyegbado et al., 2002). Some literature has reported the utilization of BA as a base catalyst in the synthesis of biodiesel. Researchers previously reported the BA utilization as a source of K_2CO_3 catalysts for the synthesis of biodiesel from coconut oil (Imaduddin et al., 2008). Other researchers also reported the influence of ash of palm EFB in palm oil transesterification to biodiesel (Yoeswono et al., 2007).

Transesterification is usually carried out using homogeneous catalyst (sodium or potassium hydroxide). However, the process has few drawbacks, in this situation the use of heterogeneous catalyst is a better solution. Therefore, a new process using heterogeneous catalyst has been developed for environment-friendly and reduction of production cost. There are many types of heterogeneous catalysts from waste, such as waste egg, crab, and oyster shells; bone and ash (Boey et al., 2009a; Nakatani et al., 2009; Chakraborty et al., 2010; Boey et al., 2011b, and Obadiah et al., 2012). Baby clam (*Paphia undulata)* is a species of saltwater clam, this species inhabits inshore shallow sandy seabed in Southeast Asia. *Paphia undulata* is second most important bivalve in Malaysia in term of total production. Estimated potential annual production is 20,000 metric tonnes (Sin and Mahmood, 2013). On the other hand, capiz (*Placuna* *placenta*) is a successful source with abundant and diverse populations. *Placuna placenta* is a highly asymmetrical bivalve with a characteristically thin, translucent shell often used in handicrafts such as lampshades. It lives mostly on mangrove coasts from the Arabian sea to the coast of China. Populations are concentrated in the Gulf of Aden [12°N, 48°E], the coast of India [21°N, 78°E], the Malaysia Peninsular [3°N, 101°E], the southern coasts of China [19°N, 109°E], and the northern coasts of Borneo [4°N, 114°E] to the Philippines [14°N, 121°E]. The major compound of capiz is calcium carbonate (Suryaputra et al., 2013), therefore baby clam and capiz could be potential sources of CaO since they consist of >90 % of $CaCO_3$ and upon heat treatment the $CaCO_3$ could be easily converted to CaO.

The utilization of oil and catalyst from waste sources could also counter the environmental damage. Furthermore, within the last 5 years, many research works have focused on the exploitation of waste materials as catalysts for the production of biodiesel. They include shells, ashes, rock, and bone (Xie et al., 2009; Boey et al., 2011d; Ilgen, 2011, and Obadiah et al., 2012). Due to their abundance and low cost, the exploitation of such waste materials has become very attractive. As such, this work focusing on feedstock and catalysts from waste sources in the preparation of methyl esters.

1.2 PROBLEM STATEMENT

There are some problems that need to be encounter in order to produce biodiesel and one of the main problem is the major cost for the biodiesel production which mainly due to the cost of feedstock. Using a low cost oil for biodiesel production become very attractive, in this work the feedstock been sourced from waste oil is waste palm cooking oil (WPCO) as well as palm olein, while oil extracted from decanter cake also was investigated as a new waste source. On the other hand, waste oil is low in quality feedstock as such need a suitable catalyst to tolerance the moisture and FFA. Typically, production of biodiesel by transesterification using typical catalyst including NaOH, KOH or their alkoxides. This work involved the production of biodiesel also utilization waste sources as a catalyst, the catalyst derived from waste sources such as from ash and shells which is cost effective with good availability. Other than that, solid catalyst which has the capability to tolerate the moisture and fatty acid in the feedstock and it also can be recycled. By utilizing the waste matters, the cost of the production biodiesel could be decreased, and natural mineral resources could be utilized as well.

1.3 OBJECTIVES

The objectives of this study are:

i. To utilize catalysts produced from boiler ash, baby clam shell and capiz shell in transesterification of refined, bleached and deodorized palm olein (RBD-PO) and waste palm cooking oil (WPCO).
ii. To study the reusability of the catalysts and their tolerance towards moisture and FFA in waste palm cooking oil.
iii. To compare methyl ester conversion between single step (*in situ*) method using ultrasound irradiation and mechanical stirring methods using decanter cake (DC) as a feedstock.

1.4 SCOPE OF STUDY

Based on the objectives, the major scope of this experiment is to find out the effectiveness of catalyst from waste sources to transesterify the low cost feedstocks. In this experiment the boiler ash, baby clam shell and capiz shell as a waste catalysts were utilized to transesterify refined, bleached and deodorized palm olein (RBD-PO) and waste palm cooking oil (WPCO). The reusability and capability of the catalysts from the boiler ash and mixed shell (baby clam and capiz) toward moisture and FFA that are present in the WPCO were also investigated. *In situ* transesterification of decanter cake (DC), as a new feedstock, by ultrasound and mechanical stirring using boiler ash as a catalyst was studied. In addition, the engine performance of WPCO B10 was compared to petro-diesel fuel using diesel engine (YANMAR NF19-SK) was investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

Increasing concerns on the potential of global climate change, declining air and water quality, and human health are inspiring the development of biodiesel, as a renewable, cleaner burning diesel alternative. The alternatives to diesel fuel must be technically feasible, economically competitive, environmental acceptable and readily available (Mahanta and Shrivastava, 2008). Many of these requisites are satisfied by vegetable oil or in general by triglyceride. Indeed, vegetable oils are widely available from a variety of sources and they are renewable (Encinar et al., 2007).

Biodiesel fuel based on vegetable oil, such as methyl or ethyl ester, have the following advantages over diesel fuel: high cetane number, produce lower carbon monoxide and hydrocarbon emissions, are biodegradable and non-toxic, provide engine lubricity to low sulfur diesel fuels and and so is environmentally beneficial (Ma and Hanna, 1999; Demirbas, 2003, and 2005). Biodiesel contains electronegative elemental oxygen, therefore it is slightly more polar than diesel fuel, and as a result the viscosity of biodiesel is higher than that of diesel fuel. The heating value of biodiesel is lower than diesel fuel due to the presence of elemental oxygen (Deshpande and Kulkarni, 2012).

The high cost of biodiesel production, which is 1.5 to 3 times higher than that of petroleum diesel, is an obstacle in the use of biodiesel (Zhang et al., 2003; Haas et al., 2006, and Liu et al., 2012). Biodiesel can be blended with diesel to reduce the particulate emissions from the engine as well as the cost impact of biodiesel. Biodiesel can be either used in its pure form (B100) or can be blended with mechanical stirring diesel (e.g. B5, B10 and B20). Biodiesel can also be used as an additive because it is a very effective lubricity enhancer (Ball et al., 1999). Biodiesel also exhibits potential for compression-ignition engines without the need for engine modification (Wang et al., 2000, and Kumar et al., 2010).

Biodiesel also can reduces the life-cycle greenhouse gas (GHG) emissions by displaces the petroleum. The GHG emissions benefits of biodiesel are especially significant, because carbon dioxide (CO_2) released during fuel combustion is offset by the CO_2 captured by the plants from which biodiesel is produced. The CO_2 in the air absorbed by the plant when it grows. In addition, when the biodiesel can be obtained from the oil extracted from plant as soybeans, when it burned, the CO_2 and other emissions are released and returns to the atmosphere. The CO_2 concentration in the atmosphere does not increase because the CO_2 will be reuse by plant when it grows.

Sheehan et al. (1998) studied the total life cycles of CO_2 released at the tailpipe biodiesel and petroleum diesel based on the combustion of fuel in the bus. As shown in Figure 2.1, the overall life cycle emissions of CO_2 from B100 are 78.45% lower than those of petroleum diesel. B20, the most commonly used form of biodiesel in the US, reduces net CO_2 emissions by 15.66% per gallon of fuel used.

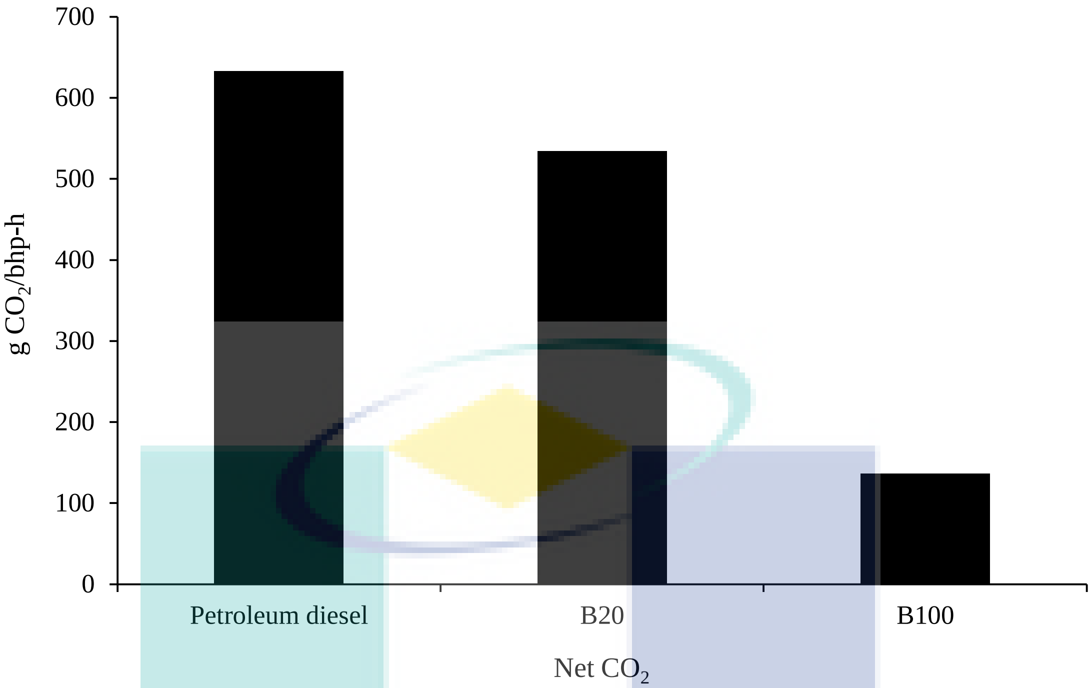


Figure 2.1: Comparison of net CO_2 life cycle emissions for petroleum diesel and biodiesel blends

Source: Sheehan et al. (1998)

2.2 HISTORICAL BACKGROUND ON BIODIESEL PRODUCTION

Transesterification of triglycerides in oils is not a new process. Transesterification of vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Life for the diesel engine begin on August 10, 1893 in Augsburg, Germany when famous German inventor Dr. Rudolf Diesel published a paper entitled "The theory and construction of a rational heat engine". He demonstrated his compression ignition engine by using peanut oil the first biodiesel as a prototype engine on his prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base. August 10th has been declared International Biodiesel Day. In 1900 Diesel again demonstrated his engine at the World Fair in Paris, France and received the Grand Prix (highest prize). In 1912 speech, Rudolf Diesel said "*The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time*" (Haas and Foglia, 2005).

Research into the use of transesterified sunflower oil and refining it to diesel fuel standard was initiated in South Africa in 1979. While, the process to produce fuel quality engine tested biodiesel was completed and published international in 1983. By November 1987, Gaskoks, an Austrian Company, put up the first pilot plant for biodiesel, obtained the technology from the South Africa, Agricultural Engineers. On 12 April 1989, the establishing of the first industrial biodiesel plant, with capacity of 30,000 tonnes of rapeseed annually. Moreover, throughout the 1990s, biodiesel plants were opened in many European Countries, such as the Czech Republic, France, Germany and Sweden (Haas and Foglia, 2005).

2.3 GLOBAL BIODIESEL PRODUCTION

In recent years, the annual increases in biodiesel production, shown in Table 2.1, in addition global biodiesel demand is predicted to grow by 15%/year to 85 Mt by 2020. In the short term at least 11 countries (Germany, France, Italy, UK, Spain, Netherlands, US, Argentina, Brazil, Indonesia and Malaysia) are expected to exceed a production of 1 Mt/year.

Table 2.1: Predicted annual increases in biodiesel production (Mt)

Producer	2008-2010	2011-2015
EU	1.7	1.2
USA	0.8	0.4
South America	1.1	1.1
Asia-Pasific	1.1	1.4
World	5.0	4.7

Source: Gunstone (2007)

There are many sources could be use as a feedstock to produce biodiesel. Table 2.2 presents different feedstock from different countries that are used in the production of biodiesel.

Table 2.2: Edible, non-edible and waste potential feedstock for biodiesel process in worldwide

Country	Potential Feedstock
USA	Soybeans/waste oil/peanut
Canada	Rapeseed/animal fat/soybeans/yellow grease and Tallow/mustard/flax
Mexico	Animal fat/waste oil
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Linseed oil/sunflower
Greece	Cottonseed
UK	Rapeseed/waste cooking oil
Sweden	Rapeseed
Ireland	Frying oil/animal fats
India	*Jatropha*/*Pongamia pinnata* (karanja)/soybean/ Rapeseed/sunflower/peanut
Malaysia	Palm oil
Indonesia	Palm oil/*Jatropha*/coconut
Singapore	Palm oil
Philippines	Coconut/*Jatropha*
Thailand	Palm/*Jatropha*/coconut
China	*Jatropha*/waste cooking oil/rapeseed
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/tallow

Source: Atabani et al. (2013)

2.3.1 Biodiesel in Europe

Biodiesel is the most important biofuel in the EU, on volume basis, represents about 70 % of the total transport biofuels market, it is due is main European solution to reduce emissions from transport. Most biodiesel in the EU is used in urban public bus and truck fleets and increasingly so also in private cars. Biodiesel produced on an industrial scale in the EU primarily as rapeseed methyl ester. The total biodiesel capacity of the EU amounted to 2.25 Mt in 2004, located mainly in Germany, France and Italy, is rapidly been extended of 16 Mt for EU by mid-2008. Germany is the leading producer and consumer in the region, followed by France (Smith et al., 2013).

Figure 2.2 showing the overall EU production decreased in 2012, reaching 9.6 million tonnes. This represents a 10% decline compared to 2011. In 2009, the European Commission defined a 10% use of renewable in the transport sector, to which biodiesel will be the major contributor. Hence, decrease in European production is balanced by higher uncompetitive imports. Argentine and Indonesian biodiesel imports took over imports originating from the USA. In 2009, the European Commissions imposed imports duties against subsidised US biodiesel. While the imposition of measures should have contributed to the European industry's recovery, in fact, massive imports from Argentine and Indonesia took over the US market share. In 2011, these two countries alone represent over 90% of the international market partners of the European territory and 95% of EU biodiesel imports in 2012.

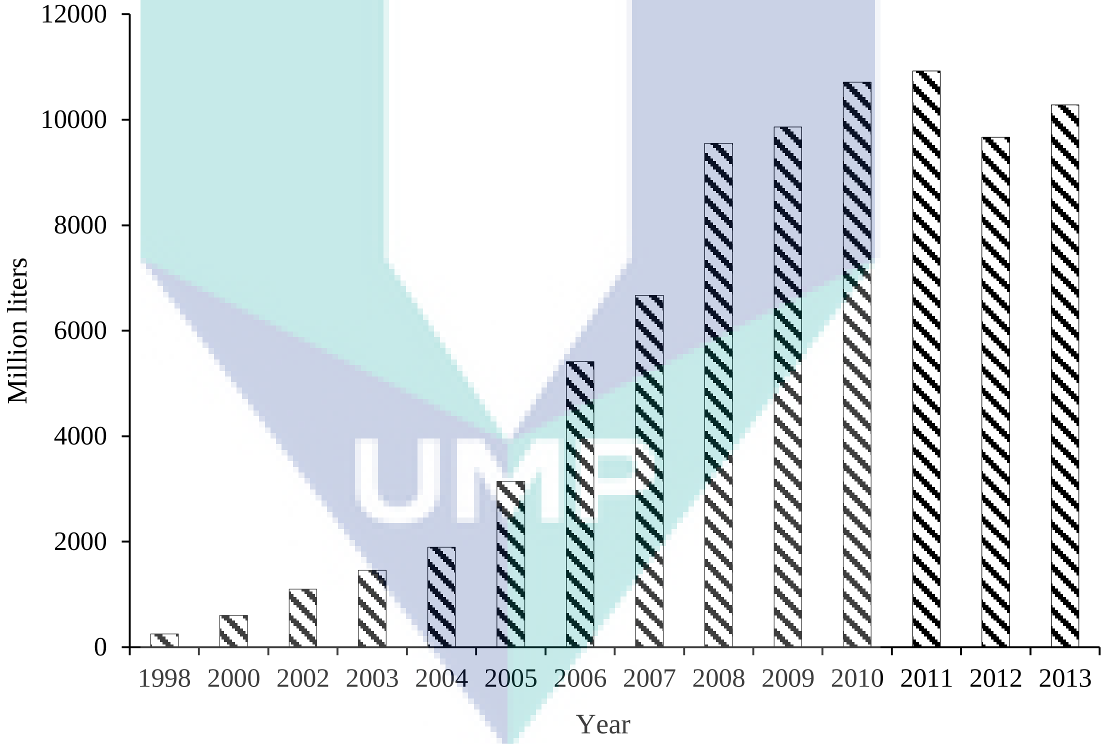


Figure 2.2: Biodiesel production in EU

Source: Smith et al. (2013)

a) Mandatory Requirement in Europe to use Biodiesel

Nowadays, biofuels are not competitive with the fossil fuel due to the relatively low price of crude oil. Biofuels are usually produced and used locally, but this situation has changed in Europe. Under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) most industrialised countries have committed themselves to limit o reduce their emissions of greenhouse gases (CO_2, CH_4, N_2O, HFCs, PFCs, SF_6) by 5.2% in relation to the base year 1990 or 1995. The EU committed to cut its GHG emissions within 2008-12 by 8% from their 1990 level. Ambitious self-imposed climate change objective were defined by most EU member states. In May 2003, the EU outlined the Biofuels Directive (EU Directive 2003/30/EC) on the promotion and use of biofuels and other renewable fuels for transport. Biodiesel should substantially reduce petroleum used and GHG generated compared with their petroleum-derived alternatives. The general EU policy objectives considered most relevant to the design of energy policy are (i) the competitiveness of the EU economy, (ii) the security of energy supplies, and (iii) environmental protection (Smith et al., 2013).

2.3.2 Biodiesel in United States

The most common sources of oil for biodiesel production in the United State are soybean oil, much of the early support for biodiesel in US came from the American Soybean Association. However, the vegetable oil crops cannot realistically satisfy US (or indeed global) demand for fuel consumption. The combined vegetable oil, animal fat and yellow grease production (primarily recycled cooking oil from restaurants) represent one third of the U.S. total fats and oils production. The United States is the world’s large single biodiesel market by 2010. The rapid growth of US biodiesel production, from a more 0.5 Mgal in 1999, to 7 Mgal (2000) and to over 25 Mgal (2004) are presented in Figure 2.3. While in 2003 to 2004, it lead stagnant, but rapidly increased in 2005 to about 700 Mgal in 2008.

Biodiesel fuel is mainly used for transportation, similar to diesel fuel. Monthly biodiesel production had both sharp increases and decreases in 2009 and 2010 due in part to the expiration and reinstatement of Federal tax credits and renewable fuels standards affecting biodiesel. Annual biodiesel production was 516 million gallons in 2009. Production fell to 343 million gallons in 2010 but then rebounded to 967 million gallons in 2011, the production came from 113 active biodiesel plants. Soybean oil was the largest biodiesel feedstock in 2011, at 4,136 million pounds consumed. The next three largest biodiesel feedstocks during 2011 were canola oil (847 million pounds), yellow grease and other recycled feedstocks (665 million pounds), and white grease (533 million pounds) according to data released by the U.S. Energy Information Administration (EIA. 2014).

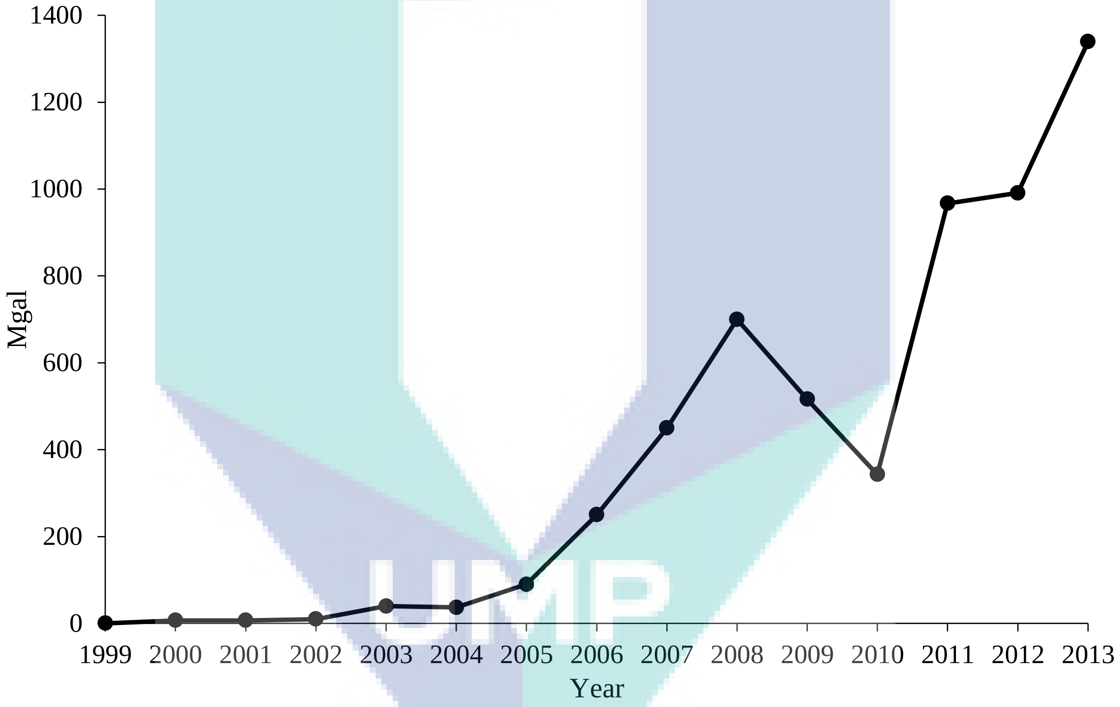


Figure 2.3: US biodiesel production

Source: Bart et al. (2011)

2.4 BIODIESEL IN MALAYSIA

Malaysia is one of the major global producers of palm oil. It produced nearly 19 million tonnes of crude palm oil in year 2013 (MPOB, 2014). As such, Malaysia has very high potential to cater for the global demand of biofuel as it benefits from vast agricultural land and a tropical climate, in which oil palm plantations are very feasible. As the major palm oil producer in the world, biodiesel production will certainly add value to the local palm oil industry. Development in biodiesel will certainly lessen Malaysia’s dependency on foreign crude oil imports. And now, Malaysia has set its sights on promoting and producing the palm oil for purpose of making biodiesel. Biodiesel can be found in the market from the month of June 2011 onwards. The supply of the new fuel was started at Putrajaya followed by Negeri Sembilan, Selangor, Kuala Lumpur and Malacca as well. Biodiesel is implemented nationwide by 2013 and it is a greener alternative to regular diesel. “*Time is needed by the Petroleum companies in order to build blending facilities in order to mix palm methyl ester with regular petroleum-based diesel*”, Minister Tan Sri Bernard Dompok said. The programme is taken as the initiative to reduce the greenhouse gases and also would elevate the nation's image internationally as one of the countries which started renewable energy programmes.

A good news, very recently, FELDA IFFCO Sdn Bhd has agreed to sell its biodiesel facility in Cincinnati, Ohio, to United States-based refiner Marathon Petroleum Corp (MPC). MPC signed an agreement to purchase the plant, which currently produces several products, including biodiesel and glycerin, from Felda IFFCO. The capacity of the plant is 4,100 barrels per day. The transaction is expected to close in April 2014, it said in a statement. However, details of the transaction were not disclosed. MPC senior vice-president of supply, distribution and planning, Mike Palmer, said the company has been a producer and large blender of ethanol for many years, and this acquisition will broaden its renewable fuels portfolio with a quality asset (*The Star Online*, 2014).

2.5 PROCESS OF SYNTHESIZING BIODIESEL

Among the available biodiesel production technologies; dilution/blending, micro-emulsification, thermal cracking and pyrolysis; transesterification seems to be the best choice, as the physical characteristics of fatty acid esters are very close to those of diesel fuel and the process is relatively simple. The advantages and disadvantages of different methods in biodiesel production is presented in Table 2.3.

Table 2.3 : Different methods of biodiesel production

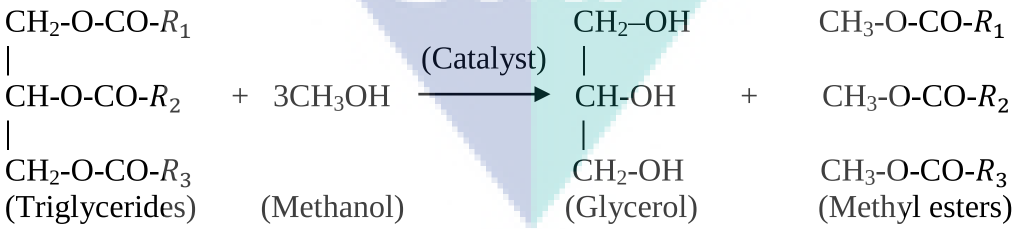
Methods	Definition	Advantage	Disadvantage
Micro-emulsions	A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles	Better spray patterns during combustion Fuel viscosity is lowered	Lower energy content Lower cetane number
Direct use and blending	Direct use as diesel fuel or blend with diesel fuel	Liquid nature-portability Heat content (~ 80 % of diesel fuel) Readily available; renewability	Higher viscosity Higher volatility The reactivity of unsaturated hydrocarbon chains
Thermal cracking (pyrolysis)	The conversion of long-chain and saturated substance to biodiesel by means of heat	The final product are similar to diesel fuel in composition	Energy intensive and hence higher cost
Transesterification	The reaction of a fat or oil mix an alcohol with catalyst to form esters and glycerol	Renewability; higher cetane number; lower emissions; higher combustion efficiency	Disposal of glycerol and waste water

Source: Leung et al. (2010)

2.5.1 Transesterification Process

Transesterification is a catalytic process of alcohol displacement from an ester to another. Although three moles of methanol are required, stoichiometrically, since transesterification is a reversible process, excess methanol is proposed to shift the reaction forward. Transesterification between triglyceride and alcohol is commonly known as alcoholysis, and, if methanol is used, then it is called methanolysis. The methanolysis of oil, together with a suitable catalyst, produces fatty acid methyl esters and glycerol. At the end of the reaction, the latter settles down to form the bottom layer. It is important to note that the main purpose of transesterification is to lower the viscosity and at the same time to increase the volatility of the oil. The overall transesterification process is normally a sequence of three consecutive steps, which are reversible reactions. From triglycerides, the first step is the formation of diglycerides, followed by the conversion of diglycerides to monoglycerides and finally from monoglycerides the formation of three moles of methyl ester and a mol of glycerol.

Common method for converting oils to produce biodiesel is by transesterification. Transesterification is the chemical reaction between triglycerides and short-chain alcohol in the presence of catalyst to produce mono-ester. The long- and branched-chain triglyceride molecules are transformed to mono-esters and glycerine. The production of biodiesel by transesterification with catalyzed by both homogenous and heterogeneous catalysts. Although non catalytic transesterification is possible, via supercritical methanol, catalytic transesterification is commonly accepted as an industrial process due to its lower operational cost (Leung et al., 2010). The chemical reaction is shown in equation in Figure 2.4.



$$\begin{array}{lcccccc}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & & & CH_2\text{–}OH & & CH_3\text{-}O\text{-}CO\text{-}R_1 \\
| & & & \text{(Catalyst)} & | & & \\
CH\text{-}O\text{-}CO\text{-}R_2 & + & 3CH_3OH & \longrightarrow & CH\text{-}OH & + & CH_3\text{-}O\text{-}CO\text{-}R_2 \\
| & & & & | & & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & & & & CH_2\text{-}OH & & CH_3\text{-}O\text{-}CO\text{-}R_3 \\
\text{(Triglycerides)} & & \text{(Methanol)} & & \text{(Glycerol)} & & \text{(Methyl esters)}
\end{array}$$

Figure 2.4: Chemical reaction for transesterification process

During the transesterification process, the glycerine portion of the oil molecules is replaced by alcohol and eventually removed from the mixture in the washing and drying process where biodiesel is formed (as shown in Figure 2.4).

a) *In situ Transesterification*

In situ transesterification is different from the mechanical stirring reaction. The concept of *in situ* transesterification was considered of oil-containing in material directly contacts with catalyst alcohol and co-solvent in the reaction. That is, extraction and transesterification directly instead in one step reaction, the co-solvent acting as an extraction and alcohol as a transesterification reagent. Harrington and D'Arcy-Evans, (1985) claimed that *in situ* transesterification of sunflower seed produced higher methyl ester than mechanical stirring method and both processes yielded similar quality of fatty acid esters.

Kildiran et al. (1996) and Qian et al. (2008) reported that *in situ* transesterification is inactive without catalyst. Georgogianni et al. (2008) observed that by using sunflower as a feedstock, the conversion of methyl ester was very high 97% when using methanol and sodium hydroxide as a catalyst. However, Shuit et al. (2010) observed by using *Jatropha curcas* as a feedstock, the very high methyl ester content was achieved at 99.8%, with 0.2% sulphuric acid, 300:1 methanol to oil molar ratio for 24h, using *n*-hexane as a co-solvent. Boey et al. (2011a) reported by using *in situ* transesterification of spent bleaching clay (SBC) that the optimum condition was obtained at 5.4 wt% KOH, methanol to oil mass ratio of 5.9:1 and 1:1 mass ratio of co-solvent (petroleum ether or ethyl methyl ketone).

b) *Ultrasonic Assisted in Transesterification*

In the last two decades, many researchers used ultrasound to produce biodiesel. Biodiesel normally produced in batch reactors that use heat and mechanical stirring as energy input. Ultrasounic irradiation is a useful tool for emulsification of immiscible liquids. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge one liquid to the other. This effect can be employed for biodiesel production. The low frequency ultrasound is an efficient, time saving and economically functional, offering a lot of advantages over the mechanical stirring. Ultrasounds can be a valuable tool for the transesterification of tryglicerides to prepare the biodiesel at industrial scale (Stavarache et al., 2005).

Stavarache et al. (2005) reported, ultrasonic transesterifcation can achieve a biodiesel yield in excess of 99%. The processing time can be reduced from the mechanical stirring 1 to 4 hour batch processing to less than 30 second. In the industry, ultrasonication can reduce the separation time from 5 to 10 h using mechanical stirring agitation, to less than 60 minutes. This method also helps in decreasing the amount of catalyst required by up to 50% due to increased chemical activity in the presence of the cavitations formed due to ultrasonication. Ultrasonication also significantly reduces the amount of excess alcohol required for processing along with increasing the purity of the glycerine formed.

The molar ratio of alcohol:oil used is only 6:1. Normal chain alcohols react fast, while secondary and tertiary alcohols show some or no conversion after 60 min of reaction. Surprisingly, 40 kHz ultrasounds are much more effective in the reduction of the reaction time (10–20 min). Using 28 kHz give slightly better yields (98–99%), but longer reaction time, while higher frequencies are not useful at all for the transesterification of fatty acids (Stavarache et al., 2005, and Gude and Grant, 2013).

2.6 WASTE SOURCES OF FEEDSTOCK TO BIODIESEL PRODUCTION

Biodiesel feedstock could be originated from vegetable oils or waste oils containing ester of monocarboxylic acids which are triglycerides. Currently, biodiesel seems to be more costly than petro-diesel, which is largely due to the high cost of the feedstock. The feedstock is the biggest input when making biodiesel. There are few types of feedstock from edible and non-edible oil which are very familiar and common in the biodiesel industries such as soybean oil, *Jatropha* oil, palm oil, sunflower oil, rapeseed oil, canola oil and others. Feedstock from plants usually high in cost, nevertheless they are easy to use. In addition, the concern of food starvation arises if edible oil is used. On the other hand, limited supply and deforestation issue surface for non-edible feedstock. The utilization of oil from waste sources could also counter the environmental damage. Due to their abundance and low cost, the exploitation of such waste materials has become very attractive. The right selection of feedstock could counter this problem, to some extent, by lowering the overall production cost. As a solution, waste/used oil could be one of the best choices in order to produce biodiesel with a comparable cost to petro-diesel. Many studies have investigated the use of waste cooking oil (WCO); animal fats including chicken fats, pork, lard, tallow and grease, and spent bleaching clay (SBC). In view of this, a comprehensive report on the utilization of feedstock from waste is presented in this review and tabulated, as shown in Table 2.5.

2.6.1 Animal Fats and Grease

Animal fats and grease could be a suitably affordable feedstock for biodiesel (Demirbas, 2009). The availability of a large quantity of animal fats and the ease of collecting them from slaughter houses or meat processing units make animal fats one of the desired choices. The fatty acid distribution of animal fats, greases and vegetable oils are presented in Table 2.4, proving the very small differences in terms of the fatty acid distributions among these sources.

Table 2.4: Fatty acids distribution of animal fats, greases and vegetable oils.

Product	**Fatty acid distribution (%)**								**Σ**	**Ref.**
	$C_{14:0}$	**$C_{16:0}$**	**$C_{16:1}$**	**$C_{18:0}$**	**$C_{18:1}$**	**$C_{18:2}$**	**$C_{18:3}$**	**Others**		
Chicken fat	-	19.82	3.06	6.09	37.62	31.59	1.45	0.37	100	Alptekin and Canakci, 2010
Tallow	3.10	23.80	4.70	12.70	47.20	2.60	0.80	5.10	100	Wyatt et al., 2005
Pork Lard	1.30	23.50	2.60	13.50	41.70	10.70	-	6.70	100	Wyatt et al., 2005
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67	5.62	100	Canakci, 2007
Brown grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	4.47	100	Canakci, 2007
Rapeseed oil	-	3.49	-	0.85	64.40	22.30	8.23	0.73	100	Alptekin and Canakci, 2010
Sunflower oil	-	5.40	0.10	2.90	18.70	72.90	-	0.00	100	Wyatt et al., 2005
Soybean oil	-	10.58	-	4.76	22.52	52.34	8.19	1.61	100	Alptekin and Canakci, 2010

Table 2.5: Comparison of reaction conditions and performance of various types of feedstock from waste sources in the production of biodiesel.

Feedstock from waste sources	**Physical properties**			**Cat.**	**Reaction conditions**				**Conv. (C) or Yield (Y) (%)**	**Pretreatment feedstock**	**Ref**
	WC	**SV**	**AV**		**T(˚C)**	**MeOH:Oil (mol:mol)**	**Cat. (wt.%)**	**t (h)**			
Homogeneous base catalyst											
WSCO	0.42	188	-	KOH	87	90:1	6	2	-	Heated at 122 ˚C	Demirbas, 2009
Mixtures WFO and PL	WFO =0.05 PL = 0.03	-	WFO =0.82 PL = 0.71	NaOH	90	6:1	0.8	1	Y = 88	WFO = vacuum filtered, dehydrated with Na_2SO_4 anhydrous. PL = heated at 100 ˚C	Dias et al., 2008
Animal fat (PL, BT, CF)	-	-	-	NaOH	65	6:1	0.4	0.5	C (PL = 98.7%, BT = 98.8%, CF = 99.4%)	-	Wyatt et al., 2005
Homogeneous acid catalyst											
WCO	-	-	75.92	H_2SO_4	95	20:1	4	10	C ≥ 90	Filter	Wang et al., 2006
WCO	-	-	-	H_2SO_4	80 70	162:1 245:1	1.9 3.8	4 4	Y = 98.9 Y = 99	-	Zheng et al., 2006
Two-step: Acid-esterification (A) catalyst followed by base-transesterification (B) catalyst											
WCO	-	-	75.92	Ferric sulfate followed by KOH	95 (A) 65 (B)	10:1 (A) 6:1 (B)	2 (A) 1 (B)	4 (A) 1 (B)	C = 97.2	Filter	Wang et al., 2006
UFSO	-	-	-	H_2SO_4 followed by NaOH	50 (A) 60 (B)	0.3:1 (A) (v/v) 0.2:1 (B) (v/v)	0.75(A) 1 (B)	1 (A) 4 (B)	Y = 97	2 l water added and heated over anhydrous Na_2SO_4	Chakraborty et al., 2010
Heterogeneous base catalyst											
WPCO	-	-	-	BA	60	18:1	5.35	0.5	Y = 71.7	Heated at 120 ˚C	Chin et al., 2009
WCO	0.65	223	7.70	K_3PO_4	60	6:1	4	2	Y = 97.3	-	Guan et al., 2009
SBC	-	-	-	CaO	65	0.5:1(wt/wt)	6	2.5	C = 98.6	-	Lim et al., 2009
WCO	0.00	-	5.08	Sr/ZrO_2	115.5	29:1	2.7	2.8	Y = 79.7	-	Omar and Amin, 2011

Heterogeneous acid catalyst											
WCO	-	-	30	ZS/Si	200	18:1	3	10	Y = 98	-	Jacobson et al., 2008
WCO	1.9	207	3.6	TiO_2- MgO	150	30:1	5	6	Y = 79.9	Heated at 120 ˚C	Wen et al., 2010
				Enzymatic catalyst							
WPCO	0.9	-	0.1	Novozym 435	40	4:1	4	12	Y = 88	-	Halim and Kamaruddin, 2008
WCO	-	191	54.3	Immobilized *Penicillium expansum*	35	1:1	Not clearly specified	7	Y = 92.8	-	Li et al., 2009
WCO	-	299	143.6	immobilized *Candida* lipase	45	3:1	25	-	Y = 91.1	H_3PO_4 was added	Chen et al., 20009

WC = Water content (wt.%), SV = Saponification value (mgKOHg^{-1}), AV = Acid value (mgKOHg^{-1}), Cat. = Catalyst, T = Temperature, MeOH = Methanol, t = reaction time, Conv. = Conversion, WSCO = Waste sunflower cooking oil, WFO = Waste frying oil, PL = Pork lard, BT = Beef tallow, CF = Chicken fat, WCO = Waste cooking oil, UFSO = Used frying soybean oil, WPCO = Waste palm cooking oil, SBC = Spent bleaching clay, BA = Boiler ash.

In general, a major disadvantage of animal fats and grease utilized as feedstock in transesterification is that they provide products with poorer cold temperature properties than virgin vegetable oil and contain high FFA (Wyatt et al., 2005). Improving the cold properties of biodiesel using white sesame oil was investigated in which the researcher used methyl stearate, isopropyl stearate, methyl oleate and isopropyl oleate as pour point depressants (Satapimonphan and Pengprecha, 2012). The most effective results were shown by isopropyl oleate at 30 wt.%. The cloud and pour points decreased from 1 ˚C to -6.6 ˚C and 0 ˚C to -8 ˚C, respectively. In addition, another study to improve the cold flow properties using surfactants and detergent fractionation was investigated by Wang et al. (2011). The effect of different surfactants was studied, including sugar esters, silicone oil, polyglycerol ester, and diesel conditioner. Another solution to improve the cold properties, involves blending biodiesel with poor cold properties with biodiesel with higher cold properties or using cold point depressants (Kleinová et al., 2007).

Nevertheless, for the case of high FFA, the feedstock can be treated via esterification to lower the FFA content. To deal with the high FFA in feedstock, the researchers carried out esterification as a pretreatment step to convert the FFA to ester. In a related study, esterification was carried out using acids (sulphuric, hydrochloric and sulphamic acids) to esterify chicken fat with 13.45% FFA. After pretreatment, the FFA level in the feedstock was reduced to less than 1%. The authors reported that sulphuric acid gave the best result among the three acid catalysts, in the following conditions: 20% sulphuric acid, methanol to oil molar ratio 40:1 at 60 ˚C for an 80 min reaction. Sulphamic acid did not have any significant effect in reducing the FFA (Alptekin and Canakci, 2010).

2.6.2 Spent Bleaching Clay

Spent bleaching clay (SBC), which is a waste from edible oil refineries, could be an affordable feedstock similar to waste cooking oil, animal fats and grease. Bleaching clay is used to remove soap, metals, polymers and colouring substances in the palm oil refinery. SBC contains a high amount of oil, approximately 20%-40% and the availability of SBC at refineries makes clay an attractive feedstock material for biodiesel (Ong, 1983). Its benefits can be further harnessed by the construction of a sizeable biodiesel plant adjacent to oil refineries. Another advantage is that the adsorbed oil on the clay is comparatively better in quality compared to other waste feedstock. Annually, 600,000 metric tonnes or more SBC is used worldwide. In Malaysia alone, with a CPO production of 19.2 million tonnes in 2013 (MPOB, 2014), it is estimated that about 190,000 tonnes of SBC is generated.

In situ biodiesel production from residual oil from SBC was investigated by Mat et al. (2011). The researchers compared two different catalysts to synthesize biodiesel from SBC oil. Sodium hydroxide and sulphuric acid were used as catalysts, and hexane was used to extract the oil from the SBC. The yield of biodiesel resulting from the use of an alkali catalyst was higher than that from the acid catalyst, and the reaction time using the alkali catalyst is much shorter. In another related study, the transesterification of SBC using different solvents was explored (Lim et al., 2009). The authors used different polar and non-polar solvents, such as methanol, ethanol, petroleum ether and hexane to convert the adsorbed oil on SBC to biodiesel. Among them, ethanol gave the highest extracts, which contains polar components and triglyceride. However, for the purpose of transesterification, triglyceride without other components is preferred. As such, the non-polar solvent, together with moderate extracts, provides the best extraction solvent, which extracts triglyceride (without polar components) from SBC with the least FFA content.

2.6.3 Decanter Cake

Decanter cake (DC), a solid waste produce when the crude palm oil is centrifuged for purification where the supernatant is the pure palm oil and the sediment is the DC. DC typically contains moisture (about 76%, on wet basis), residual oil (about 12%, on dry basis) and nutrients (about 6%). There are previous reports on the use of DC in the area of bio-fertilizer, biofuel and cellulose (Kandiah, 2012, and Razak et al., 2012). DC, with residual oil, with appreciable magnitude (3% of DC is generated for every million tonnes of fresh fruit bunch) could be a potential feedstock for production of biodiesel (methyl ester).

2.6.4 Waste Cooking Oil

Waste cooking oil (WCO) is any vegetable oil that has been previously used for frying or cooking and which is deemed unhealthy to reuse (See et al., 2006). As such, one of the ways to add value to WCO is by utilizing it as a feedstock in transesterification. Table 2.6 depicts that WCO is the most inexpensive feedstock as it can be readily collected from households, hotels and restaurants. The price of these waste oils is two to three times cheaper than virgin vegetable oils (Demirbas, 2009).

Table 2.6: Average international price of virgin vegetable oils, waste grease and fat in 2007

Feedstock	Price (US$/tonnes)
Crude palm oil	543
Rapeseed oil	824
Soybean oil	771
Refined cottonseed oil	782
Crude corn oil	802
Crude tea seed oil	514
Waste cooking oil	224
Yellow grease	374
Poultry fat	256

Source: (Demirbas, 2009)

However, the drawback of used/waste oil is the presence of high free fatty acids (FFA) and water content. The quality of this type of oil can be improved by several pretreatments, especially for waste oil and fat with FFA content over 2.5% and moisture beyond 0.5% (Canakci and Gerpen, 2001). Excess FFA and moisture must be removed from the feedstock as they will affect the transesterification reaction through saponification reaction, and, eventually, decrease the yield and complicate the product separation.

Commonly, alkali catalysts can tolerate FFA up to 2.5 wt.%, however, feedstock with FFA over 2.5 wt.% needs a pretreatment to bring down the FFA prior to transesterification. Three main ways have been identified to remove water in the oil. Heating the oil is one of the preferred methods, where the waste oil is heated at 100 ˚C for 15 min with continuous stirring (Pazouki et al., 2010). Chemical treatment is also an option where magnesium sulphate is used to absorb the water (Felizardo et al., 2006) and warm water or water vapour is also used to deal with the moisture in the waste oil (Cvengroš and Cvengrošova, 2004).

2.7 EXTRACTION TECHNIQUES

There are many techniques to extract oil that can be used as feedstock nowadays. Every of this technique has its own benefit and drawback, depending on what is the material being extracted. Among the most popular techniques had been used in many extraction activities are electromechanic, enzymatic, expeller, osmotic and supercritical. The solvent extraction method and ultrasonic is cheaper and easier for conducted residual oil from decanter cake (DC).

2.7.1 Mechanical Stirring Soxhlet Extraction Method

Soxhlet extraction is the technique of removing one constituent from a solid by means of a liquid solvent. It is also called leaching. Soxhlet extraction has long been investigated as a technique for extracted of feedstock for biodiesel production, especially in non-edible oil such as Jatropha seed, *Pmgamia pinnata*, *Cerbera odollam* (Sea mango), *Coriandrum sativum* L., *Moringa oleifera* (Achten et al., 2008; Mahanta and Shrivastava, 2008; Kansedo et al., 2009b, and Sarin et al., 2009).

Mahanta and Shrivastava (2008) and Achten et al. (2008) indicated that Soxhlet extraction with *n*-hexane can be used to extract the oil from *Jatropha* seed and *Pmgamia pinnata*. It is reported that this method could produce about 41% and 95–99% of oil yield respectively. Moreover, several other studies conducted by Kansedo et al. (2009a) and Sarin et al. (2009), extracted the oil from *Cerbera odollam* (sea mango), Coriander (*Coriandrum sativum L.*), *Moringa oleifera* and *Guizotia abyssinica L.* using Soxhlet extractor with *n*-hexane as the solvent.

Some frequently used solvent are *n*-hexane, petroleum ether, ethanol and benzene. *n*-hexane is the most popular solvent due to its relatively cheaper cost and has smaller polarity level as a solvent. In selecting the solvent, things to consider are polarity level, toxicity level, volality and the price. Ethanol is chosen because it has longer carbon than methanol and the longer the carbon chains the smaller is the polarity level. In the way, it is easier to extract the oil.

2.7.2 Ultrasonic Extraction Method

Ultrasonic extraction method is a new extraction method, this method could be suggested as an alternative to mechanical stirring extraction technique due to its inexpensive, simplicity, shorter extraction time and less-energy usage. The use of ultrasonic cause the cavitation bubbles in solution, acoustic cavitation phenomenon which created by passing ultrasound waves through solvent system causing higher efficiency of the technique. This phenomenon permits better penetration of the solvent into the sample, increases the release of the solutes from the matrix to the solvent. (Morelli and Prado, 2012).

Many researchers reported the use of ultrasound-assisted extraction to extract oil from matrix to produce biodiesel. Yustianingsih et al. (2009) extracted oil from rice bran to produce biodiesel. Zhang et al. (2003) compared both ultrasonic-assisted and mechanical stirring methods for oil extraction from flaxseed and concluded that ultrasound is more efficient than the mechanical stirring method for oil extraction. In addition, the comparison from other method in extraction of soybean oil was investigated, and it concluded that the ultrasound-assisted technique gave highest oil yield of 93.3% (Luthria et al., 2007).

2.8 CATALYSTS IN TRANSESTERIFICATION

2.8.1 Homogeneous Catalyst

Transesterification of triglycerides catalyzed by base homogeneous alkali catalyst is common process in the industrial biodiesel production, due to (i) the low cost of the catalyst, (ii) the good conversions can be achieved in shorter reaction time at moderate temperature, and (iii) widely available. Base homogeneous catalysts such as alkaline metal hydroxides (Ma and Hanna, 1999) like as NaOH and KOH are most often used in the reaction because their availability and low cost. Another sources as alkoxides (Singh et al., 2006) and carbonate (Arzamendi et al., 2008) also can used. However, the alkoxides are more expensive and also difficult to handle because of their hygroscopic nature. Nevertheless, this catalyst is limited only used for feedstock with less than 0.5 wt.% FFA (Wang et al., 2006) or acid value less than 1 mg KOH/g (Felizardo et al., 2006). Some researchers are reporting that base homogeneous catalyst can tolerate higher content of FFA, while a feedstock still in ranging from 0.5 wt.% to the less 2 wt.%)

Singh et al. (2006) investigated the effect of alkaline (NaOH, KOH, CH_3ONa and CH_3OK) in the transesterification reaction of canola oil. The catalyst amount, reaction time, temperature and methanol:oil also studied. The author found, that there were significant different in methyl ester conversion among the four catalysts in the same conditions. The potassium catalyst gave better performance in large extent of soap formation and methyl ester conversion than the sodium-based catalyst. In addition, the methoxide catalysts gave higher methyl ester conversion than hydroxide catalysts. Unfortunately, the cost of methoxide catalysts is more expensive, about five to six times higher than that of hydroxides catalysts.

The mechanism of triglyceride and methanol catalyzed by homogeneous base catalyst is presented in Figure 2.5. As a basic site of base catalyst, surface basic site extracts H^+ from methanol to form methoxide, production of the active species (Figure 2.5(a)), which is easily extracted by reactants in chemical reactions. The mechanism of transesterification of tryglyceride to biodiesel in the presence of methoxide anion is as follows: In the first step, the methoxide anion in the catalyst attaches to the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate (Figure 2.5(b)). In the second step, the tetrahedral intermediate picks up an H^+ atom. In the last step, the rearrangement of the tetrahedral intermediate results in the formation of biodiesel and diglycerol (Figure 2.5(c)).

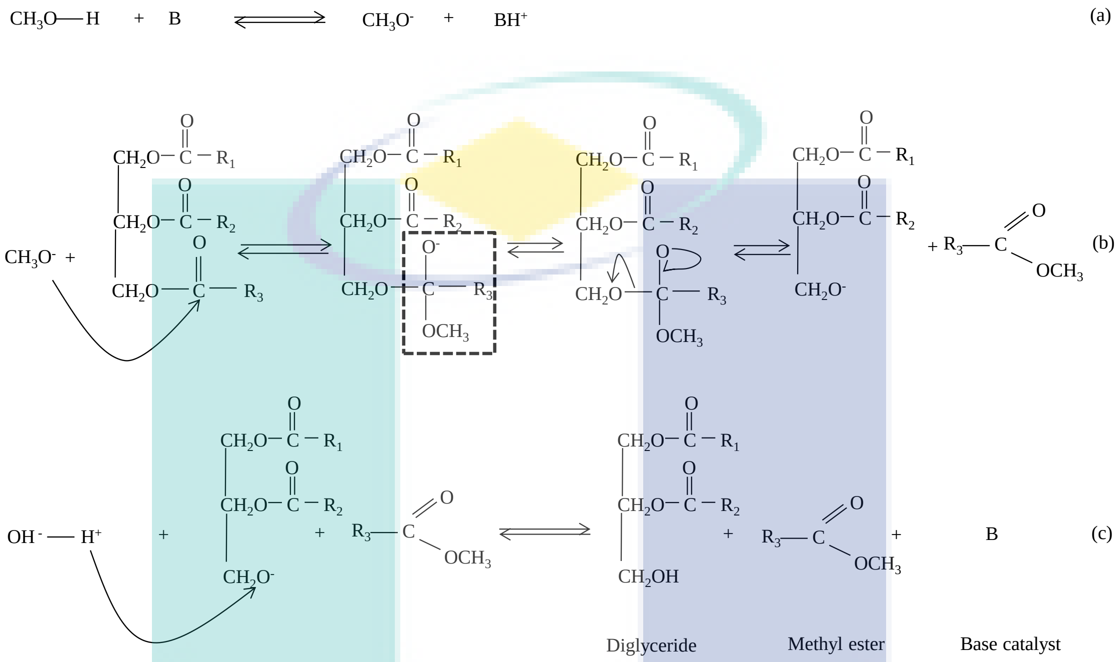


Figure 2.5: Possible mechanism of transesterification of WPCO catalyzed by homogeneous base catalyst

Source: Lam et al., 2010

There are some advantages of acid homogeneous catalyst compare to base homogeneous catalyst, (i) acid catalyst is insensitive to the presence of FFAs in the feedstock (Kulkarni and Dalai, 2006), and (ii) can catalyzes esterification and transesterification simultaneously (Jacobson et al., 2008). Nevertheless, the acidic catalyst has disadvantages, namely; requirement of high reaction temperature and alcohol to oil molar ratio, difficult in catalyst separation, and environmental and corrosion problem makes this catalyst not popular for commercial applications. Freedman et al. (1986) investigated effect of H_2SO_4 as catalyst in transesterification, the methyl ester conversion at 99 % was achieved with conditions of 1 mol% of H_2SO_4, 30:1 methanol:oil molar ratio and 69 h reaction duration. The list the variation of base and acid homogeneous catalyst in transesterification of biodiesel is presented in Table 2.7.

Table 2.7: Transesterification reaction catalyzed by homogeneous catalysts

Catalysts	References
	Homogeneous base catalysts
Potassium hydroxide	Singh et al., 2006, and Vicente et al., 2004
Sodium hydroxide	Singh et al., 2006; Ma and Hanna, 1999, and Vicente et al., 2004
Potassium methoxides	Singh et al., 2006, and Vicente et al., 2004
Sodium methoxides	Freedman et al., 1986; Singh et al., 2006; Ma and Hanna, 1999, and Vicente et al., 2004
	Homogeneous acid catalysts
Sulphuric acid	Freedman et al., 1986
Hydrochloric acid	Ayhan, 2008

2.8.2 Heterogeneous Catalyst

Various types of heterogeneous catalysts such as alkaline earth metal oxide and solid acid catalysts have been explored for transesterification as well as esterification reactions. The main advantages of this catalyst in transesterification are (i) lower production cost due to catalyst reusability, and (ii) higher tolerance moisture and FFA. calcium oxide (CaO) is alkaline metal oxide getting much attention due to its relative high basic strength, low solubility in methanol and can synthesized from low-cost sources like shells, limestone and bones (as presented in section 2.9.1, 2.9.3 and 2.9.4). Kouzu et al. (2008) reported that CaO obtained from $CaCO_3$ at 900 ˚C for 1.5 h, The methyl ester conversion was achieved at 93% in the optimal conditions of methanol:oil molar ratio 12:1 for 1 h reaction time. The possible mechanisms of triglyceride and CaO is also presented in Figure 2.6. As a basic site of CaO solid base catalyst, surface O^{2-} extracts H^+ from methanol to form methoxide and surface OH^- (Figure 2.6 (a)). The mechanism of transesterification of tryglyceride to biodiesel similar to KOH, the methoxide anion in the catalyst attaches to the carbonyl carbon atom of the triglyceride molecule and the next picks up an H^+ to form diglyceride and methyl ester (Figure 2.6 (b)) and (Figure 2.6 (c)).

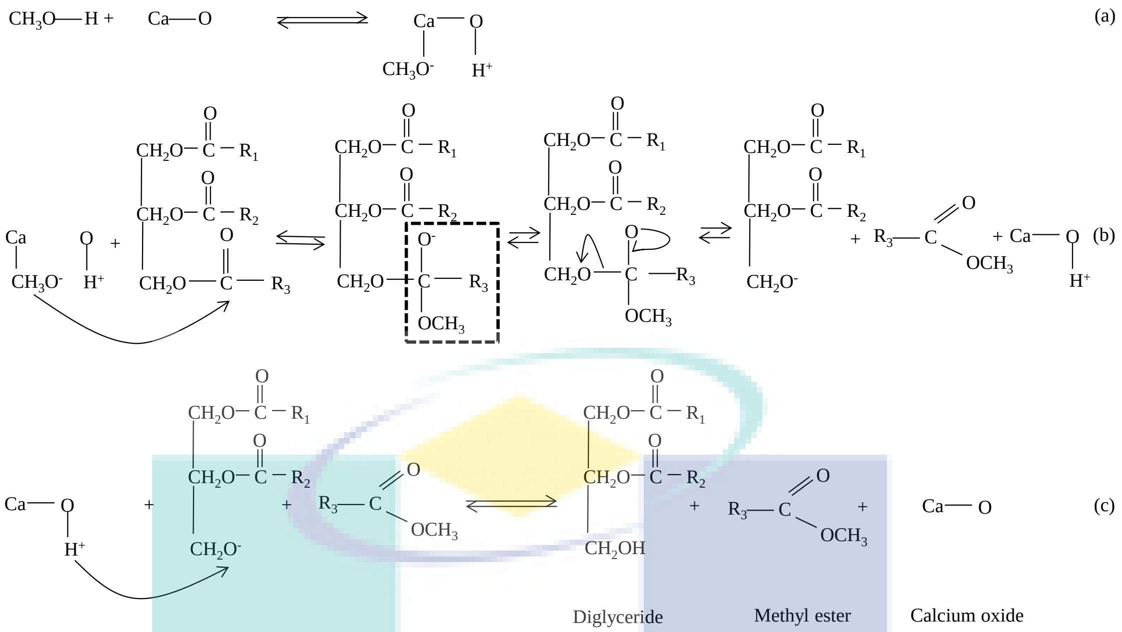


Figure 2.6: Possible mechanism of transesterification of WPCO catalyzed by CaO

Source: Lam et al., 2010

The exploring of a new and sustainable of solid catalyst for transesterification of biodiesel continually was studied. The researchers believed that heterogeneous acid catalysts have strong potential to replace of homogeneous acid catalysts. The advantages of these catalysts are (i) more tolerance to FFA content, (ii) occurence of esterification and transesterification simultaneously, (iii) washing step is not required, (iv) easy in separation of catalyst from the reaction (v) easy in regeneration and recycling of the catalysts and (iv) less corrosion problems. In fact, the researchers have not utilizing these solid acid catalysts widely due to its limitation of slow reaction rate and possible undesirable side reactions. The heterogeneous acid catalysts were reported by previous study like the use of zirconium oxide (ZrO_2) and titanium dioxide (TiO_2) as a solid acid catalyst for transesterification, it is due to strong surface acidity. The acidity properly can coating of surface this metal oxide with anions like sulphate such as sulfuric acid (H_2SO_4). Miao and Gao (1997) investigated of ZrO_2 with acidic solution of H_2SO_4 using impregnation method. The authors reported that the catalyst is promising in transesterification of palm kernel oil and crude coconut oil with higher FFA. with methyl ester content over 85%,. The list of various heterogeneous catalysts is presented in Table 2.8.

Table 2.8: Transesterification reaction catalyzed by heterogeneous catalysts

Catalysts	References
	Heterogeneous base catalysts
CaO	Kouzu et al., 2008
MgO	Demirbas, 2008
SrO	Liu et al., 2007
KF/CaO-MgO	Fan et al., 2012
	Heterogeneous acid catalysts
SO_4^{2+}/ZrO_2	Miao and Gao, 1997
ZrO_2-Al_2O_3	Furuta et al., 2004
SO_4^{2+}/SnO_2	Gutierrez-Baez et al., 2004

2.9 CATALYSTS FROM DIFFERENT WASTE SOURCES IN TRANSESTERIFICATION REACTION

A comprehensive summary on the utilization of catalyst from waste is presented in Table 2.9. The utilization of oil and catalyst from waste sources could also counter the environmental damage. Furthermore, within the last five years, many research works have focused on the exploitation of waste materials as catalysts for the production of biodiesel. They include shells, ashes, rock, and bone. Due to their abundance and low cost, the exploitation of such waste materials has become very attractive.

Table 2.9: Summary of various types of waste catalysts in transesterification.

Waste sources	Catalyst	Preparation conditions		Reaction conditions				Conv.(C) or Yield (Y) (%)	Reusability C/Y (%)	Ref
		Calcination temperature (˚C)	Calcination duration (h)	T(˚C)	MeOH:Oil (mol:mol)	Catalyst (wt.%)	Reaction duration (h)			
Mollusc Shells										
Mud crab (*Scylla serrata*)	CaO	900	2	65	0.5:1 (wt/wt)	5	2.5	C = 98.8	15(C ≈ 94)	Boey et al., 2009a
Cockle (*Anadara granosa*)	CaO	900	2	65	0.54:1 (wt/wt)	4.9	3	Y ≥ 96.5	3 (C ≥ 96.5)	Boey et al., 2011d
Biont (turtle)	KF-CaO	500	-	70	9:1	3	3	Y = 97.5	-	Xie et al., 2009
Shrimp	KF-CaO	450	-	65	9:1	2.5	3	C = 89.1	-	Yang et al., 2009
Oyster	CaO	700	3	65	6:1	25	5	C = 98.4	-	Nakatani et al., 2009
Freshwater mussel	CaO	900	4	70	12:1	5	1.5	Y = 96	7 (Y ≥ 90)	Hu et al., 2011
Sea snail (*Turbonilla striatula)*	CaO	900	3	65	9:1	3	6	Y = 93.3	2 (Y ≥ 80)	Boro et al., 2011
Exoskeleton (*Pila globosa*)	CaO	900	2.5	60	10:1	4	5	C = 97.8	-	Agrawal et al., 2012
Snail	CaO	900	3.5	60	6:1	2	8	C = 99.58	-	Birla et al., 2012
Golden apple snail and *Meretrix venus*	CaO	800	2-4	60	12:1	10	2	Y ≥ 90	-	Viriya-empikul et al., 2010
Clam (*Mereterix mereterix*)	CaO	900	3.5	60	6:1	3	3	C ≥ 97	-	Nair et al., 2012
Egg Shells										
Chicken	CaO	800	2-4	60	12:1	10	2	Y ≥ 95	-	Viriya-empikul et al., 2010
Chicken	CaO	1000	2	65	9:1	3	3	Y = 95	13	Wei et al., 2009
Chicken	CaO	900	2	60	9:1	3	3	Y = 96	14 (Y = 88)	Jazie et al., 2013
Quail	CaO	800	-	65	12:1	0.03	2	C ≥ 98	5 (C ≥ 98)	Cho and Seo, 2010
Ashes										
BA	K_2O	105	2	60	15:1	3	0.5	C = 90	-	Boey et al., 2011b
BA	KOH	550	4	65	15:1	1.5	20	C = 98.54	5 (C ≥ 97-85)	Yaakob et al., 2012
KOH/BA	KOH	550	4	65	15:1	0.75	15	C = 99.45	5 (C ≥ 98-93)	Yaakob et al., 2012
Coal fly ash loaded with KNO_3	K_2O	500	5	160	15:1	15	5	C = 86.13	3 (C = 47-24)	Babajide et al., 2010
Coal fly ash loaded KNO_3	K_2O	500	5	70	15:1	15	8	C = 87.5	-	Kotwal et al., 2009
Coal fly ash loaded egg shell	CaO-Al_2O_3 and SiO_2	1000	2	70	6.9:1	1	5	Y = 96.97	16	Chakraborty et al., 2010
Rocks										
Alum	$KAl(SO_4)_2$	550	-	170	18:1	7.09	12	Y = 92.5	-	Aderemi and Hameed, 2009
Dolomite	$CaMg(CO_3)_2$	850	2	67.5	6:1	3	3	Y = 91.8	5 (Y≥ 90-82)	Ilgen, 2011
Dolomite	$CaMg(CO_3)_2$	800	2	60	30:1	6	3	C = 98.6	7 (C ≥ 90)	Ngamcharussrivichai et al.,

										2010
Calcite	$CaCO_3$	800	2	60	30:1	6	3	C = 46.8	-	Ngamcharussrivichai et al., 2010
Bones										
Rohu fish (*Labeo rohita*) bone	$\beta\text{-}Ca_3(PO_4)_2$	997.42	2	70	6.27:1	1.01	5	Y = 97.7	6	Chakraborty et al., 2011
Sheep bone	hydroxyapatite	800	-	65	18:1	20	4	C = 96.78	5 (C = 83.7)	Obadiah et al., 2012
Cuttlebone	$CaCO_3$	800	2	60	30:1	6	3	C = 24.1	-	Ngamcharussrivichai et al., 2010

T = Temperature, MeOH = Methanol, Conv. = Conversion, BA = Boiler ash

2.9.1 Shells

a) Mollusc Shells

Calcium oxide derived from mollusc shells has been proven to be a potential heterogeneous catalyst for biodiesel production. Boey et al. (2009a,b) investigated the use of waste mud crab shells (*Scylla serrata*) as a catalyst for the transesterification of palm olein and the report revealed that the calcined shell contains mainly CaO (Boey et al., 2009a,b). Under the optimal conditions of 0.5:1 (mass ratio of MeOH:oil); catalyst amount, 4-5 wt.% and reaction temperature 65 ˚C, the calcined catalyst could be reused several times without much reduction its effectiveness. The performance of waste crab shells was comparable to the laboratory grade CaO. A similar observation was noticed for the catalyst from waste cockle shells (*Anadara granosa*), in which the calcined shell (900 ˚C, 2 h) could transesterify palm olein (Boey et al., 2011d). Both of the waste catalysts recorded 98.2-99.0% methyl ester conversion in 3 h reaction time.

Xie et al. (2009) investigated the carbonization of biont shell (from turtle shells). The catalyst was prepared via a series of treatments; incomplete carbonization at 500 ˚C, followed by impregnation in KF, for 6 h at 25 wt.%, and, finally, thermal activation at 300 ˚C. The authors reported by observation at CO_2-TDP spectra that strong basicity sites were formed on the catalyst after the impregnation of KF. Chitin, the major constituent of the biont shell formed the active sites after reaction with KF. The report concluded that the heterogeneous catalyst from biont shell exhibited an excellent activity as well as stability under mild reaction conditions. Similar work has been reported using shrimp shells (Xie et al., 2009). The catalyst was prepared in a similar manner as the biont shell, except for the carbonation temperature (450 ˚C) and activation temperature (250 ˚C). While using biont shell recorded a yield of 97.5% in 3 h (3% catalyst), this waste reported a conversion of 89.1% in 3 h (2.5% catalyst).

Nakatani et al. (2009) investigated the use of waste oyster shells as a catalyst in the transesterification of soybean oil. In a 5 h reaction, a methyl ester content of 98.4% was achieved. Similar to mud crab and cockle shells, the main constituent of the calcined oyster shell is CaO. Sea snail shells (*Turbonilla striatula*) were also found to be a source of CaO in the investigation by Boro et al. (2011). The calcined (800 ˚C, 4 h) shell was able to transesterify mustard oil with a yield of 93.3 wt.%, in a 6 h reaction. In terms of reusability, the catalyst was stable until the second cycle and exhibited a sharp reduction for the third and fourth cycles. However, the authors found that the used catalyst can be reactivated upon calcination at 900 ˚C for 3 h.

Another CaO source was derived from calcined waste freshwater mussel shells, from the work of Hu et al. (2011). The catalyst was prepared by calcination (900 ˚C, 4h) then impregnation in deionized water before being thermally activated again (600 ˚C, 3h). In this way, a ‘honey-comb’ catalyst structure was obtained, which recorded the highest surface area at 23.2 m^2g^{-1}. The resultant catalyst was able to yield 90% methyl ester in 1.5 h of reaction time. Interestingly, the catalyst can be reused seven times before the yield dropped below 90%, maintaining 80% yield up to the twelfth cycle and 60% yield at the seventeenth reuse.

Calcium oxide can also be derived from waste egg shells, snails (golden apple), and clams (*Meretrix venus*) (Viriya-empikul et al., 2010). The calcined (800 ˚C, 2-4 h) shells were able to produce methyl ester content over 90%, in 2 h reaction time; egg shells and snail shells have higher initial activities.

b) Egg Shell

Chicken and quail egg shells were found to be a reliable source of CaO, consisting of 85-95% of calcium carbonate and 15-5% other components ($MgCO_3$, phosphate, organic matter and a small amount of metal) in dry egg shells . The catalytic performance was comparable to laboratory grade CaO in transesterification. In a 3 h reaction time, Wei et al. (2009) achieved 95% biodiesel yield and reported that the catalyst can be reused 13 times without any significant loss of activity. Viriya-empikul et al. (2010) also reported the good performance of egg shells in transesterification. Chicken egg shell contains the highest amount of calcium and has the larger surface area as compared to golden apple snail and meretrix venus shell. Recently Semwal et al. (2011) prepared the metal oxide $CaTiO_3$ using egg shell by calcination at 1050 ˚C for 3.5 h; yielding over 95% methyl ester content. The metal oxide catalyst was stable for four cycles of reuse without any major structural changes as confirmed through XRD. It proves that regardless of the origin, CaO could catalyze the reaction with success. Calcium oxide from these waste sources compliments where they could be co-used with laboratory grade CaO.

2.9.2 Ashes

a) Empty Palm Fruit Bunch-Based Boiler Ash

Empty palm fruit bunch (EPFB) fibre (dry basis) consists mainly of glucan (42.85%), xylan (24.01%), lignin (11.70%) and other components. As for oxides, EPFB contains potassium oxide as the major constituent, followed by silica, calcium oxide and others (Konsomboon et al., 2011). The ash was successfully utilized by Boey et al. (2011b) as a catalyst in the transesterification of palm olein. With oven drying (105 ˚C, 2h), 3 wt.% ash was capable of transesterifying palm olein at 90% conversion in a 0.5 h reaction time. However, since the ash acts as pseudo-heterogeneous, it is intolerant to the presence of moisture and FFA at 1 wt.% in the feedstock.

The transesterification reaction of palm oil with methanol using a methanolic extract of boiler ash (BA) as a homogeneous catalyst was reported by Imaduddin et al. (2008). In contrast, Yaakob et al. (2012) used BA as a heterogeneous catalyst. They made a comparison between BA and the BA doped with 20 wt.% KOH and used *Jatropha curcas* oil for the transesterification. Optimum conditions for the BA-catalyzed reaction were 20 wt.% BA; MeOH:oil molar ratio 15:1 at 65 ˚C, for 90 min; a maximum oil conversion of 98.5% was achieved and the report showed that the KOH/BA catalyst reaction has better activity than the BA alone; 99.5% conversion in the much shorter reaction time of 45 min at 15 wt.%. The reusability study of the catalyst indicated that KOH/BA is a better catalyst for repeated use. After five cycles, the conversion of both catalysts was more than 85%. The decreased activity of the catalyst after the fifth run was confirmed by XRF analysis due to the absence of metals like K and Ca, which indicates leaching of the active ingredients.

b) Fly Ash

Fly ash as an inorganic waste generated from coal combustion processes has a typical chemical composition (on dry basis), of around 55% SiO_2, 30% Al_2O_3 and other oxides (Ojha et al., 2005). It is obvious that the oxides of both silica and alumina could work excellently as a catalyst support. Consequently, researchers have used thermally activated fly ash as a support for loading CaO for chemical production. This supported catalyst gave higher conversions of up to three cycles and the catalyst was able to be reused without much loss in the activity. The presence of the high amount of SiO_2 and Al_2O_3 prompts its potential applicability as a low-cost catalyst support. In a recent work, fly ash supported CaO has been employed as a recyclable solid base catalyst (Jain et al., 2010). Fly ash supported heterogeneous CaO catalyst from egg shells have been investigated to transesterify soybean oil (Chakraborty et al., 2010). Fly ash supported a CaO catalyst prepared by wet impregnation method, with 30 wt.% CaO loading and followed by calcination at 1000 ˚C for 2h. A maximum FAME yield of 97% was achieved with 6.9:1 MeOH:oil molar ratio. The study of the reusability of catalyst showed higher catalytic activity in which the catalyst showed remarkable repeated usability of 16 times without major loss in activity; indicating a high degree of catalyst stability. However, the catalyst became completely deactivated after being used more than 18 times. Fly ash-based base catalyst was investigated by Kotwal et al. (2009), in the transesterification reaction of sunflower oil. The catalyst was prepared by the mechanical stirring wet impregnation method using KNO_3. In the work, fly ash loaded with 5 wt.% KNO_3, followed by calcination at 500 ˚C was able to convert the oil at 87.5% in 8 h reaction time. However, the catalyst suffered from being reused, probably due to the leaching of active species. Similarly, Babajide et al. (2010), reported that fly ash loaded with 5 wt.% KNO_3 could transesterify sunflower oil to about 86% but at an elevated reaction temperature of 160 ˚C. Similar to the previous study, the catalyst also suffers with respect to its reusability.

2.9.3 Rocks

Alum ($KAl(SO_4)_2$) has a traditional role in water treatment and potential as a catalyst in the transesterification of palm oil. Aderemi and Hameed (2009) reported the preparation of alum as a catalyst in the transesterification of palm oil. The alum successfully transesterified the oil to 92.5%, with a catalyst at 7.09 wt.% and MeOH/oil molar ratio 18:1 in 12 h reaction time at an elevated temperature of 170 ˚C. Another potential catalyst with high carbonate content originating naturally are dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$). At present, the low cost of dolomite is the main reason of major domestic usage in cement manufacturing and landfill. While dolomite consists of 23.5% Ca, 12.1% Mg, 63% CO_3 and 1.4% other components (Fe, SiO_2, PO_2, SO_4) (Ilgen, 2011), calcite contains high purity of $CaCO_3$ (over 91 wt.%) (Ngamcharussrivichai et al., 2010). Both dolomite and calcite could be easily transformed to CaO and MgO by thermal activation. Comparison of dolomite and calcite has been reported by Ngamcharussrivichai et al. (2010), in the transesterification reaction of palm kernel oil (PKO). In their study, the dolomite successfully transesterified the PKO, over 98% methyl ester, under the reaction conditions of: 6 wt.% catalyst, MeOH/oil molar ratio 30:1 in 3 h reaction at 60 ˚C. Meanwhile, calcite performed at 46.8% methyl ester under the same reaction conditions. The calcined dolomite at 800 ˚C for 2 h could be reused up to seven cycles without much loss in the activity.

2.9.4 Bones

Bone from waste Rohu fish (*Labeo rohita*) has been reported as another low-cost heterogeneous catalyst for the synthesis of biodiesel from soybean oil (Chakraborty et al., 2011). The analysis of TGA and XRD revealed that a significant portion of the main component of fish scale, hydroxyapatite, could be transformed into β-tri-calcium phosphate when calcined above 900 ˚C for 2 h, with optimal conditions of MeOH/oil molar ratio, 6.27:1, catalyst at 1.01 wt.% for 5 h. This compound was able to yield 97.7% of methyl ester. The reusability of the catalyst shows that it could be reemployed up to six times. Similar work has been reported using sheep bone (Obadiah et al., 2012); the calcined bone at 800 ˚C, transformed calcium phosphate of the bone into hydroxyapatite with an increase in surface area. In a 4 h reaction, methyl ester content of 96.8% was obtained under the reaction conditions of: methanol to oil 18:1 (molar ratio) and 20% catalyst at 65 ˚C. The catalyst was stable for five cycles at 83.7% conversion. On the other hand, cuttle bone (calcined at 800 ˚C for 2 h) could also catalyze transesterification of PKO but with much lower conversion (24%) although the bone contains over 91 wt.% $CaCO_3$ (Ngamcharussrivichai et al., 2010). Increasing the calcinations temperature of the bone to above 800 ˚C may increase the methyl ester conversion.

2.10 THE EFFECT OF FREE FATTY ACID AND MOISTURE IN TRANSESTERIFICATION

Two major impurities that affect the quality of oils are free fatty acid (FFA) and moisture. For the transesterification used homogeneous catalyst, the reaction must be free of moisture (< 0.06% w/w) and FFA, it was allowed is < 0.5% of FFA (Freedman et al., 1986, and Ma and Hanna, 1999). Wright et al. (1944) noted that the triglycerides should have an acid value less than 1, and material should be substantially anhydrous. The NaOH was required for neutralize the FFA if acid value greater than 1. The presence in the reaction can lead to saponification reaction, the soap formation reaction as shown in Figure 2.7:

$$\begin{array}{cccccccl} \mathrm{RCOOH} & + & \mathrm{XOH} & \rightleftharpoons & \mathrm{RCOO^{-}X^{+}} & + & \mathrm{H_2O} & (\mathrm{X = Na\ or\ K}) \\ \text{Fatty acid} & & \text{Hydroxide} & & \text{Soap} & & \text{Water} & \end{array}$$

Figure 2.7: Saponification reaction of fatty acid

Meanwhile, the presence of moisture can lead to hydrolysis of the ester to produce fatty acids and methanol, as shown in the following reaction (Figure 2.8):

$$\begin{array}{ccccccc} \mathrm{RCOOCH_3} & + & \mathrm{H_2O} & \rightleftharpoons & \mathrm{RCOOH} & + & \mathrm{CH_3OH} \\ \text{Ester} & & \text{Water} & & \text{Fatty acid} & & \text{Methanol} \end{array}$$

Figure 2.8: Hydrolysis reaction of ester

In short, the presence of FFA or moisture or both will lead to the soap formation reaction (saponification). The soap promotes the formation of stable emulsions, which lowers the yield of methyl esters and, at the same time, complicates the downstream separation process of the products (methyl esters and glycerol). In addition to the lower yield, extra processing is required to remove the FFA, moisture and the soap resulting from the reaction mixture. In a previous report, an increase in FFA content from 5 to 33% decreased the yield from 90% to as low as 58% (Canacki and Gerpen, 2001).

The heterogeneous catalysts showed better water tolerance than homogeneous catalysts, the presence of water in the reaction system could change the Lewis base site in (metal –O– group) into Bronsted base sites (metal –OH group) (Yan et al., 2009). So, amount of water caused CaO as heterogeneous catalyst to form $Ca(OH)_2$ that is capable of extracting H^+ from methanol. Thus, generating additional methoxide anion which is strongly basic and promotes base catalyzed transesterification. While, on another site, a basic site of CaO solid base catalyst, surface O^{2-} also extracts H^+ from H_2O to form surface OH (Figure 2.9 (a)). Then, the OH^- attaches to the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate (Figure 2.9 (b)). In the next step, the rearrangement of the tetrahedral intermediate divides into two molecules: diglyceride and fatty acid (Figure 2.9 (c)). This fatty acid lead saponification reactionas presented in Figure 2.7.

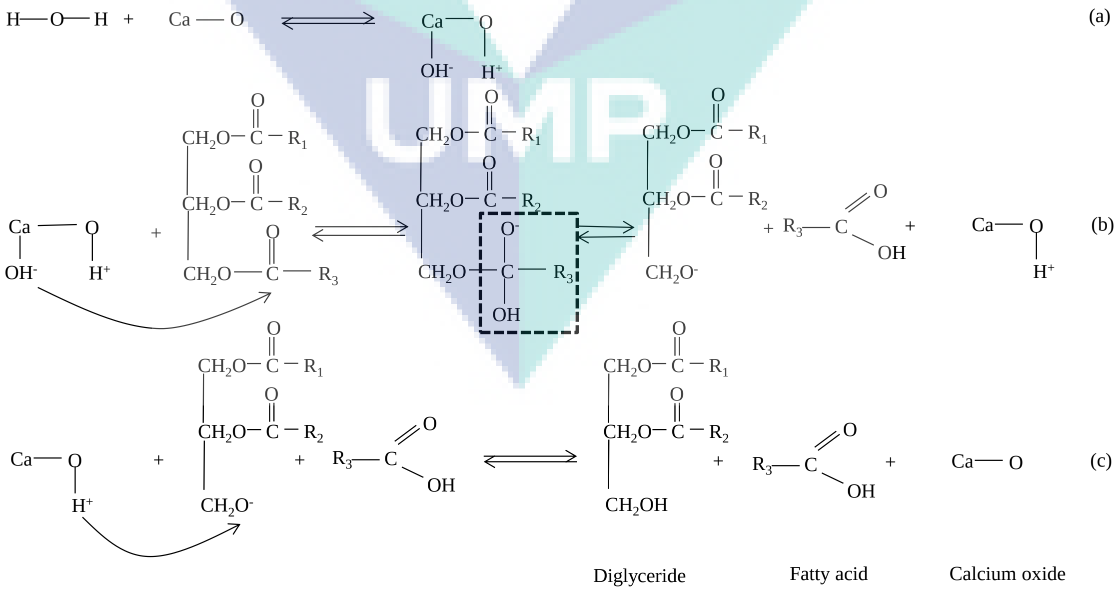


Figure 2.9: Presence of water in transesterification reaction using CaO catalyst

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

Refined, bleached and deodorized palm olein (RBD-PO) was manufactured by Yee Lee Edible Oils Sdn. Bhd. (Shah Alam, Selangor) and purchased from a local grocery. Waste palm cooking oil (WPCO) was collected from cafeteria surrounding Universiti Malaysia Pahang (UMP). Decanter cake (DC) and boiler ash (BA) were supplied by Oil Palm Mill (LKPP Corporation Sdn. Bhd), Gambang. Baby clam (*Paphia undulata*) was obtained from local market and capiz (*Placuna placenta*) shell was collected from Langkawi beach. Analytical grade methanol and *n*-hexane were purchased from MERCK (Germany). Chloroform, petroleum ether (PE) (40-60 ˚C) and Thin Layer Chromatography (TLC) (20 x 20 cm, silica gel 60 F254) of HPTLC grade were purchased from MERCK (Germany). The chemicals thus were purchased from Sigma-Aldrich company (Switzerland) include phenolphthalein ($H\_ = 8.2$), 2,4-dinitroaniline ($H\_ = 15.0$) and 4-nitroaniline ($H\_ = 18.4$), methyl heptadecanoate as an internal standard GC grades (> 99.1%). Methanol (anhydrous, ≥ 99.8%), hexane (anhydrous, ≥ 99.8%) was purchased from Hamburg (Germany).

3.2 PREPARATION OF FEEDSTOCK

RBD-PO was used without any pretreatment. The WPCO was filtered using a laboratory scale vacuum to remove any visible proteins and solids. WPCO ready to use as feedstock. Residual oil from decanter cake was extracted using Soxhlet set-up with various solvents extracted using *n*-hexane, petroleum ether, mix *n*-hexane:PE, methanol and ethanol. The method was adapted with modification from Ahmad et al. (2001).

Approximately 20 g DC sample was weight in Soxhlet thimble with about 4 g of fine sand (to improve solvent drainage). The mixture was covered with a layer of cotton wool (to aid in solvent distribution). The thimble was then placed in the Soxhlet butt tube and extracted with 50 ml of co-solvent. In this study, the extraction solvent was collected for 3 h, there was no future increase in weight of product over 3 h.

The yellow-brown supernatant layer was transferred into a pre-weighed flask, rotary evaporation was used to remove the co-solvent. The process was repeated three times and the accumulated supernatant solution was evaporated. The percentage of oil content was calculated using equation (3.1):

$$\text{Oil content (\%)} = \frac{M_1 x\ 100}{M_0} \tag{3.1}$$

where M_1 is the mass of DC oil extracted in gram.

M_0 is the mass of DC sample used in gram.

3.3 CHARACTERIZATION OF FEEDSTOCK

3.3.1 Determination of Acid Value (PORIM Test Methods (p1), 1995)

Approximately 20 gram of oil (RBD-PO) was weighed into 250 ml Erlenmeyer flask. Then 50 ml neutralised isopropanol was added into flask. The solution was heated on the hot plate to about 40 ˚C, shaken gently and titrating with standard potassium hydroxide solution until the first permanent pink solution for 30 s. The determination was done in triplicate. The acid value was calculated using the formula expressed in equation (3.2):

$$\text{Acid value (mg KOH/g sample)} = \frac{56.1 \text{ x V x M}}{\text{m}} \tag{3.2}$$

where V is the volume of standard potasium hydroxide in mL.

M is the molar concentration of standard potassium hydroxide used

m is the weight of sample in gram

Firstly, the potassium hydroxide was standardized with potassium hydrogen phthalate, the procedure as follows: The potassium hydrogen phthalate was dried in an oven at 120 ˚C until constant. Weight out 0.4 of potassium hydrogen phthalate directly into conical flask and added 50 ml water and phenolphthalein indicator. Heated and swirl till the salt has completely dissolved, then titrated with potassium hydroxide to the first appearance of a permanent pink colour. The normality of the alkali was calculated with formula:

$$\text{Normality of the alkali} = \frac{\text{W x } 10^3}{\text{v x } 204.2} \tag{3.3}$$

where W is the weight of potassium hydrogen phthalate

v is the volume of potassium hydroxide in ml

To neutralise isopropanol, 50 ml of isopropanol is poured in the Erlenmeyer flask, then heated on the hot plate, 0.5 ml of phenolphthalein added, then neutralised by dropwise addition of 0.1 N potassium hydroxide until a faint, but permanent pink colour is obtained. The procedure repeated for determination of acid value of WPCO and DC oil.

3.3.2 Determination of Free Fatty Acid (PORIM Test Methods (p1), 1995)

The determination of free fatty acid of feedstock was prepared following the procedure described in section 3.3.1, was done in triplicate. The free fatty acid of DC oil was calculated using the following equation (3.4):

$$\text{Free fatty acid (\% as palmitic acid)}: \frac{25.6 \text{ x N x V}}{\text{W}} \tag{3.4}$$

While, the free fatty acid content of RBD-PO and WPCO was expressed as percentages of oleic acid by the equation (3.5):

$$\text{Free fatty acid (\% as oleic acid)}: \frac{28.2 \text{ x N x V}}{\text{W}} \tag{3.5}$$

where N is the normality of a standard potassium hydroxide solution

V is the volume of standard potassium hydroxide solution in ml.

W is the weight of sample in grams

3.3.3 Determination of Water Content

Water content of DC was determined by heating balance (MX-50). 5 gram sample solid was dried in measuring balance and was set temperature at 200 ˚C until the constant weight.

3.3.4 Determination of Viscosity

The viscometer Brookfield DV-II+Pro was used to determine viscosity of oil and methyl ester.

3.3.5 Determination of Density

The Kyoto-kem DA-640 was used to determine the density of the oil.

3.3.6 Deterioration of Bleachability Index Analysis

Deterioration of Bleachability Index (DOBI) is an indication of the bleachability of the crude palm oil based on the amount of carotenes still present in the crude oil and the amount of secondary oxidation products (Siew, 1994). A good easily bleached crude palm oil will have a DOBI of 4, while average quality crude will exhibit a DOBI of 2.5 to 3.Table 3.1 below, shows the refinability of CPO according to DOBI values.

Table 3.1 Refinability of CPO according DOBI values

DOBI	Grade
<1.7	Poor
1.8-2.3	Fair
2.4-2.9	Good
3.0-3.2	Very good
>3.3	Excellent

Source: Siew (1994)

DOBI can be measured using UV-visible spectrophotometer and it is a numerical ratio of spectrophotometric absorbance at the wavelength at 446 nm to absorbance at 269 nm. The measurement is carried out on 1% concentration solution of crude palm oil in isooctane. The experimental procedures for the determination of DOBI value are as follows (Boey et al., 2011a).

About 0.1 g of completely melted and homogenised crude palm oil sample was weighed into 25 ml volumetric flask. Then dissolved in *n*-hexane (0.5 – 1.0 % concentration) and make-up to the desired volume. Oil solution was filled in a 10 mm cuvettes and measured its absorbance at 269 nm and 446 nm against pure solvent using spectrophotometer. The DOBI value was calculated using the following equation (3.6) :

$$\text{DOBI} = \frac{Abs\ 446}{Abs\ 269}\ (in\ a\ 10\ mm\ quartz\ cell) \tag{3.6}$$

3.4 CATALYSTS PREPARATION FOR TRANSESTERIFICATION

3.4.1 Boiler Ash as a Catalyst in Transesterification

Boiler ash was obtained and dried in an oven at 105 ºC until constant weight, to remove water and then filtered through 100 mesh sieve. The filtered ash was then calcined to remove the remains of carbon and other impurities. Calcination BA was done at different temperatures (500, 700 and 900 ˚C) and durations (2, 4 and 6 h). Approximately 2 g of catalyst sample was weight in a crucible and was then placed in the furnace. For this study, an electrical furnace (Nabertherm, 30-3000 ˚C) was used, and the obtained catalyst was labelled as BA.

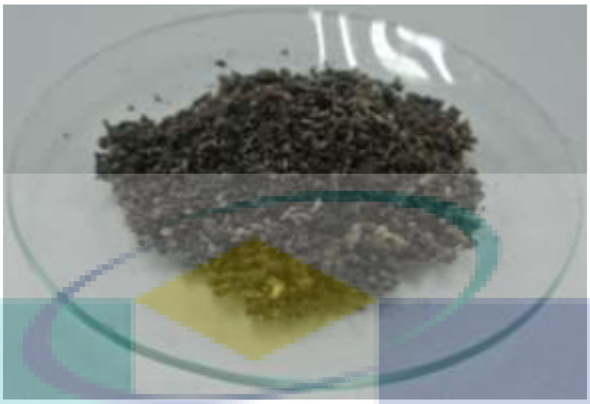


Figure 3.1: Boiler ash

3.4.2 Baby Clam Shell as a Catalyst in Transesterification

Baby clam (*Paphia undulata*) (Figure 3.2) shell was cleaned using warm water to remove dirt, fibrous matters and proteins. Then the shell dried in an oven at 105 ˚C until constant weight. The shell was then crush by mortar and pestle until powder, for futher fine crush using a dry-mill blender and sieved through 100 µm mesh. The catalyst was calcined to remove the remains of carbon and other impurities at different temperature (500, 700 and 900 ˚C) and duration (3, 5 and 7), by following the procedure in section 3.4.1. The catalyst obtained was labelled as BC-CaO.

Figure 3.2: Baby clam (*Paphia undulata*) shell

3.4.3 Capiz Shell as a Catalyst in Transesterification

Catalyst from capiz (*Placuna placenta*) (Figure 3.3) shell was prepared following the procedure described in section 3.4.2, and calcined folowing the procedure described in section 3.4.1. The catalyst obtained was labelled as C-CaO.

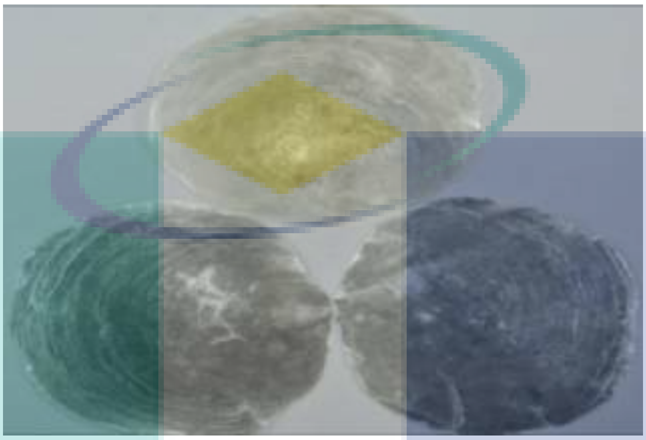


Figure 3.3: Capiz (*Placuna placenta*) shell

3.5 CATALYSTS CHARACTERIZATION

3.5.1 Thermal Gravimetric Analysis of the Catalysts

About 7 mg of catalyst was analysed by Mettler Toledo thermogravimetric analysis (TGA)/differential thermal analysis (DTA) 851e, to determine the thermal stability and major compounds of catalysts. The TGA was set to range from 25 to 900 °C with 10 ºC/min heating rate, under N_2 environment.

3.5.2 X-ray Diffraction Analysis of the Catalysts

The crystalline of the waste catalysts were determined by X-ray Diffraction (XRD) techniques. This method was based on the fact that every crystalline material has its own characteristic diffractogram. XRD patterns were identified by X-ray diffraction (Rigaku) with CuKα radiation in the range of 2θ from 2˚ to 60˚ at a scanning speed of

3˚ per minute. All the samples were fully dried before XRD diffactograms were measured.

3.5.3 Surface Analysis (BET Method) of the Catalysts

The surface analysis of the catalysts was determined by Micromeritics ASAP 2000. The sample was degassed at 105 ˚C prior to analysis and the adsorption of N_2 were measured at -196 ˚C. The surface area was calculated using Brunauer-Emmett-Teller (BET) equation over the pressure range of P/P_0 = 0.01-0.30, where a liner relationship was sustained.

3.5.4 Fourier Transform Infrared Analysis of the Catalysts

The Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum 100) was used to investigate the functional groups of catalysts. Each waste catalysts sample was mix with standard KBr. The samples were then scanned transmittance mode from 4000 to 400 cm^{-1}. All spectra were referenced against the background spectrum.

3.5.5 Scanning Electron Microscopy Analysis of the Catalysts

The morphology of catalyst was observed by scanning electron microscopy (SEM) ZEISS (EVO50).

3.5.6 X-ray Fluorescence Analysis of the Catalysts

X-ray fluorescence (XRF) analysis was performed on Bruker, S8 Tiger using pressed-pellet (pressure at 8.0 Pa) method to determine the elemental and oxide composition of catalysts.

3.5.7 Basicity Analysis of the Waste Catalysts using Hammett Indicators

Basic strengths of the catalyst were determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H_= 8.2), 2,4-dinitroaniline (H_= 15.0) and 4-nitroaniline (H_= 18.4). About 25 mg of catalyst was shaken with 1 mL of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted.

3.6 TRANSESTERIFICATION REACTION

The transesterification of feedstock (i.e.: RBD-PO and WPCO) into biodiesel using waste catalyst (i.e.: BA, BC-CaO, C-CaO) was carried out in a 50 ml one-neck round bottom flask equipped with reflux condenser, thermometer, and magnetic heating mantle, as shown in Figure 3.4. In a typical reaction, 10 g of oil was added in round bottom flask onto mixture of calcined catalyst and methanol. The transesterification experiments were carried out at temperature 65 ± 2 ˚C and stirred vigorously for 1 h for BA and 3 h to BC-CaO and C-CaO. Reaction parameter (catalyst amount, methanol to oil molar ratio and reaction time) were studied to determine the optimum conditions.

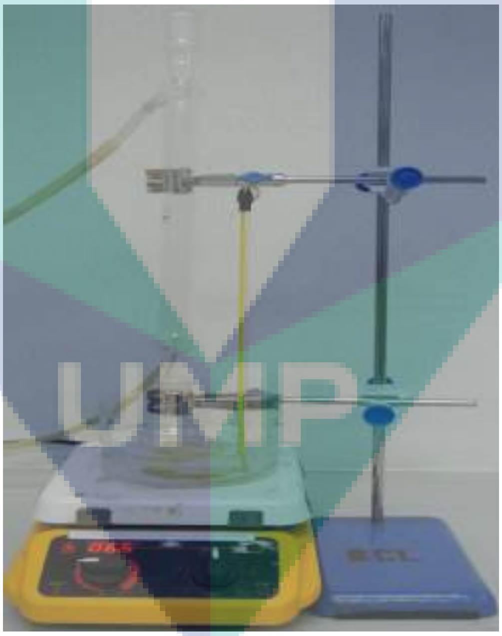


Figure 3.4: Transesterification reaction

After completion, the reaction mixture was allowed to cool, successful transesterification reaction produces two liquid phases: methyl ester and crude glycerine. The glycerol being separated by gravity. Centrifugation (6000 rpm, 15 min) was used to further separate the layers (methyl esters, glycerol and catalyst). The top layer (methyl esters) was carefully transferred to a pre-weighed round bottom flask and the residual methanol in the layer was evaporated out using a rotary evaporator at 80 °C. The methyl esters obtained was then weighed and transferred into an amber vial and refrigerated until the next use. The methyl esters content in the final product is quantified using GC and GC-MS

3.7 ANALYSIS OF METHYL ESTER

3.7.1 Qualitative Analysis of Methyl Ester

In order to ensure the complete transesterification process, the qualitative analysis using Thin Layer Chromatography (TLC) was used. The TLC was performed on an aluminium sheet coated with silica gel 60 (DC- Fertigplatten Kieselgel 60 F254). A mixture of solvent containing chloroform and petroleum ether (with ratio 3:2) was used to developing solvent and iodine vapour was used for visualization of the spots. The achievement of reaction was judged by the disappearance of triglyceride spots and the formation of methyl esters. The spot of mixture internal standard methyl heptadecanoate (C_{17}) and oil was used as comparison of the formation of methyl ester, as shown in Figure 3.5.

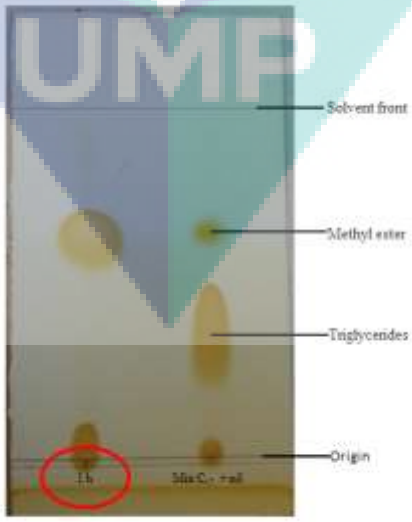


Figure 3.5: TLC plate showing of methyl ester and mixture standard C_{17} and oil in 1 h, using BA as a catalyst and RBD-PO as a feedstock

3.7.2 Quantitative Analysis of Methyl Ester

The methyl ester content in biodiesel was determined using gas chromatography-flame ionization detector (GC-FID) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) method. In this study, GC-FID (Agilent 7890A) with capillary column DB-wax (length 60 m x diameter 0.25 mm x film thickness 0.25 µm) and a flame ionization detector operated at 300 ˚C was used. Helium was used as the carrier gas with a linear velocity of 40 cm/s. The injector temperature was 250 ˚C at split ratio of 60:1. The initial oven temperature was 190 ˚C with an equilibration time of 2 min. After isothermal period, the oven temperature was increased to 230 ˚C at a heating rate of 10˚C/min and held for 8 min. About 20 mg of methyl ester sample was weight in a vial and added of 400 µL of internal standard dilute in heptane 10 mg/ml concentration. The vial was then shake well to homogenous mixture. Sample volume of 1 µL was injected into GC. The methyl ester content of biodiesel was calculated by following the European regulation procedure EN 14103 and using methyl heptadecanoate as an internal standard. The methyl esters content was calculated using the following formula:

$$\text{Methyl ester content (\%)} = \frac{A_{total} - A_{ISTD}}{A_{ISTD}} \text{ x } \frac{C_{ISTD} \text{ x } V_{ISTD}}{W_{sample}} \text{ x } 100\% \qquad (3.7)$$

where A_{total} is the total peak area of methyl esters

A_{ISTD} is the area of methyl heptadecanoate

V_{ISTD} is the volume of methyl heptadecanoate

C_{ISTD} is the concentration of methyl heptadecanoate

W_{sample} is the weight of sample

^{1}H-NMR spectrum of methyl ester was obtained using a Bruker (Billerica, MA) AV-500 spectrometer operating at 500 MHz with a 5-mm broadband inverse Z-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA, USA) as solvent and reference. Knothe (2005) reported methyl ester protons appears at 3.6 ppm and the protons on the carbons next to the glyceryl moiety ($R\text{-}CH_2$) appears at 2.3 ppm. An equation of methyl ester content was calculated by following formula:

$$\text{Methyl ester content (\%)} = \frac{2\,A_{ME}}{3\,A_{\alpha-\mathrm{CH2}}} \text{ x } 100 \qquad (3.8)$$

where A_{ME} is the integration value of the protons of the methyl ester

$A_{\alpha\text{-CH2}}$ is the integration value of the methylene protons

3.8 CATALYST ACTIVITY

The catalytic tests of major fatty acid of feedstock (in this study oleic acid; $C_{18:1}$) used each catalyst were measured by using turnover frequency (TOF) analysis under the optimal reaction conditions in transesterification. The TOF value was calculated using the following equation (3.9) (Xu et al., 2013):

$$r = \frac{\dfrac{\mathrm{n}_{\mathrm{C18:1}} \text{ x cov.\% } C_{18:1} \text{ x } \mathrm{M}_{\mathrm{C18:1}}}{\mathrm{W}_{\mathrm{Cat}}}}{\mathrm{t}} \qquad (3.9)$$

where $\mathrm{n}_{\mathrm{C18:1}}$ is the molarities of oleic acid in mol.

Cov.% $C_{18:1}$ is the % $C_{18:1}$ converted to methyl oleat

$M_{C18:1}$ is the molecule weight of $C_{18:1}$ in g mol^{-1}.

W_{cat} is the weight of the catalyst in gram

t is the duration of reaction in second

3.9 TRANSESTERIFICATION USING MIXED-SHELL-CaO CATALYST

Baby clam (*Paphia undulata*) and capiz (*Placuna placenta*) shell was prepared following the procedure described in section 3.4.2, and calcined in a furnace (900 ˚C for 2 h) following the procedure described in section 3.4.1, to be used as a source of CaO to replace the use laboratory grade CaO. The mixture waste catalysts obtained was labelled as BC-C-Mixed-900, then employing the optimum conditions for BC-C-Mixed-900. The waste cooking oil (WPCO; 10 g) was transesterified using mixture waste catalyst at different condition; mixture (1:1) mass ratio of baby clam and capiz shell. The procedure described in section 3.6.

3.10 REUSABILITY, REGENERATION AND LEACHING STUDY OF WASTE CATALYSTS IN WPCO

In order to examine the potential reusability of the catalyst, used catalyst was tested for its catalytic activity. For reuse experiments, the used solid catalyst that recovered by centrifugation was regenerated by washing with methanol followed by hexane. The dried used catalyst at 105 ˚C for overnight, then directly used as a catalyst for the repeated reactions. For the regeneration catalysts, after washing, the catalysts were calcined at 500 ˚C of 5 h for BA catalyst and 900 ˚C of 2 h for BC-C-mixed catalyst.

The leaching test of catalysts was carried out in this study. The calcined catalyst was placed in contact with methanol and kept under stirring conditions at 65 ˚C for 1 h for BA catalyst and 3 h for BC-C-mixed catalyst. Then, the stirring was stopped, the catalyst was filtered out, and the treated methanol was placed in contact with WPCO. In other words, the transesterification reaction was carried out with catalyst dissolved in methanol.

3.11 TOLERANCE OF WASTE CATALYSTS TOWARDS OF WATER AND FFA IN WPCO

Water and FFA tolerance of waste catalysts with addition of 0-5 wt.% from weight oil in varying of methanol to oil molar ratio and catalyst loading was investigated. The WPCO was transesterified with 3 wt.% of BA-500 and 5 wt.% BC-C-mixed-900 in the varying of methanol to oil molar ratio with reaction duration 1 and 3 h for BA-500 and BC-C-mixed-900, respectively. In the varying of catalyst amount, the optimal methanol to oil molar ratio was used, 1:9 and 1:12 for of BA-500 and 5 wt.% BC-C-mixed-900, respectively. In this study the free fatty acid was used is oleic acid.

3.12 *IN SITU* TRANSESTERIFICATION OF DC USING ULTRASOUND IRRADIATION AND MECHANICAL STIRRING METHODS

Transesterification reaction was carried out in a 250 ml three-neck round bottom flask equipped with reflux condenser, thermometer, and magnetic heating mantle, with the constituent of 10 g DC (1.35 g oil, at oil content 13.5 wt.%), 20% wt.% BA catalyst (0.27 g, based on oil weight), 7.91 g of methanol to give the molar ratio of methanol to oil of 150:1 and a co-solvent (*n*-hexane:PE mixture at 1:1, 5 g respectively):DC weight. The transesterification experiments were carried out at temperature 65 ˚C and stirred vigorously for 1 h.

The resultant mixture was then placed in a test tube and centrifuged at 6000 rpm for 10 min. Three layers were formed; the top was co-solvent, followed by methanol and the DC layer at the bottom. The co-solvent and methanol layers were pipetted out separately, then about 3 ml of each PE and hexane were added into the test tube, homogenize and centrifuge then the resultant top co-solvent layer was added to the portion of co-solvent that was pipetted out earlier. The step was repeated twice to obtain a total amount of accumulated co-solvent. Upon solvent evaporation, pure ME was obtained. The resultant ME was subjected to chromatographic analysis for quantification using GC-FID (Agilent 7890A) following the European procedure EN 14103.

The *in situ* transesterification of DC using ultrasonic irradiation was compared using bottle reactant was immersed in the ultrasound water bath (Bransonic at a working frequency of 42 kHz and the power supply of 235W) with the temperature set at 65 ºC for 1 h.

3.13 DETERMINATION OF FUEL PROPERTIES OF THE METHYL ESTER PRODUCTS

The fuel properties of methyl ester of density, viscosity, flash point, heating value, cold point and sulphur content was determined. The density and viscosity procedure was presented in section 3.3.4 and 3.3.5.

3.13.1 Determination of Flash Point

Flash point is the measure of flammability of a fuel. Higher flash point ensures safer storage and transportation of the fuel. The flash point is defined as the minimum temperature at which a fuel produces sufficient vapor to ignite momentarily and give the first flash. Petrotest PM4: Close cup Pensky-Martens apparatus was used to determine flash point using ASTM method D 93.

3.13.2 Determination of Higher Heating Value

Higher heating value (HHV) of biodiesel was measured using IKA C-200 oxygen bomb calorimeter using ASTM D240. Approximately 0.2 g of biodiesel was placed into a quartz crucible inside the combustion chamber. Pure oxygen gas was introduced into the chamber until 30 bar pressure was achieved. Two litres of tap water at temperature range of 20–23 ˚C was added inside the calorimeter surrounding the chamber. After five minutes of stirring, the water temperature became stable and the samples were ignited. The changes in water temperature were monitored until it remained constant. Differences of initial and final temperature were used to calculate the heating value of the samples. The calorimeter heat capacity was calibrated using benzoic acid as reference.

3.13.3 Determination of Cold Point

The cold point of biodiesel was determined based on ASTM D2500. The biodiesel inside to water batch, the temperature of which can be controlled. The temperature was observed using thermometer of temperature range -50 ˚C to 200 ˚C. Initially the sample was heated to 130 ˚C to destroy any crystal nuclei present. The sample was cooled on stirring until a temperature is reached where the sample shows no movement after 5 s.

3.13.4 Determination of Sulphur Content

The sulphur content of biodiesel was determined using C, N, O, S analysis. The composition of C, H, S and N elements in biodiesel were determined by Elementary CHONS Analyzer. The oxygen content of biodiesel not include in this analysis.

3.14 EMISSION ANALYSIS

The performance of the biodiesel produced by the transesterification process was evaluated on a Euro 4 diesel engine mounted on a steady state engine test bed. The type engine was a horizontal single cylinder 4 stroke diesel engine (YANMAR NF19-SK). The general specification was Bore = 110 x 106 mm, stroke maximum = 1007 cm^3, clearance volume = 61.78 cm^3, compression ratio = 16.3:1, fuel injection release pressure = 135 bar, max power = 19.0 PS / 2400 rpm. Emissions were measured using a Horiba EXSA 1500 system, measuring CO_2, CO and NOx. The test procedure was to run the engine speeds at 1200, 1500, 1800, 2100 & 2400 rpm. At each of these settings the torque, fuel consumption and emissions were measured for each of the diesels, the standard diesel forming the benchmark.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF FEEDSTOCK

4.1.1 Characteristics of RBD-PO, WPCO and O-DC

The characterization results of feedstock RBD-PO, WPCO and oil extracted from decanter cake (O-DC) in term of acid value, free fatty acid (FFA), water content, density, viscosity are presented in Table 4.1. As stated, DC oil has the highest acid value, FFA, water content and viscosity compared to WPCO and RBD-PO. Higher acidity in O-DC is justified since it consists of crude palm oil which contains comparatively higher FFA, the reported range of free fatty acid content of crude palm oil was 2.3–6.7% (Saad et al., 2007, and Tan et al., 2009). However, the relatively high moisture content in CPO may be related with heating duration of palm fruit and the quantity of water added during boiling process. In contrast, the RBD-PO used in this study has very low acid value and FFA; obviously RBD-PO is refined through a number of processes until it reached FFA of 0.08 % (Refaat, 2011), in agreement with PORIM standard specifications for processed palm oil, the FFA content of RBD-PO should be lower than 0.1% (Tan et al., 2009). The waste palm cooking oil (WPCO) from RBD-PO has higher FFA at 3.45 mg/KOHg. This could be the result of the heat and water which accelerates the hydrolysis of triglycerides during the frying process, eventually increases the FFA content and water content in the oil (Marmesat et al., 2007).

The relatively of high viscosity of oil can be related to the chain length and degree of saturation of the fatty acid content in triglycerides. The increasing viscosity of triglycerides is increasing fatty acid chain length. The viscosity of decanter cake higher than RBD-PO and WPCO, because of unsaturated fatty acid content in the O-DC. Unsaturated oils have double bonds in the hydrocarbon chains, where the double bonds that produce ‘kinks’ in the molecule. These ‘kinks’ prevent the molecules getting as close to each other and forming as many Van der Waals interactions, thus increasing the viscosity of the oil.

Table 4.1: Quality parameters of oils

Test	Unit	RBD-PO	WPCO	O-DC
Acid value	(mg/KOHg)	0.16	3.45	13.80
FFA	(%)	0.08	1.67	6.30
Water content	(wt.%)	0.09	0.11	0.30
Density	(g/cm^3)	0.91	0.91	0.91
Viscosity	(cP)	62.7	64.00	90.1

The characterization of WPCO from different sources is presented in Table 4.2. Although the WPCOs were from different origins, they were quite similar to each other, with the exception of the acid value, FFA and viscosity. Many researchers have linked for this case with the transesterification process, such as temperature, duration of heating, heating pattern (continuous or intermittent), turnover rate and also for the food subjected at frying, i.e. lipid composition, will change some physical and chemical properties (acid value and FFA content) in oil after frying (Machado et al., 2007, and Refaat, 2011). However, continuously using the same oil or fat for frying will change physical properties in the oil, such as (i) an increase in viscosity, (ii) an increase in specific heat, (iii) a decrease in surface tension, and (iv) the colour tends to be darker (Cvengroš and Cvengrošova, 2004).

Table 4.2: Characterization of WPCO from different sources

Test	Unit	$WPCO_1$	$WPCO_2$	$WPCO_3$	Present work
Acid value	(mg/KOHg)	4.77	6.69	2.51	3.45
FFA	(%)	2.39	3.36	1.23	1.67
Water content	(wt.%)	0.12	0.12	0.12	0.11
Density	(g/cm^3)	0.91	0.91	0.91	0.91
Viscosity	(cP)	68.20	69.20	67.6	64.00

$WPCO_1$= WPCO from restaurant Kuantan, $WPCO_2$= WPCO from restaurant Gambang and $WPCO_3$= WPCO from domestic

The compositions of fatty acid of RBD-PO are reported in Table 4.3. The most abundant fatty acid is the oleic acid, the similar observation was reported by (Rustan and Drevon, 2005) and (Lam et al., 2010). RBD-PO has long been investigated as a feedstock in the production of biodiesel (Kansedo et al., 2009, and Noiroj et al., 2009), especially in Indonesia and Malaysia which are the major palm oil producing countries in the world. RBD-PO used in this study contains 42.4 % saturated and 57.6 % unsaturated fatty acids.

Similar to RBD-PO, the palm olein is the major composition of WPCO used in this study, as WPCO is probably derived from the virgin RBD-PO. The properties of WPCO are presented in Table 4.3, in which higher content of unsaturated fatty acid is 66.2 %. The composition of fatty acid in WPCO resembles the composition of chicken fat. The WPCO could be used to fry chicken which justify the presence of palmitoleic acid ($C_{16:1}$). Originally in RBD-PO the palmitoleic acid is not usually present.

Table 4.3: Fatty acid composition of RBD-PO, WPCO and chicken fat

Fatty acid	**Composition (%)**		
	RBD-PO	**WPCO**	**Chicken fat**
	Present work	**Present work**	**Previous work** (Boey et al., 2011c)
Saturated			
Lauric ($C_{12:0}$)	0.1	0.9	-
Myristic ($C_{14:0}$)	1.0	1.0	0.6
Palmitic ($C_{16:0}$)	37.0	28.2	24.7
Stearic ($C_{18:0}$)	4.3	3.7	4.5
Arachidic ($C_{20:0}$)	0.2	Traces	-
Sub total	42.6	33.8	29.8
Unsaturated			
Myristoleic ($C_{14:1}$)	-	-	0.2
Palmitoleic ($C_{16:1}$)	-	4.8	6.3
Oleic ($C_{18:1}$)	45.2	42.3	44.1
Linoleic ($C_{18:2}$)	12.2	18.1	18.4
Linolenic ($C_{18:3}$)	Traces	1.0	0.2
Gardoleic ($C_{20:1}$)	-	-	1.0
Sub total	57.4	66.2	70.2
Total	100.0	100.0	100.0

The composition of fatty acids in O-DC as crude palm oil is present in Table 4.4, and was compared to crude palm oil from previous work (Siew, 1994). Major fatty acid content in O-DC is palmitic acid (35.9 %). The fatty acid distribution of O-DC has slightly higher unsaturated at 54% versus 46% of saturated fatty acids. Similar result was document by Siew (1994), where value of unsaturated fatty acid (45.8-53.5 %) is higher than of saturated (45.8-54.1%) in crude palm oil.

Table 4.4: Fatty acid composition of O-DC compared to crude palm oil previous work

	Composition (%)	
Fatty acid	**Present work**	**Previous work** (Siew, 1994)
Saturated		
Lauric ($C_{12:0}$)	0.5	0.1-0.4
Myristic ($C_{14:0}$)	1.1	1.00-1.40
Palmitic ($C_{16:0}$)	43.9	40.9-47.5
Stearic ($C_{18:0}$)	Traces	3.8-4.8
Sub total	45.5	45.8-54.1
Unsaturated		
Oleic ($C_{18:1}$)	41.6	36.4-41.2
Linoleic ($C_{18:2}$)	11.5	9.2-11.6
Linolenic ($C_{18:3}$)	1.4	0.2-0.7
Sub total	54.5	45.8-53.5
Total	100.00	

4.1.2 Characteristics of DC and Extraction of O-DC

Utilization of waste/used oils in transesterification reaction should be given priority as a way to cater solution for the ‘food-for-fuel’ crisis. Among the waste vegetable oils, animal fats and biomass sources, waste cooking oil have attracted much attention as a potential resource for production of an alternative for petroleum-based diesel fuel. Though, new waste feedstock alternatives as source are still being sought. A large range of industrial wastes, both natural and synthetic, are disposed without extracting the useful components from them. Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. The previous investigated of spent bleaching clay (SBC) as a waste biomass from palm oil refinery was promised and successful as a feedstock in transesterification (Lim et al., 2009; Huang and Chang, 2010, and Mat et al., 2011). Another biomass waste from palm oil plantation is decanter cake (DC).

DC is a solid waste produced when the crude palm oil is centrifuged for purification where the supernatant is the purer palm oil and the sediment is the decanter cake. DC contains water (about 76%, on wet basis), residual oil (about 12%, on dry basis) and nutrients, cellulose, lignin and ash. There are previous reports on the use of DC in the area of bio-fertilizer, biofuel and cellulose (Kandiah, 2012, and Razak et al., 2012). The composition of decanter cake (DC) is reported in Table 4.5. Decanter cake mainly consists of C (60.3%) and O (32.6%) and other components (Si, Al, K, P, Ca, Mg). Oil adsorbed on DC is a minor by product of palm oil purification process, which could be a potential feedstock for production of biodiesel (methyl ester).

Table 4.5: Decanter cake composition using EDX analysis

Element	Composition (wt.%)
C	60.29
O	32.63
Si	1.57
Al	1.22
K	1.77
P	0.56
Ca	1.05
Mg	0.45
Total	100.00

In order to utilize residual oil from DC, the adsorbed oil has to be extracted first. For that purpose, the Soxhlet extraction method was conducted by using four different solvents (polar and non-polar). The yield of residual oil extracted are showed in Figure 4.1, where the highest yield of Soxhlet extraction was given for ethanol compared to methanol and non-polar solvents, this is in line with previous reports (Lee et al., 2000, and Lim et al., 2009). All non-polar solvents (*n*-hexane, petroleum ether and *n*-hexane:PE mixture) gave very similar extraction yields. Although ethanol and methanol are polar solvents which gave higher yield than the non-polar solvents, but the colour of the polar extractions was darker (brown) than the non-polar extraction (light yellow, cleaner and clearer). The darker colour of extracted residual oil is due to, extraction of all the coloured polar components from DC by these polar solvents. Apart from the colour difference, the difference in acidity of extracted residual oil is also noticed. As reported in previous work (Lim et al., 2009), the acidity of residual oil extracted from SBC using different solvents (polar and non-polar), showed that oil extracted using methanol has the highest FFA content (13.1%), followed by ethanol (8.9%), then *n*-hexane (6.8%) and petroleum ether (6.6%).

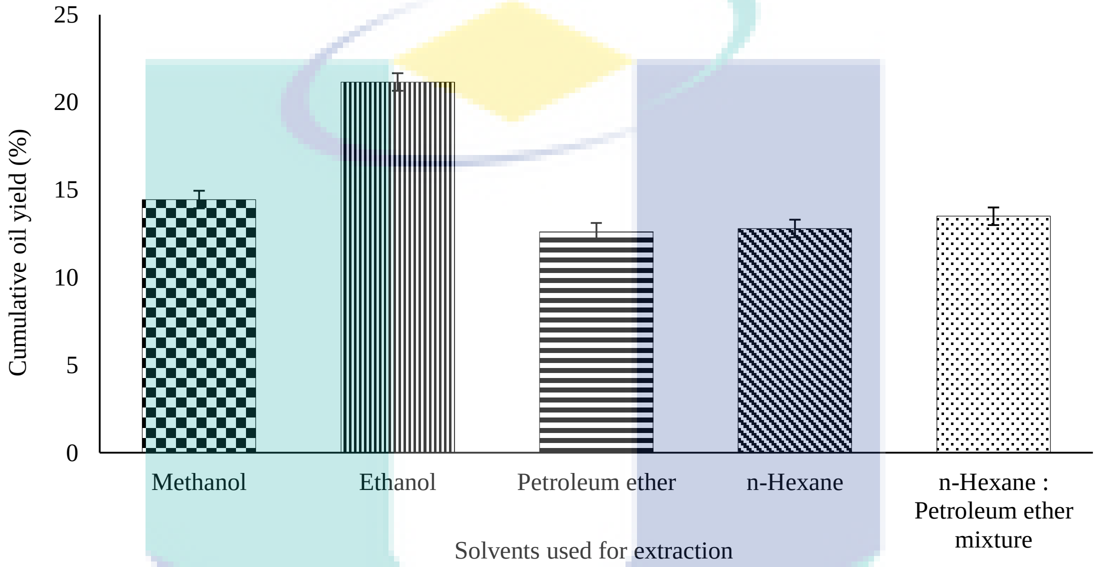


Figure 4.1: Cumulative oil yield with different solvents

The other characteristic that is deterioration of bleachability index (DOBI) analysis indicates the deterioration of the oil quality. Table 4.6 shows that the DOBI value of residual oil extracted using non-polar solvents are higher than polar solvents. According to the DOBI values and respective oil quality set by then Palm Oil Research Institute of Malaysia (Siew, 1994; tabulated in section 3.3.7), methanol recorded the lowest DOBI index of 1.5 (poor), followed by ethanol (2.1; fair), then petroleum ether (2.8; good) and same index for both *n*-hexane and mixed *n*-hexane:PE (3.3; excellent).

Table 4.6: DOBI analysis of O-DC with different solvents extracted

Solvent for extract O-DC	**DOBI Index**	**Oil Grade (Siew, 1994)**
Methanol	1.5	Poor
Ethanol	2.1	Fair
Petroleum Ether	2.8	Good
n-hexane	3.3	Excellent
Mix *n*-hexane:PE	3.3	Excellent

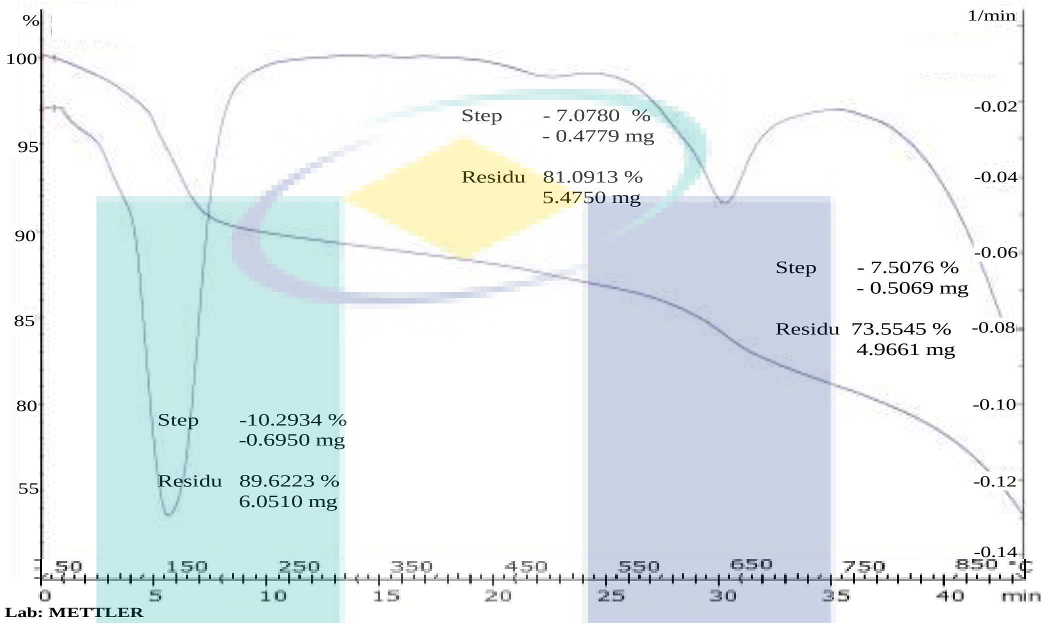
The ultrasound irradiation as a different method of oil extraction from decanter cake was also investigated. The amount of oil extracted from decanter cake with mixed solvents *n*-hexane:PE in equal mass ratio (1:1) for 1 h was at 11.5 wt.%. It is concluded that, ultrasound promises simpler process with higher product and the process can be completed in shorter reaction time compared to Soxhlet extraction methods. The higher efficiency of the extraction process using ultrasound has previously been reported by Li et al. (2004) in extraction soybean oil using mix *n*-hexane:isopropanol. The oil extraction capabilities of *n*-hexane:isopropanol mixture was 5.2% higher than of *n*-hexane

4.2 CATALYST CHARACTERIZATIONS

4.2.1 Thermal Gravimetric Analysis of the Catalysts

The thermal analysis of boiler ash (BA) as depicted by Figure 4.2 (A), shows three decomposition steps. The first mass loss is in the range of 120-340 ˚C is might be due to the surface bound water removal from the sample. Decomposition at higher temperature between 420-720 °C was 6% and it should be attributed to the carbon monoxide, volatiles such as and organic carbons that may have condensed on the sample (Khan et al., 2009). Further mass loss (15.13%) occurred between 740-900 ˚C. The decomposition of mineral component such as some of the other metal carbonates and metal oxides which present in the sample may occur during this phase. As for baby clam shell in Figure 4.2 (B), the major decomposition occur at temperature range of 600-800 ˚C, in agreement with observations by other researchers (Nakatani et al., 2009, and Wei et al., 2009) using egg shell as a catalyst. The decomposition about 42 to 44 wt.% correlates with the release of adsorbed CO_2 from catalyst (corresponds well to the molecular weight of CO_2). The weight loss indicated transformation of $CaCO_3$ to CaO. This observation is in agreement with the stoichiometry of decomposition reaction of $CaCO_3$, as depicted by Figure 4.3. The shell in this present study is in the form of calcium carbonate that decomposes into calcium oxide when calcined above 750 ˚C.

(A) BA



(B) BC-CaO

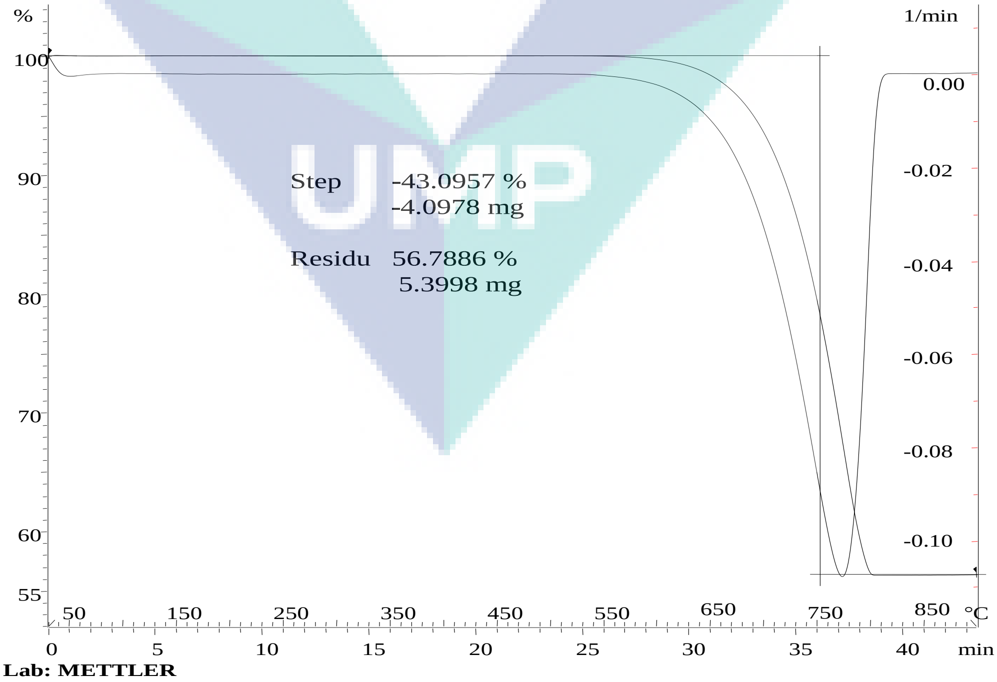


Figure 4.2: TGA thermogram of (A) BA, (B) BC-CaO and (C) C-CaO

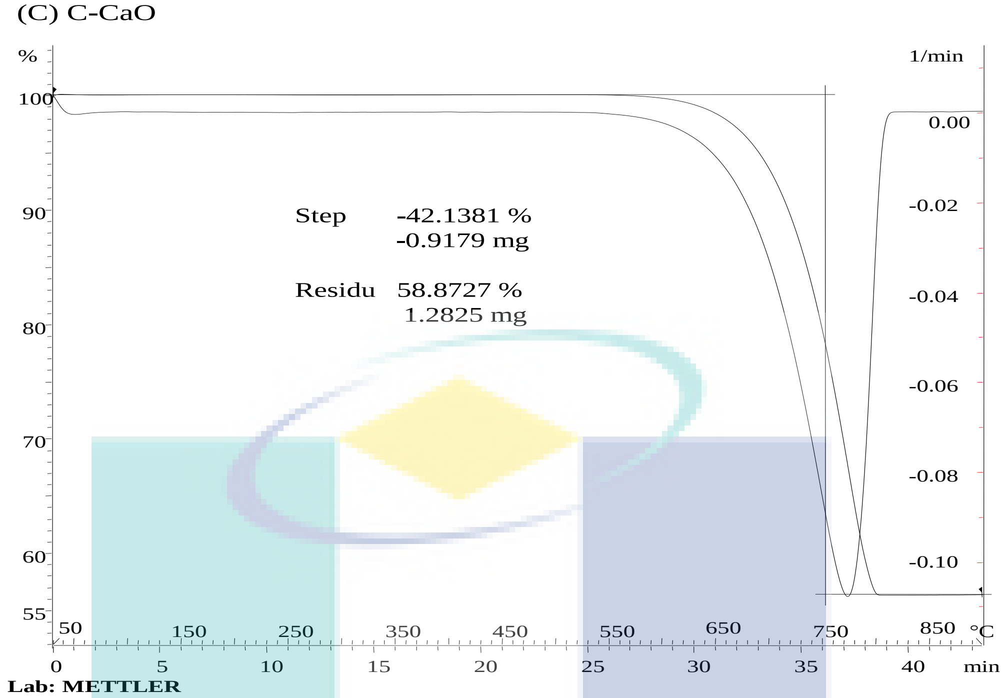


Figure 4.2 : Continued

$$CaCO_3 \xrightarrow[\triangle]{} CaO + CO_2$$

(MW = 100) (MW = 56) (MW = 44)

Figure 4.3: Decomposition of calcium carbonate

The capiz shell TGA thermograph given in Figure 4.2 (C), is similar to the TGA thermograph of BC-CaO. The major decomposition at temperature range 600-800 ˚C, is related to the transformation of calcium carbonate to calcium oxide by evolving CO_2.

4.2.2 X-ray Diffraction Analysis of the Catalysts

The XRD analysis was employed to observe the crystal structure of the BA, shown in Figure 4.4 (A). The diffractograms of BA-dried showed a minor amorphous structure; with potassium silicate as a dominant structure and other silicates such as magnesium, aluminium and calcium. Increased calcination temperature to 500 to 900 °C may have caused an increase in number of bond formations between potassium, magnesium, calcium and silicon oxide (Yang et al., 2008). The major peaks of the XRD patterns were potassium calcium silicate $K_4CaSi_3O_9$ and $K_{9.6}Ca_{1.2}Si_{12}O_{30}$.

The XRD pattern of BC-CaO, and C-CaO at different calcination temperatures are shown in Figure 4.4. (B) and (C), respectively. The pattern shows that the transformation of $CaCO_3$ to CaO occurred at temperature 800 or above, while at 700 ˚C CaO peaks just started to appear together with $CaCO_3$ structure. The dried and calcined below at temperature 700 ˚C consist only of calcium carbonate, the observation in line agreement by Wei et al. (2009). The author found that calcination of eggshell at temperature 700 ˚C consist marjory of calcium carbonate and minor calcium oxide, while below the temperature exhibit only a $CaCO_3$ structure. In contrast, Boey et al. (2011c) reported cockle shell consist CaO at temperature 700 ˚C or above. This different may arise due to different source of shell usage. These XRD pattern observations are in line well with the TGA result (section 4.2.1) where release of carbon dioxide occurred between ranges 750 to 850 ˚C.

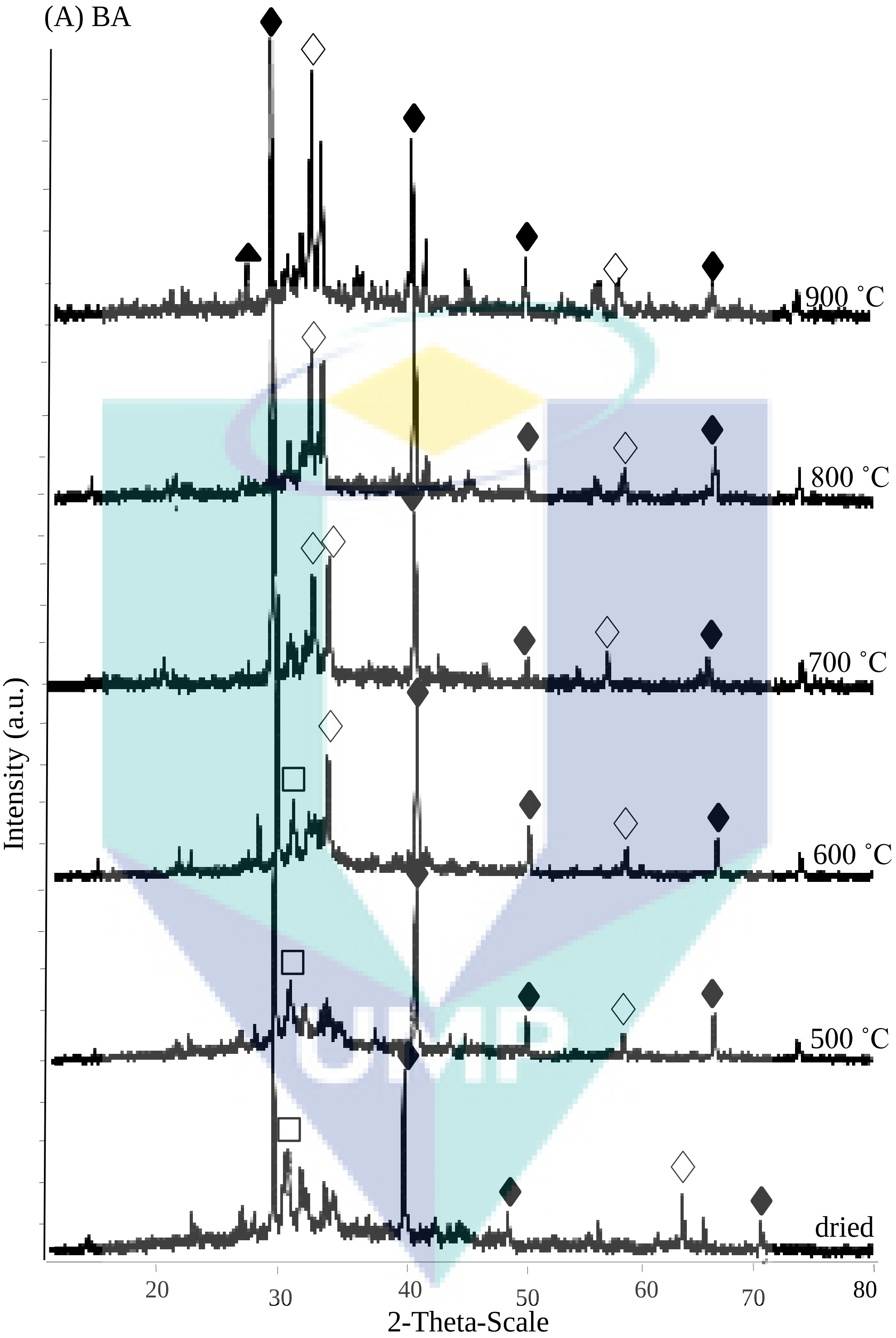


Figure 4.4: Powder XRD patterns of (A) BA, (B) BC-CaO, (C) C-CaO at various calcination temperatures ▲, K_2MgSiO_4 □, $KAlO_2$ ♦, $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ ◊, $K_4CaSi_3O_9$ ■, CaO; ●, $CaCO_3$

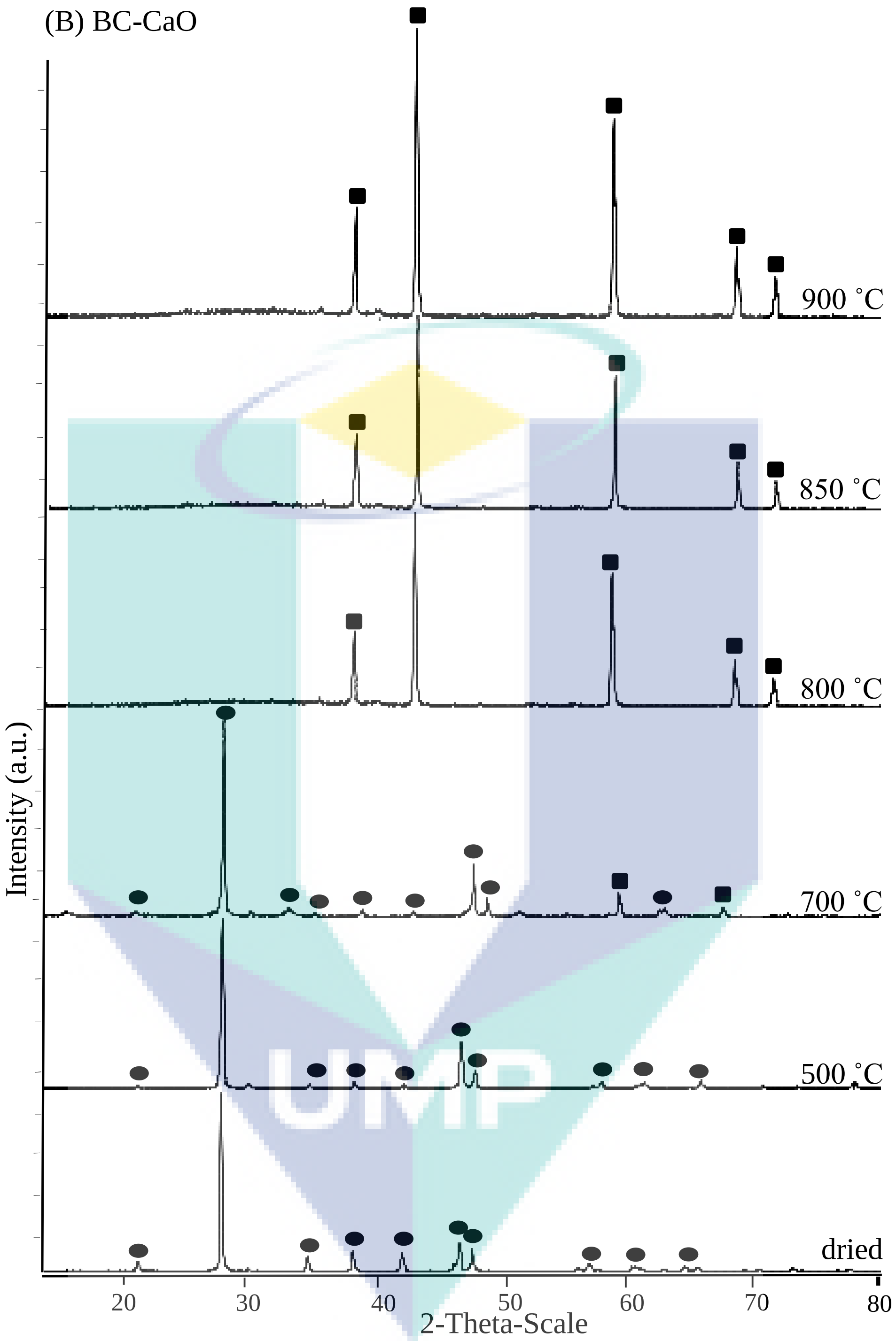


Figure 4.4: Continued

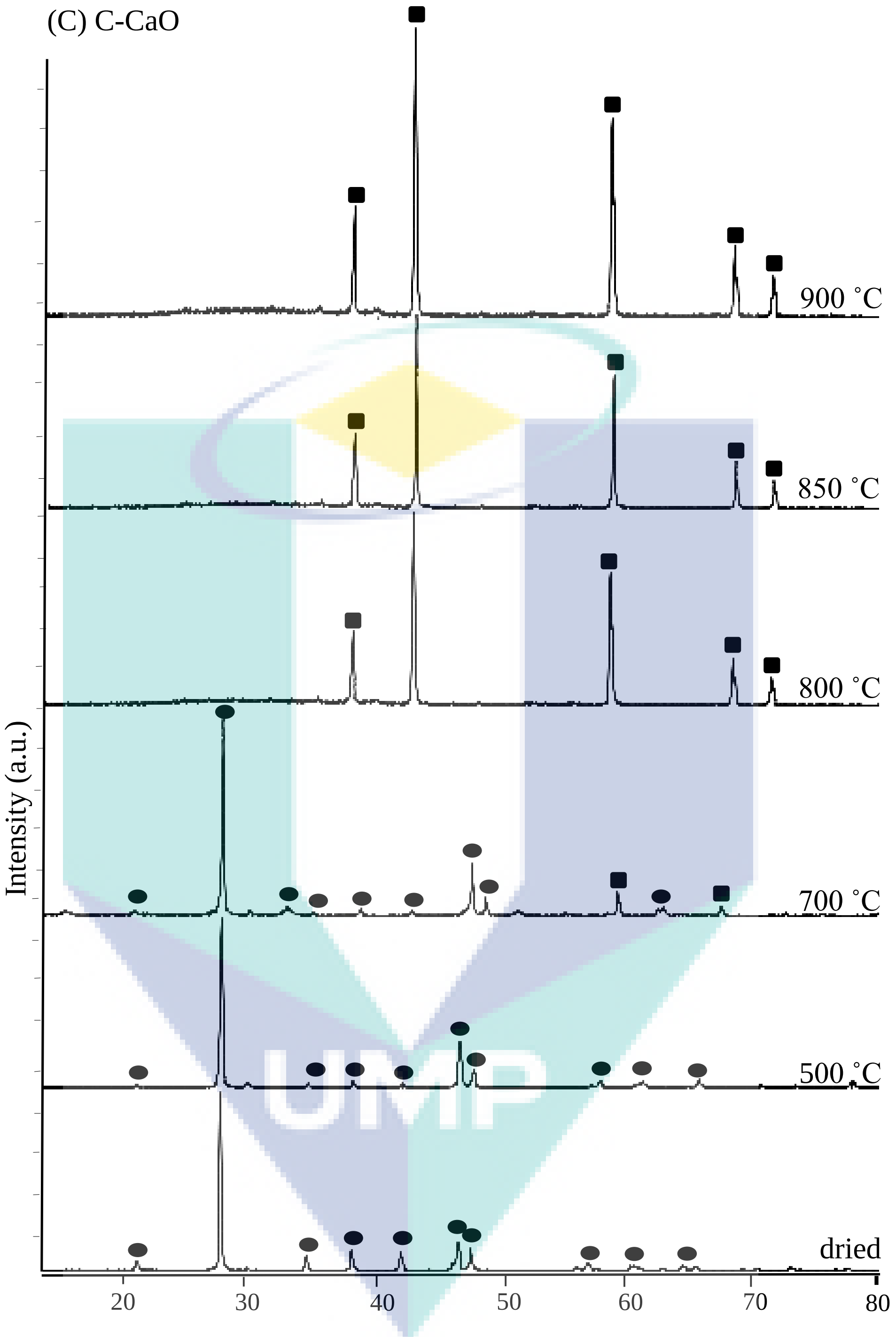


Figure 4.4: Continued

In extension of this study, mixed-catalyst from two different waste source i.e. BC-CaO-900 and C-CaO-900 was used. The catalyst was labelled as BC-C-Mixed-900. It was found that the mixed catalyst mainly is CaO same contains with their individual origin. Boey et al. (2011a) also reported that combination of waste shell from different source does not influence the characterization of the shell.

4.2.3 Surface Analysis (BET Method) of the Catalysts

Brauner, Emmett and Teller (BET) method determined the pore structure and surface area of the catalysts, BA-dried, BA-500, BC-dried, BC-900, C-dried and C-900. Table 4.7 shows the calcination of BA have reduced the surface area and pore volume, the surface area (106.6 m^2/g) and pore volume (0.032 cm^3/g) of BA-dried much higher than the surface and the pore volume of calcined BA-500 (55.86 m^2/g and 0.024 cm^3/g, respectively). The higher surface area of BA dried suggests a higher concentration of –O- and –OH- groups responsible. The decreased of surface area was probably due to the burning of the organics compound in dried catalysts. Therefore, the calcination burns the left over organics in the ash sample, consequently causing the ash to be less porous and have a reduced surface area.

However, upon the waste shells (baby clam and capiz), the surface area of dried catalysts were 1.87 and 2.19 m^2/g, respectively. Whereas much higher surface areas after calcined were recorded at 11.435 m^2/g for baby clam shell and 14.221 m^2/g for capiz shell. The thermal activation of the shell catalysts resulted in much smaller particles as well as open up the pores on the surface catalyst. It is in line was documented with previous study by Kouzu et al. (2009).

Table 4.7: Surface area, pore volume and diameter of waste catalysts dried and calcined

Catalysts	Parameters		
	Surface area (m^2g^{-1})	**Total pore volume (cm^3g^{-1})**	**Average pore diameter (Å)**
BA-dried	106.60	0.032	16.38
BA-500	55.86	0.024	12.24
BC-dried	1.87	0.009	16.30
BC-900	11.44	0.107	30.80
C-dried	2.19	0.012	18.00
C-900	14.22	0.119	29.40

Isotherms of the three catalysts (BA, BA and C) in the form of uncalcined and calcined are presented in Figures 4.5, 4.6 and 4.7, respectively. The type of isotherm of all the catalysts is of Type III, according to BDDT/BET (Brunauer, Deming, Deming, and Teller/Brunauer Emmett Teller) classification. Type III isotherm is characterised by weak gas-solid interactions. It is always regarded as not being a highly porous material. Hence, the gas uptake at lower pressure is small. it is clearly visible that all catalysts shows H1 hysteresis loop, based BDDT/BET classification. Type H1 loop characteristic of almost vertical and nearly parallel loop between the adsorption and desorption branches over a significant range of gas uptake. Normally, agglomerated or compacted spheroidal particles of fairly uniform size and array materials display this type of loop.

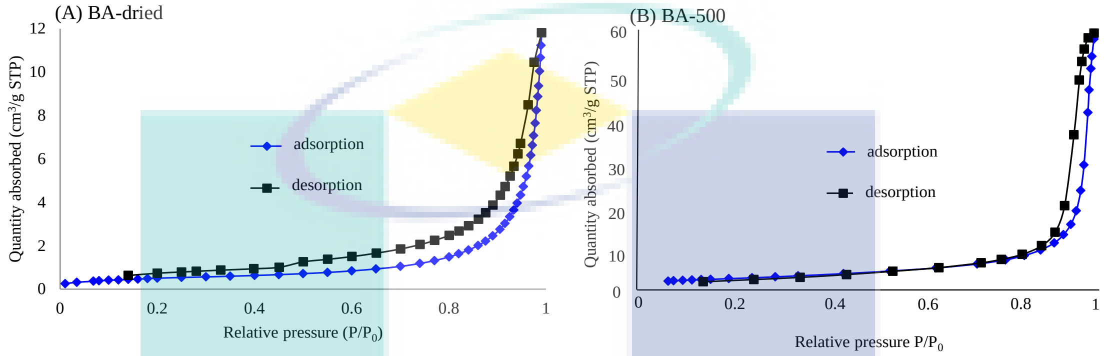


Figure 4.5: BET adsorption-desorption isotherm of BA (A) uncalcined and (B) calcined at 500 °C, 5 h

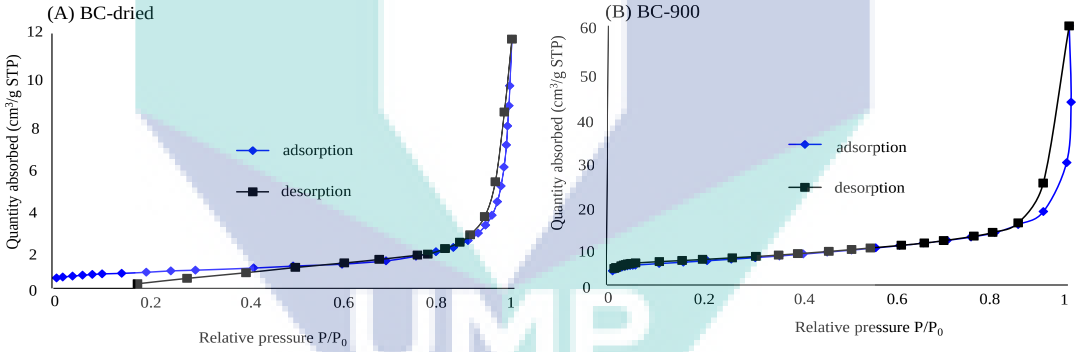


Figure 4.6: BET adsorption-desorption isotherm of BC (A) uncalcined and (B) calcined at 900 °C, 2 h

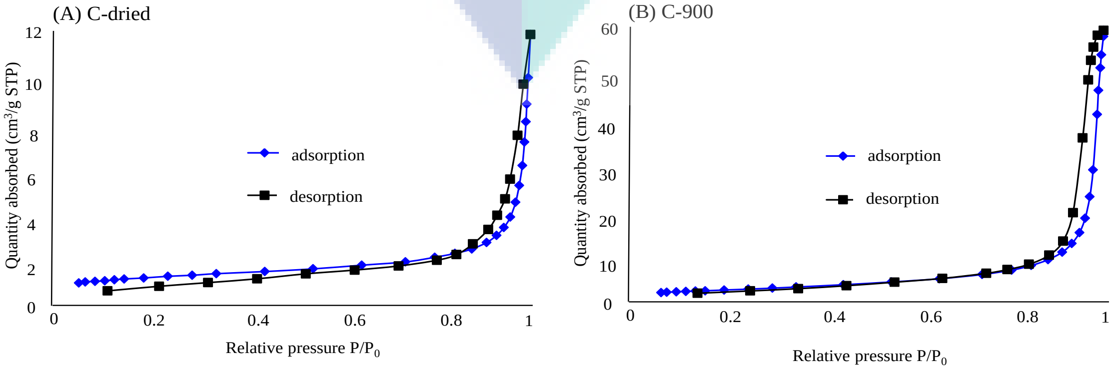


Figure 4.7: BET adsorption-desorption isotherm of C (A) uncalcined and (B) calcined at 900 °C, 2 h

4.2.4 Fourier Transform Infrared Analysis of the Catalysts

The FTIR spectra of BA-dried, BA-500, BA-700 and BA-900, is given in Figure 4.8 (A) shows the presence OH stretching and bending bands are visible at 3397 cm^{-1} in all four catalysts with various calcination temperatures and it is further confirmed by bending of OH^- at 619 cm^{-1} (Chin et al., 2009). Yin et al. (2008) has reported, the presence of this band is due to water adsorbed on surface of the catalyst. Band comparison between dried and calcine BA at 1018 cm^{-1} shows the band became sharper. This attribute is due to the alternating Si-O-Si, SiO and Al-O bond (Binitha and Sugunan, 2006). A band at 1403 cm^{-1} may be due to the presence of basic carbonates generated by adsorption of gaseous CO_2 from ambient atmosphere onto K_2O (Barbosa et al., 2000). An observation of FTIR spectra of the bands at 1018 and 1403 cm^{-1} are getting much sharper and the band at 3397 cm^{-1} much broader as the calcination temperature is reduce (900 to 500 ˚C).

The FTIR spectra of BC-CaO and C-CaO at various calcination temperatures 500 to 900 ˚C, are presented in Figure 4.8 (B) and (C). In the case at BC-CaO and C-CaO at temperature 500 to 700 ˚C has major characteristic absorption peaks at 713 and board band at 1420 cm^{-1} which can be attributed to the present of asymmetric stretch, out-of plane bend and in-plane bend vibration modes for CO_3^{2-} molecules. Afterwards, with the increased calcination temperature at 800 to 900 ºC, there is a decreasing of band at 1432 cm^{-1}, this is due to the reduction of the functional group attached to carbonate ion on calcination. A board band at 3437 cm^{-1} at temperature 500 to 700 ˚C has changed into a sharp peak at 3642 cm^{-1} at 800 to 900 ˚C. These samples attributes the present of OH^- which indicates the present of $Ca(OH)_2$ which must have formed from exposure of CaO to atmospheric air. Legodi et al. (2001) also reported carbonate bands present at 1802, 2511 and 2874 cm^{-1}. Many other previous researchers who worked with similar CaO waste shells reported the same observations (Yang et al., 2009, and Boro et al., 2011).

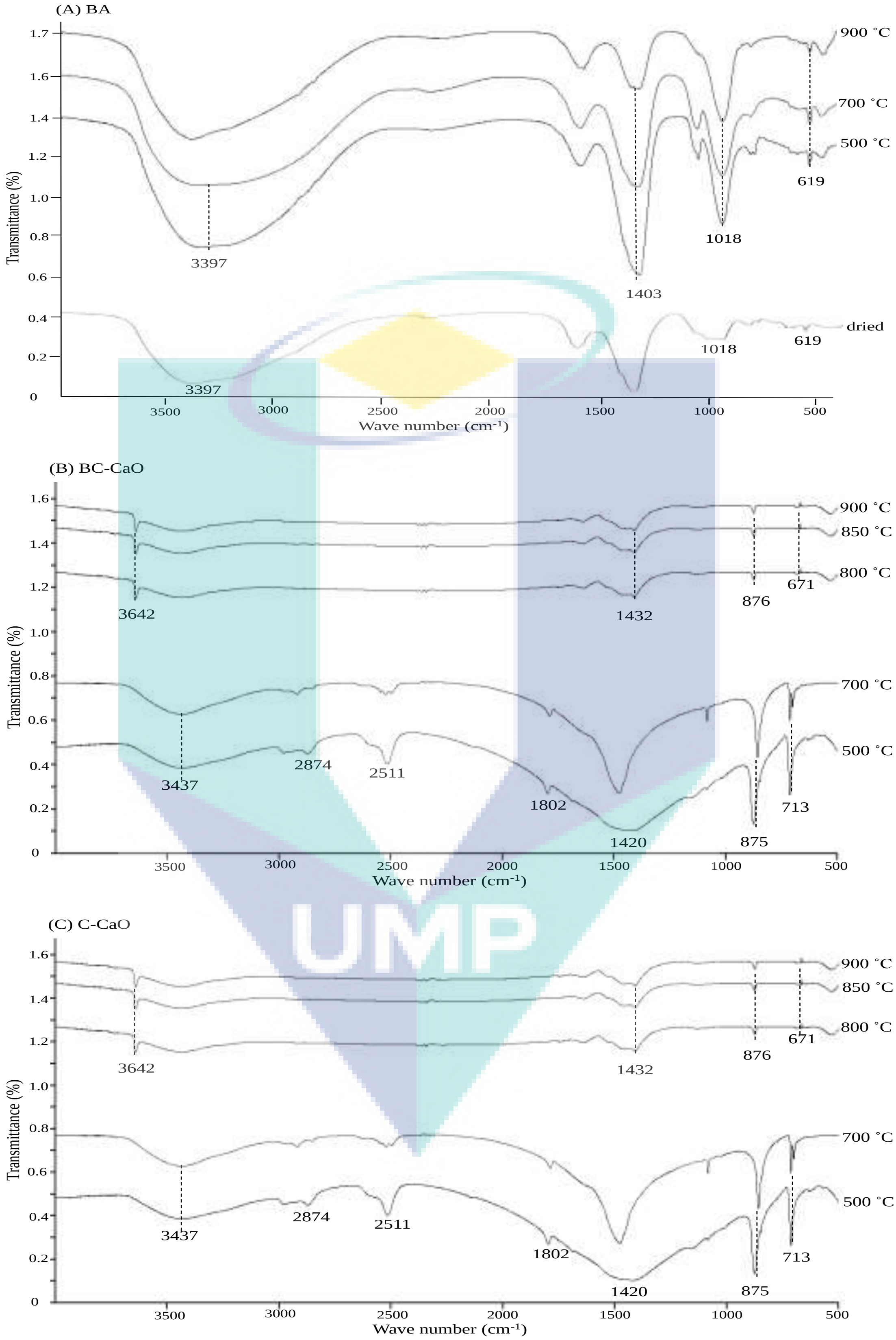


Figure 4.8: FTIR spectra of (A) BA, (B) BC-CaO and (C) C-CaO at various calcination temperature

4.2.5 Scanning Electron Microscopy Analysis of the Catalysts

The SEM micrographs of BA in different temperature are shown in Figure 4.9. The SEM micrographs of BA-dried, BA-500, BA-900 exhibited similar spongy and porous material. It can be seen from the figure, the uncalcined surface exhibited bulk morphologies without clear or defined shape. In contrast, the sample calcined at 500 ˚C, where morphologies of the catalyst with relatively smaller particles with visible pores of defined shape and size. Increased temperature to 900 ˚C, the oxide crystal can be seen at the sample. A recrystallization of the oxide accompanied by some disruptions, caused probably by at least partial decomposition of potassium oxide and formation of new phases, is documented in the SEM image of the sample calcined at 900 ˚C. It is in line with TGA result (section 4.2.1) occurred between 740-900 ˚C. However, the SEM micrographs of BC-CaO and C-CaO catalyst can be seen in Figure 4.10 and Figure 4.11, the dried catalyst exhibited bulk morphology without any clear defined shape and size. After increasing the temperature, the surface displayed relatively smaller particles with clear defined shape and size. In agreement with observations by BET result (section 4.2.3) where calcined catalyst have large surface area compared to the uncalcined catalyst.

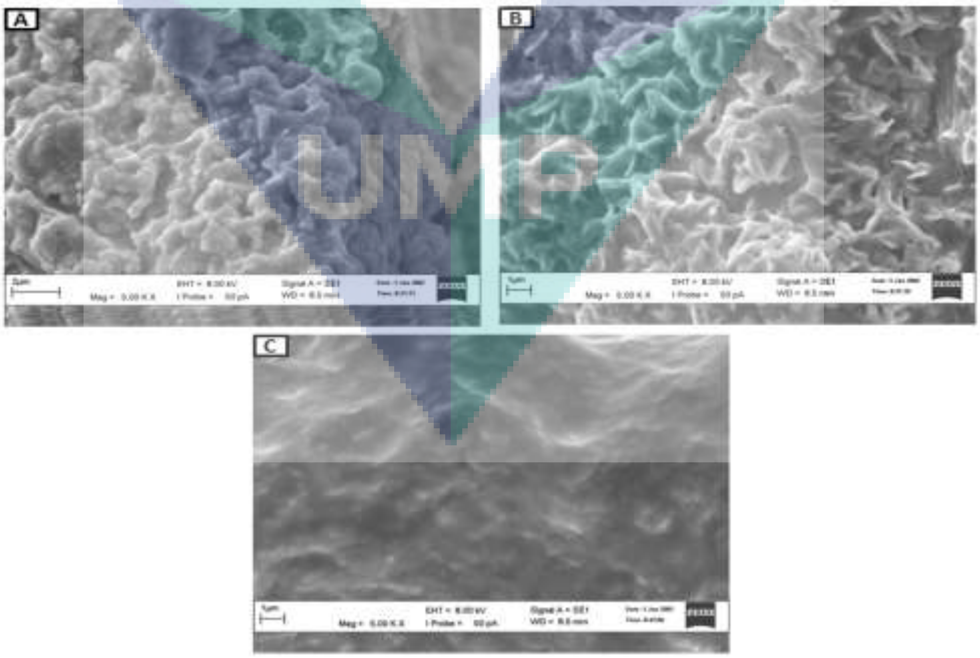


Figure 4.9: SEM image of BA (A) dried, and calcined at (B) 500 ˚C, (C) 900 ˚C, 5 h

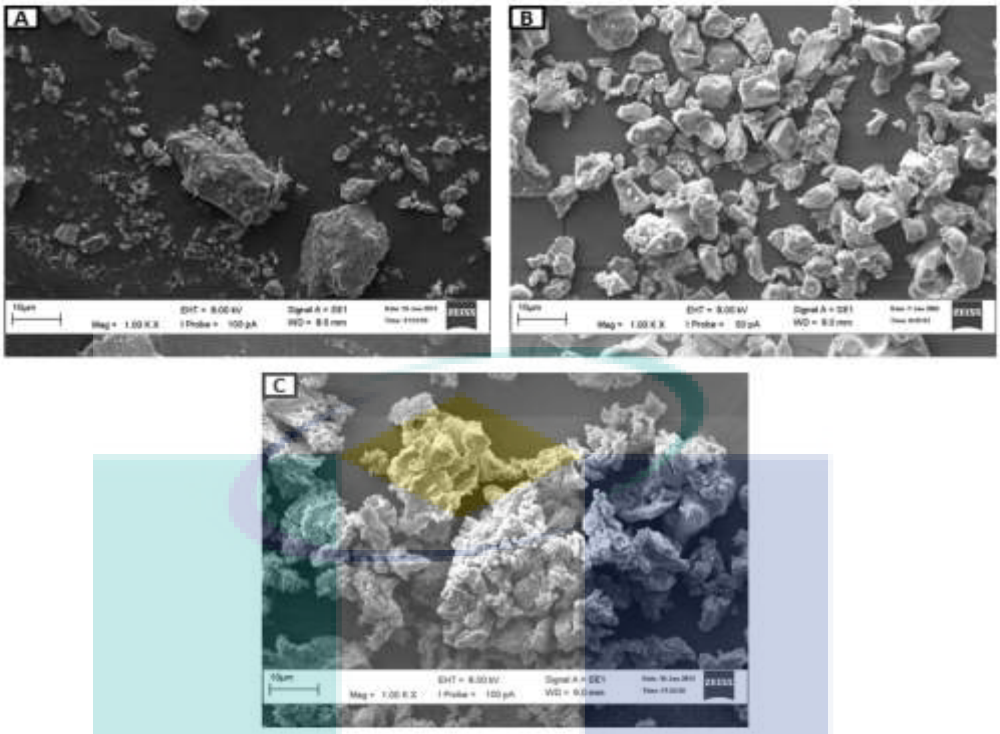


Figure 4.10: SEM image of BC-CaO (A) dried, and calcined at (B) 700 ˚C, (C) 900 ˚C, for 2 h

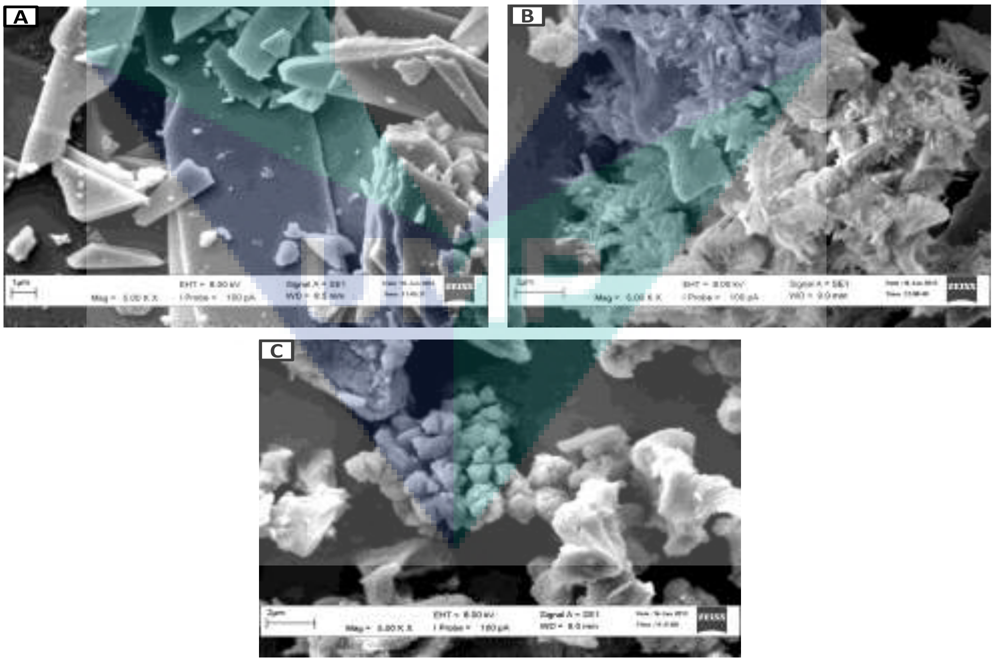


Figure 4.11: SEM image of C-CaO (A) dried, and calcined at (B) 700 ˚C, (C) 900 ˚C for 2 h

4.2.6 X-ray Fluorescence Analysis of the Catalysts

The composition of BA was investigated using XRF analysis. In line agreement by explains of XRD pattern (section 4.2.2), element contained in BA from different calcination was similar. BA consists mainly of potassium (63.65 %), calcium (9.59 %), silicate (9.39 %), chloride (8.78 %), and other oxide as reported in Table 4.8. The observation was confirmed by Chin et al., (2009) in their study of oil palm ash (OPA) by EDX, showed the presence of significant amount of potassium (40.59 %), oxygen (29.36 %) and calcium (14.56 %). The presence of different types of metal is dependent on the origins of BA (Yin et al., 2008). The mixture of metal greatly contributes to the basicity of BA in this present study, as observed in basicity analysis by Hammett indicator (section 4.2.7) where all BA has higher basicity is promised as a pseudo-heterogeneous catalyst for transesterification process, was reported by previous researchers (Chin et al., 2009; Boey et al., 2011b, and Yakoob et al., 2012). BC-CaO and C-CaO consist over 95% of CaO (tabulated in Table 4.8). These observation in line agreement with the XRD pattern results (section 4.2.2), the BC-CaO and C-CaO calcined at temperature 900 ˚C mainly consist of CaO.

Table 4.8: XRF results of waste catalysts from different sources

Catalyst	Composition (wt.%)								Total
	K	**Ca**	**Si**	**Cl**	**Mg**	**P**	**S**	**Others**[a]	
BA	63.65	9.59	9.39	8.78	3.10	2.79	1.74	0.96	100.00

[a]Other include Fe, Al, Mn, Zn, Sr, Ni, Ti, Cu, Zr, Rb, Br

Catalysts	Composition (wt.%)						Total
	CaO	**SiO_2**	**P_2O_5**	**MgO**	**Al_2O_3**	**Others**[a]	
BC-CaO	95.00	1.48	-	2.55	0.34	0.63	100.00
C-CaO	96.10	0.62	0.08	1.43	0.29	1.48	100.00

[a]Other include SO_3, Cl, Fe_2O_3, SrO, TiO_2

4.2.7 Basicity Analysis of the Catalysts using Hammett Indicators

The Hammett indicator test for all of the waste catalysts (BA, BC-CaO and C-CaO) in different calcination is shown in Table 4.9. All of the BA catalysts (dried, BA-500, BA-700 and BA-900) showed changes in both the colour of phenolphthalein ($H\_= 8.2$) from colourless to pink and the colour of 2,4-dinitroaniline ($H\_= 15$) from yellow to mauve. However, the colour of 4-nitroaniline ($H\_=18.4$) remained unchanged. The basic strength of this catalyst in the series of $15 < H\_ < 18.4$. The calcination does not affect to the strength of the catalyst itself. The detection of basicity of potassium based compounds in ash (was observed use XRD in section 4.2.2) promises the use of ash as a solid catalyst, as observed in previous work by Dooley and Ross (1992).

Table 4.9: Basicity of catalyst in different temperature towards Hammett indicators

Waste Catalysts	**Basicity(mmol/g)**		
	Phenolphthalein[a] **$H\_= 8.2$**	**2,4 dinitroaniline[b]** **$H\_= 15.0$**	**4-nitroaniline[c]** **$H\_= 18.4$**
BA			
Dried	√	√	X
500 ˚C	√	√	X
700 ˚C	√	√	X
900 ˚C	√	√	X
BC-CaO			
Dried	√	X	X
500 ˚C	√	X	X
700 ˚C	√	X	X
900 ˚C	√	√	X
C-CaO			
Dried	√	X	X
500 ˚C	√	X	X
700 ˚C	√	X	X
900 ˚C	√	√	X

Colour change for indicator is [a]colourless to pink, [b]yellow to mauve and [c]yellow to orange) √, colour changed and X, no colour changed

On the other hand, different case for BC-CaO and C-CaO was observed. All of the catalyst BC-CaO (dried, BC-CaO-500, BC-CaO 700) and C-CaO (dried, C-CaO-500, C-CaO-700), showed positive result to phenolphthalein and negative results to both

2,4-dinitroaniline and 4-nitroaniline. The basic strength of them, by the Hammett scale is between 8.2 and 15.0 ($8.2 < H\_ < 15.0$). In contrast , both the catalyst (BC-CaO-900 and C-CaO-900) showed positive result toward phenolphthalein and 2,4-dinitroaniline, but failed to change 4-nitroaniline. As such the basic strength of calcined BC-CaO-900 and C-CaO-900 ˚C, 2 h is identified as $15 < H\_ < 18.4$, same observations with previous works (Yang et al., 2009; Boey et al., 2011c, d, and Semwal et al., 2011).

4.3 TRANSESTERIFICATION OF RBD-PO AND WPCO

4.3.1 Influence of Calcination Temperature in Transesterification

To determine the effect of calcination temperature on the activity of the catalyst, all catalyst were heated or calcined at different temperatures from (dried, 500, 600, 700, 800 and 900 °C), then tested for the transesterification of WPCO. Figure 4.12 shows the transesterification reaction for 1 h using BA as a catalyst, which gives similar trend at different calcination. In contrast, for the waste shell BC-CaO and C-CaO the results shows that the catalyst calcined at temperatures above 700 °C was more active than the shells calcined at 600 °C and 500 °C. Low catalytic activity was observed for catalyst calcined below 700 °C. The increase of calcination temperature of waste shell influences the catalytic activity.

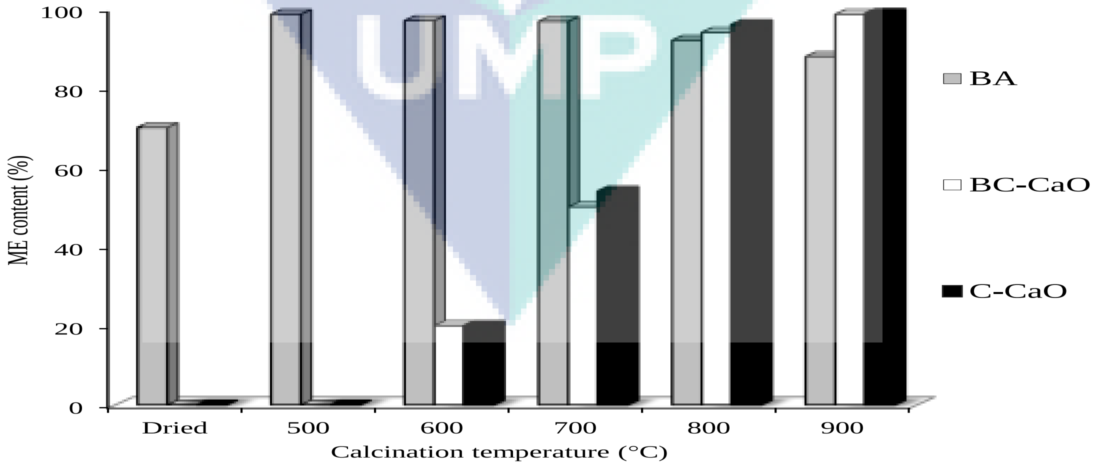


Figure 4.12: The effect of calcination temperature on methyl ester content, reaction conditions: BA-500 (MeOH:oil molar ratio 12:1, catalyst amount 3% for 1 h), BC-CaO 900 and C-CaO-900 (MeOH:oil molar ratio 12:1, catalyst amount 5% for 3 h)

4.3.2 Influence of Catalyst Amount in Transesterification

The effect of BA-500 catalyst amount was investigated by varying 0.5 to 7 wt.%, it was revealed in Figure 4.13 (A). In the illustration shown, the best catalyst amount of BA was achieved at 3% in RBD-PO and WPCO with the maximum conversion about 99.0% and 98.8%, respectively. It is because the contact opportunity of the catalyst and the reactant a direct affect to the conversion. When the catalyst amount is increased from 3 to 4 wt.%, the conversion of the methyl ester decreases, until quiet at 5% and continues to decline at 7 wt.%. It's probably, when the amount of the catalyst is increased, more products were adsorbed, causing presence of high soap content which will lead to the low activity and furthermore cause methyl esters content decreased. This amount of catalyst used is lower used than previous researches by Boey et al. (2011b) and Chin et al. (2009). The different sources of catalyst and different feedstock give different effects on methyl ester conversion. The possible mechanisms of feedstock and methanol catalyzed by BA is shown in Figure 2.5.

However, the BC-CaO-900 and C-CaO-900 have achieved 98.3 % and 98.8 % using RBD-PO, respectively. While for WPCO reached of 97.8% and 98.0% of methyl ester with catalyst amount at 5 wt.% and MeOH:oil molar ratio 12:1. Compared of BA as a catalyst, the catalyst amount of BC-CaO-900 and C-CaO-900 on the methyl ester conversion was increased step by step, the optimum condition was achieved at 5 wt.% of amount catalyst. This is because the low amount of catalyst cannot support the oil conversion. The methyl ester conversion reaches an optimal value when the catalyst amount reaches at 5 wt.%, it is due to contact opportunity between the catalyst and the reactant directly affect to the conversion. Similar with BA, after achieving the optimum condition point, the methyl ester conversion will steadily decreased. The decreasing of methyl ester content at the higher amount of catalyst is due to mass transfer limitation between the solid catalyst and the reactants. It is in agreement, in previous study where the increasing of the catalyst amount beyond the optimum value has a negative effect on the methyl ester conversion (Nakatani et al., 2009; Yang et al., 2009, and Girish et al., 2013). The possible mechanisms of feedstock and methanol catalyzed by CaO (source from shell) is shown in Figure 2.6.

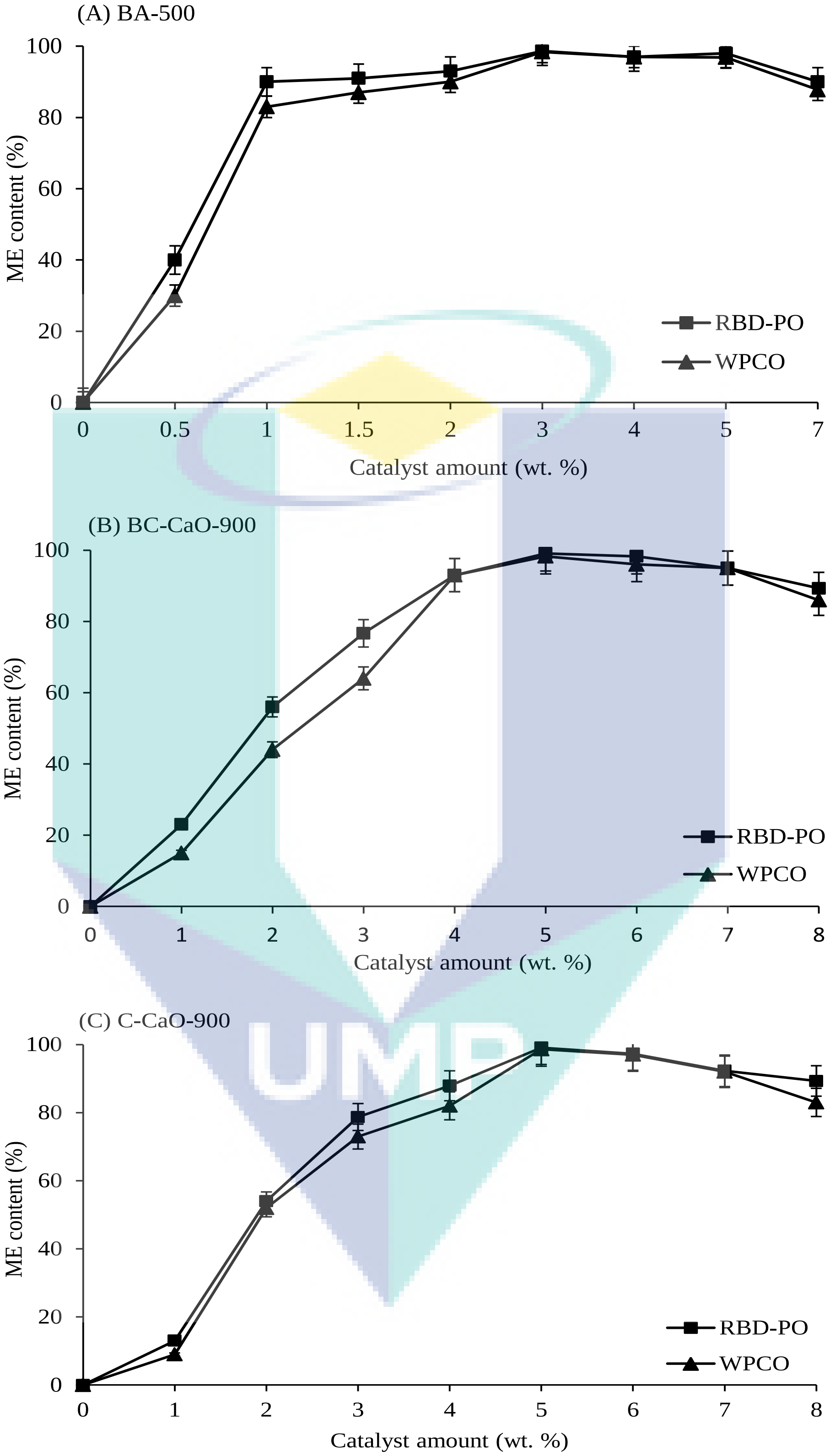


Figure 4.13: Influence of catalyst amount on methyl ester content using (A) BA-500 (MeOH:oil molar ratio 12:1 for 1 h), (B) BC-CaO-900 and (C) C-CaO-900 (MeOH:oil molar ratio 12:1 for 3 h)

4.3.3 Influence of Methanol to Oil Molar Ratio in Transesterication

The effect of MeOH:oil molar ratio was observed, seven different variation from 3:1, 6:1, 9:1, 12:1, 15:1, 18:1 and 21:1. MeOH:oil is one of the important variables that affect the transesterification reaction. Stoichiometrically, the reaction requires three moles of methanol for each mole of oil (MeOH:oil = 3:1), and with excess methanol it would shift the equilibrium towards the direction of ME production. The maximum methyl ester content was achieved at 9:1 MeOH:oil molar ratio using BA as a catalyst. From the Figure 4.14 (A), it can be seen, when the MeOH:oil molar ratio at 6:1 the conversion increased rapidly afterward and reached 71.6% and 68.7% using RBD-PO and WPCO, respectively. Then increased to 99.0% and 98.8% at MeOH:oil molar ratio 9:1. The increasing methyl ester content occurred from 6:1 to 9:1 MeOH:oil molar ratio. However, a drop of methyl ester content was seen after the MeOH:oil molar ratio at 15:1 and then was steadily decreased until 21:1 MeOH:oil molar ratio. Increasing further the molar ratio did not cause any appreciable change in the reaction activity. This may be due to the high ratio is too large and can cause the difficult separation of methyl esters and glycerol as well as complicates the methanol removal process. A similar effect was reported by Meher et al. (2006) and Anwar et al. (2010), where they found high alcohol could increases the solubility of glycerol, it is becomes more difficult to separation of glycerol and the forward reaction could to backward equilibrium. Gao et al. (2008) stated that large amount of methanol addition could dilute in the oil and also reduce of reaction rate, it is due to lower conversion of methyl ester.

The BC-CaO-900 and C-CaO-900 catalyst reached optimum MeOH:oil molar ratio at 12:1 where the methyl ester content reached (98.3% and 98.8%) using RBD-PO and (97.8% and 98.0%) using WPCO, respectively. Similar case with BA, increased MeOH:oil molar ratio caused a decrease of methyl ester content. The use of high MeOH:oil ratios will lead to excess methanol recovery to reduce the cost of production, because any loss in methanol will certainly raise the production cost. In addition, methanol vapour is fire hazard as it is highly flammable.

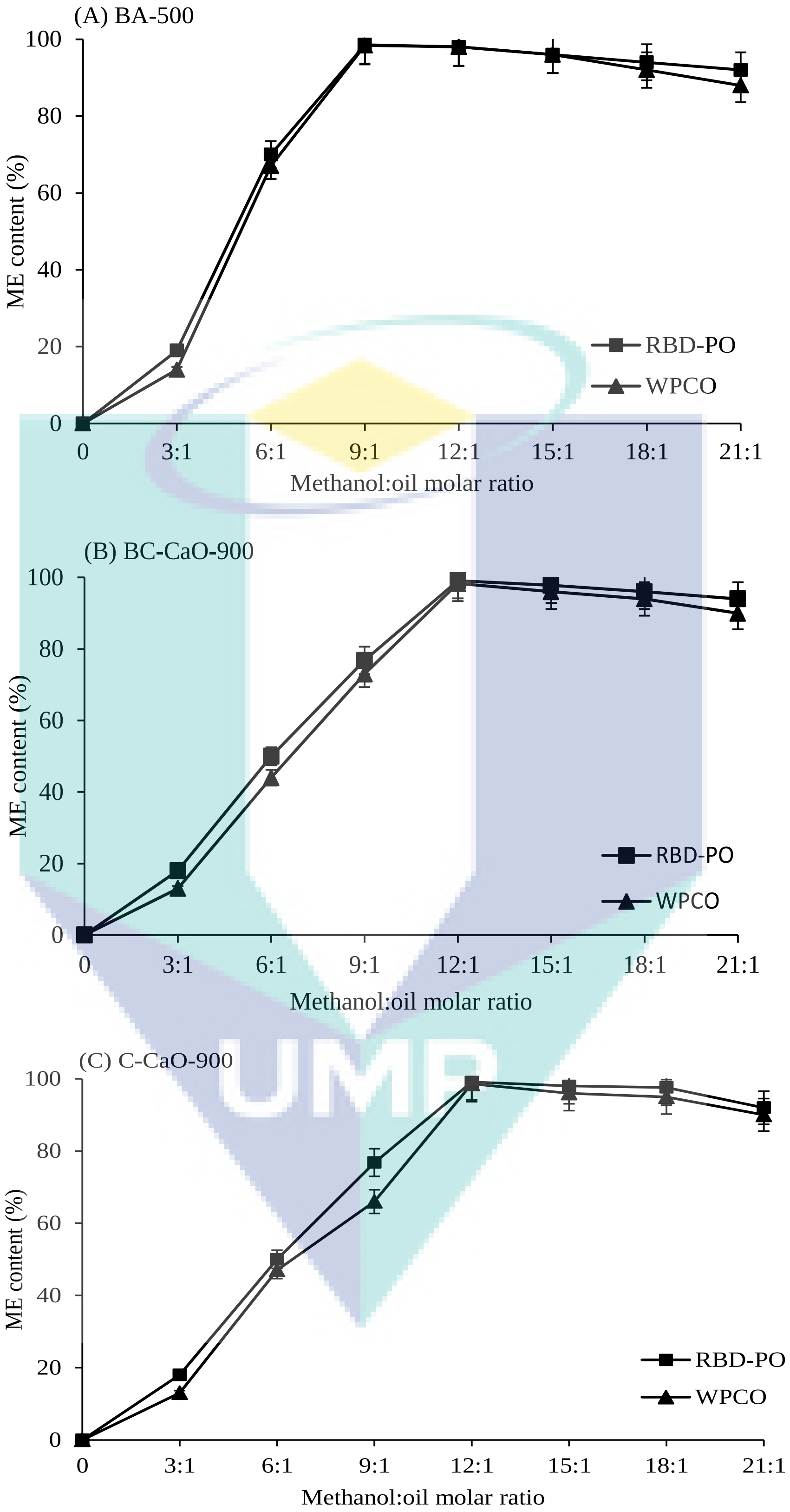


Figure 4.14: Influence of MeOH:oil molar ratio on methyl ester content using (A) BA-500 (3 wt.% catalyst for 1 h), (B) BC-CaO-900 and (C) C-CaO-900 (5 wt.% catalyst for 3 h)

4.3.4 Influence of Reaction Time in Transesterification

The effects of reaction time on the transesterification for BA-500, BC-CaO-900 and C-CaO-900 are shown in Figure 4.15 (A), (B) and (C), respectively. Figure 4.15 shows the best reaction time for BA-500 catalyst is 1 h and the best reaction time for both BC-CaO-900 and C-CaO-900 catalysts is 3 h. Transesterification using BA-500 for 30 minute the shows much higher methyl ester content above 72%. In contrast with BC-CaO-900 and C-CaO-900, transesterification for 30 minute the conversion was low at 32 % and 24%, respectively. However, the conversion increased step by step until reaction time at 3 h. Reaction time more than 3 h produces almost similar amount of methyl ester content.

The optimization using TLC plate also was investigated. The result shows the spot of triglycerides formed after 1 h reaction, while, for BC-CaO-900 and C-CaO-900 the big spot of triglycerides completely formed after 3 h reaction. If compared the reactivity of all catalysts, BA-500 more reactive than BC-CaO-900 and C-CaO-900. It is because, the BA-500 have higher basicity compared to BC-CaO-900 and C-CaO-900.

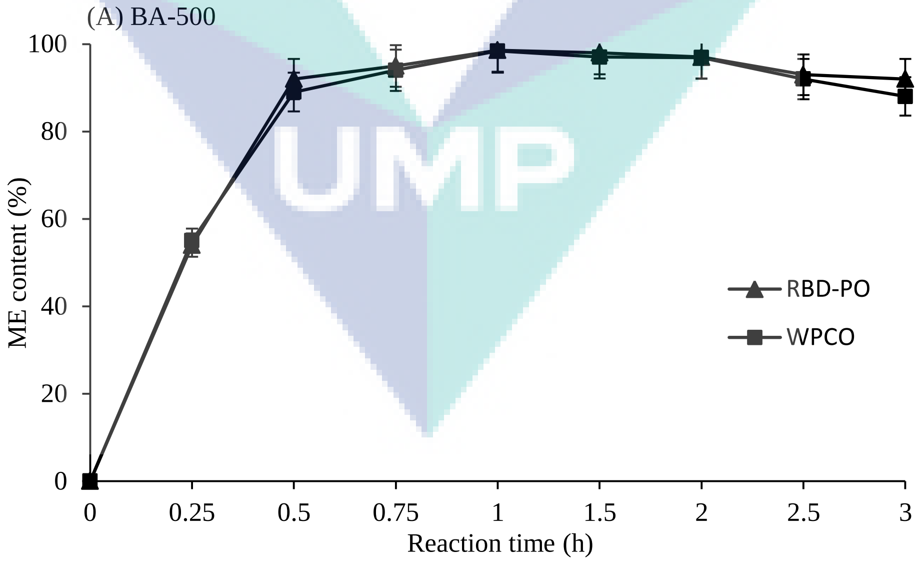
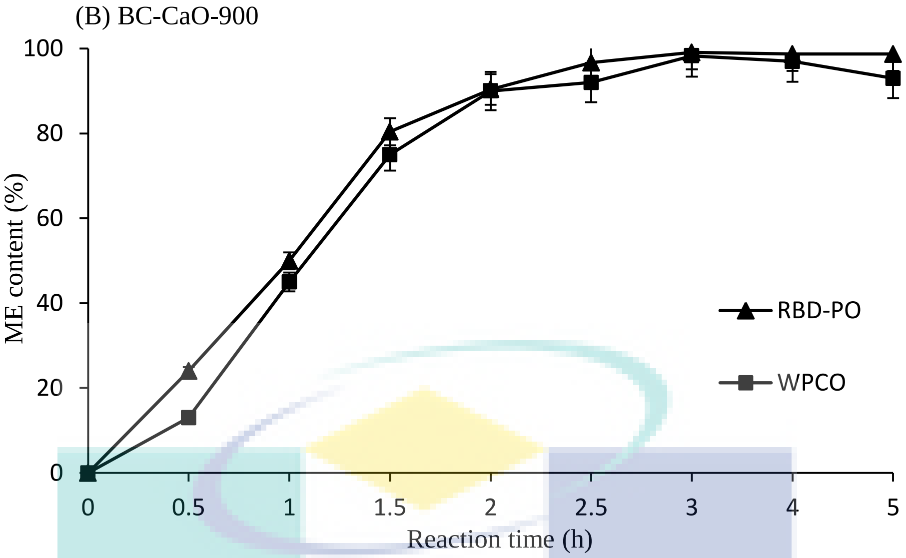


Figure 4.15: Influence of reaction time on methyl ester content using (A) BA-500 (MeOH:oil molar ratio 9:1 for 1 h), (B) BC-CaO-900 and (C) C-CaO-900 (MeOH:oil molar ratio 12:1 for 3 h)



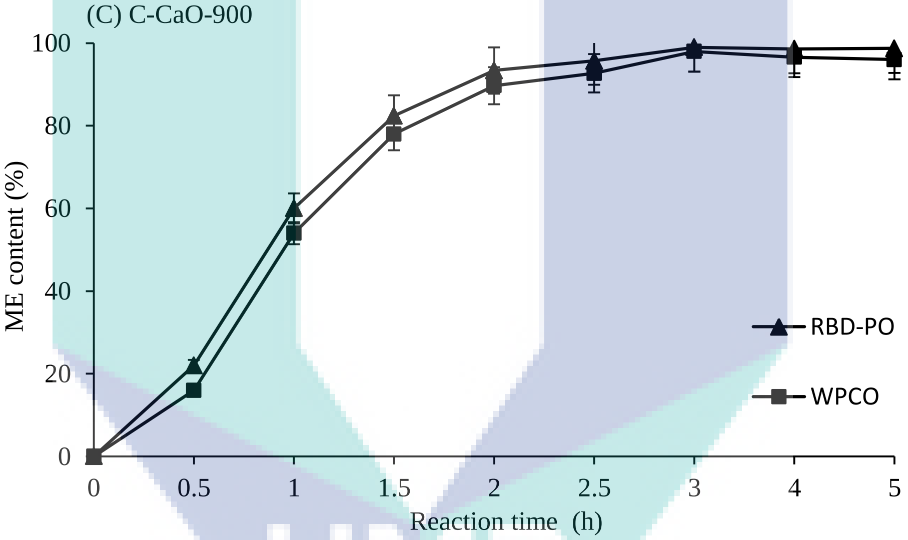


Figure 4.15 : Continued

4.4 CATALYST ACTIVITY

In order to study the effect of catalyst activity from the three catalysts (BA-500, BC-CaO-900 and C-CaO-900), experiments using different catalysts were conducted under the optimal reaction conditions. The reaction time and catalyst amount have influence on catalytic activity of transesterification. From Table 4.10, it can be seen that the lower catalyst amount at 3 wt.% and reaction time of 1 h gave maximum catalytic activity of 0.55 mol/$g_{cat}.s^{-1}$ using BA-500 catalyst. While for both BC-CaO-900 and C-CaO-900 with catalyst amount of 5wt.% and reaction time 3 h, the catalytic activity were calculated as 0.11 mol/g_{cat}.s^{-1}. This is in line with reports of Bond et al. (2006) where the kind of reaction by various types of solid catalysts is determined by the ability of surface to convert the reactants into product. In addition, the activity of the catalyst is defined as the rate of reactant(s) consumption, where the maximum rate will be achieved with combination effects of reactant and the catalyst.

Table 4.10: Catalytic performances of waste catalysts

Catalyst	ME content (%)	TOF (mol/g_{cat}.s^{-1})
BA-500[a]	98.8 ± 0.4	0.55 ± 0.002
BC-CaO-900 [b]	97.8 ± 0.4	0.11 ± 0.0005
C-CaO-900 [b]	98.0 ± 0.3	0.11 ± 0.003

[a] Reaction conditions: t = 1h, W_{cat} = 3%
[b] Reaction conditions: t = 3h, W_{cat} = 5%

4.5 TRANSESTERIFICATION USING CAO MIXED-WASTE CATALYST

The effect of mixed-catalyst from two different origin, namely, BC-CaO and C-CaO was presented in section 4.2.2. Experiment using mixed catalyst were conducted under optimum reaction condition. From Table 4.11, it can be seen that the source of catalyst as well as the mixed-catalyst have no significant effect on the methyl ester content.

Table 4.11: Methyl ester produced using CaO mixed-waste catalyst

Mixed-waste catalyst composition (BC-CaO-900:C-CaO-900)	ME content (wt.%)[a]
1:0	97.8 ± 0.4
1:1	98.6 ± 0.5
0:1	98.0 ± 0.3

[a]Reaction condition: MEOH/WPCO; catalyst amount; methanol refluxed temperature (65 ˚C); reaction period, 3 h.

The performance of mixed catalyst has similar result compared their individual performance and different origins of catalyst has no observable effect on methyl ester content produced. The similar result was observed by previous work (Boey et al., 2011c), the results have opened up the possible to combinate of waste CaO from different origin as solid catalyst in transesterifying triglycerides into methyl ester.

4.6 REUSABILITY, REGENERATION AND LEACHING OF CATALYSTS FROM WASTE SOURCES

Reusability is one of the factors in economical application of heterogeneous catalyst. The catalyst was reused without any further activation. After the transesterification reaction, the BA-500 and BC-C-Mixed-900 catalysts were decanted with simple washing with methanol followed by hexane, for 2 cycles respectively. The aim of washing with methanol is to remove glycerol and for hexane to remove methyl ester and unreacted of triglyceride in the spent catalyst. It is sufficient to clean up the spent catalyst from unwanted compounds. The argument is supported by FTIR analysis as presented in Figure 4.16, in which before the washing of the spent catalysts peaks at 1744 cm^{-1} (C=O stretching of ester) and 2854 and 2925 cm^{-1} present, indicating the –C-H stretching. It is assure that the spent catalyst still contains triglyceride, methyl ester and glycerol. This is in contrast after washing with methanol and hexane, for 2 cycles respectively, the glycerol, triglyceride and methyl ester was removed from spent catalyst.

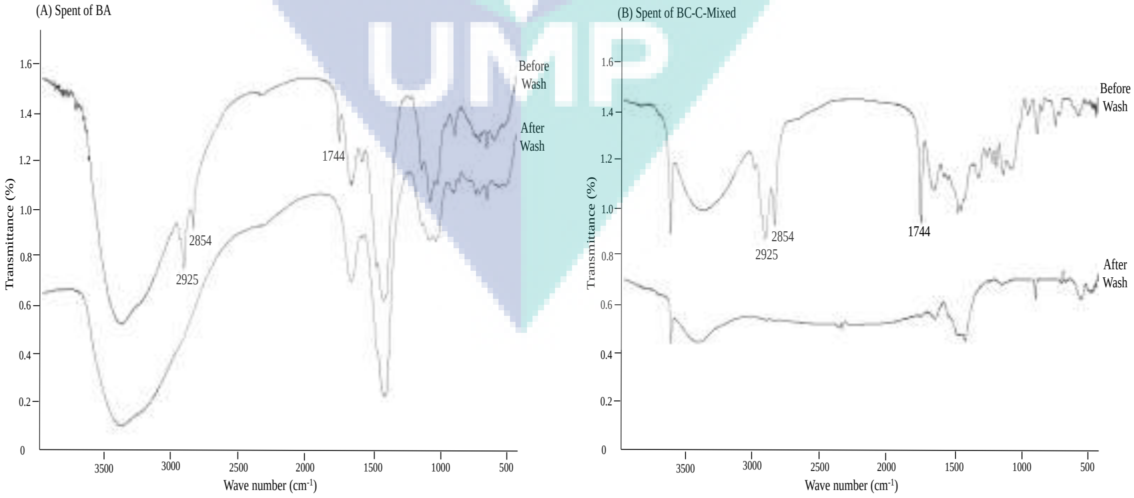


Figure 4.16: FTIR analysis of (A) spent of BA and (B) spent of BC-C-Mixed catalyst before and after washing use methanol and hexane.

4.6.1 BA-500

Transesterification of WPCO using spent BA for both uncalcined and calcined under the optimum conditions are depicted in Figure 4.17. It is found that there is no any significant different between spent and regenerated BA. The catalyst is stable up to second reusable (R_2). For the third reuse (R_3), about 10% of conversion decrease is observed and a steady decreases then after. This shows that there is catalyst leaching at third cycle onwards. The decrease in weight of catalyst from first to five cycles is due to the leaching of potassium and calcium and mass loses during washing and transferring processes. The XRD results in Figure 4.18 confirmed the observation where there is no any appreciable differences between the peaks of spent BA and regenerated BA. A study on leaching of BA was carried out following procedures presented in section 3.10. In a reaction using treated methanol and without catalyst, 63% of methyl ester is produced after 1 h of reaction. This observation confirmed that there is catalyst leaching and the catalyst act as a pseudo-heterogeneous, in agreement with a 87% conversion reported for similar reaction by Alonso et al. (2007). The authors found that there was a significant drop in potassium content from 8.16. wt.% to 2.79. wt.% from first to second runs, determined by ICP-AES.

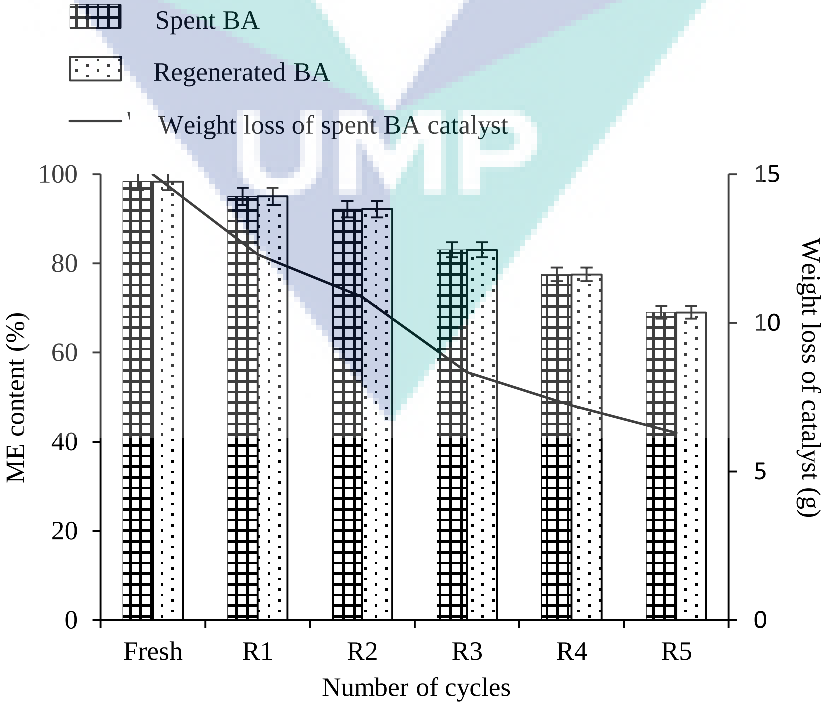
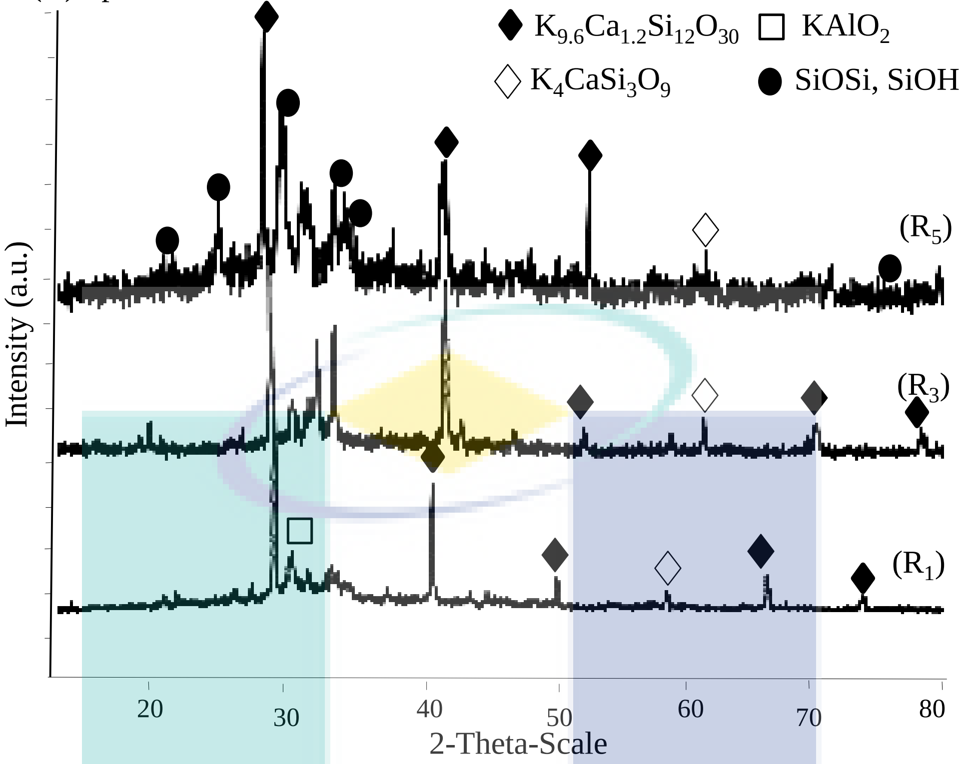


Figure 4.17: Methyl ester content from reused BA-500

(A) Spent BA



(B) Regenerated BA

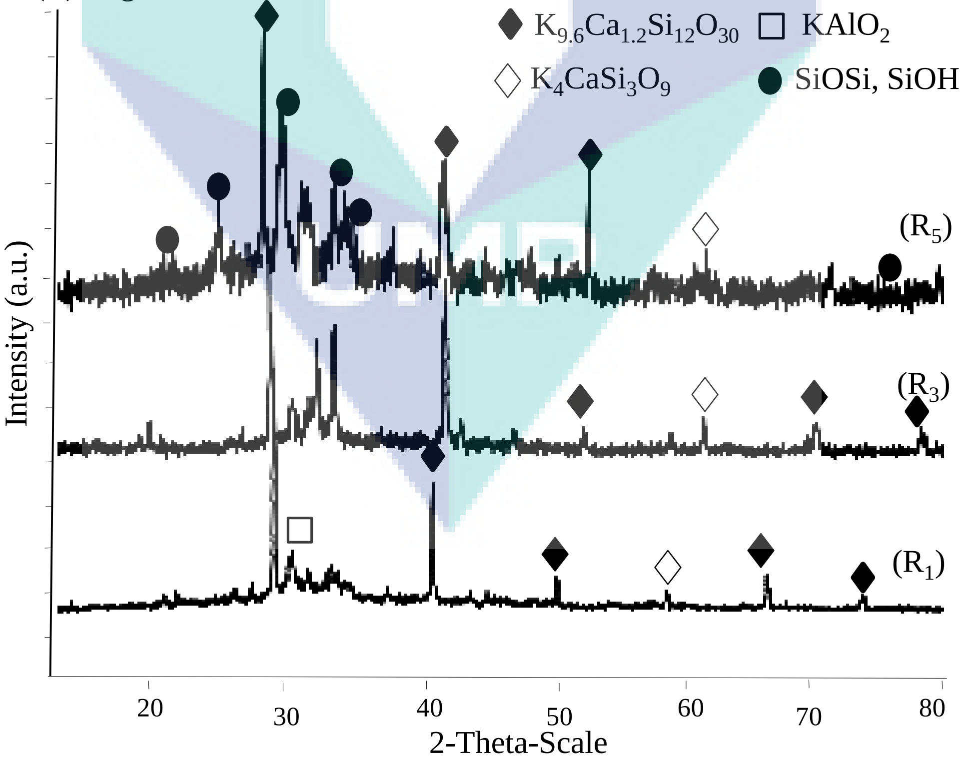


Figure 4.18: Powder XRD patterns of (A) Spent BA and (B) Regenerated BA uncalcined ▲, K_2MgSiO_4 □, $KAlO_2$ ♦, $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ ◊, $K_4CaSi_3O_9$

4.6.2 BC-C-Mixed-900

The reusability of spent and regenerated BC-C-mixed catalysts in transesterification under optimum reaction conditions was investigated, as presented in Figure 4.19. There is a significant different between spent and regenerated BC-C-mixed catalysts. In the transesterification of WPCO using spent BC-C-mixed, the ME content rapidly decrease after second cycle (R_2) and almost lost its activity at third cycle. This is in contrast with regenerated of BC-C-mixed calcined catalyst, where the ME content still maintained at 95 %, up to seventh cycle and a significant drop is observed at eighth cycle. The decrease in weight of catalyst from first to eight cycles is due to the leaching of calcium and mass loses during washing and transferring processes. In line with the XRD results of (Figure 4.20) at second and third cycles, the spent BC-C-mixed catalyst depicted the presence of $Ca(OH)_2$ and $CaCO_3$, respectively. The transformation of $Ca(OH)_2$ to $CaCO_3$ is clearly seen as the reaction proceeds from second to third cycles. As for regenerated BC-C-mixed diffractogram shows the presence of CaO, the active compound, throughout from first to eighth cycles. $Ca(OH)_2$ has lower activity compare to CaO, due to its lower basicity than CaO (Kouzu et al., 2008) and the catalytic activity is in the sequence of CaO > $Ca(OH)_2$ > $CaCO_3$. In the study soybean oil, 93% conversion is achieved in 1 h using CaO while 3.5 h is needed under $Ca(OH)_2$. As for $CaCO_3$ there is no conversion act at all in 1 h. The basicity $Ca(OH)_2$ of is $9.3 < H\_ < 15.0$ and for $CaCO_3$ is $7.2 < H\_ < 9.3$ lower than the basicity of CaO ($15.0 < H\_ < 18.4$).

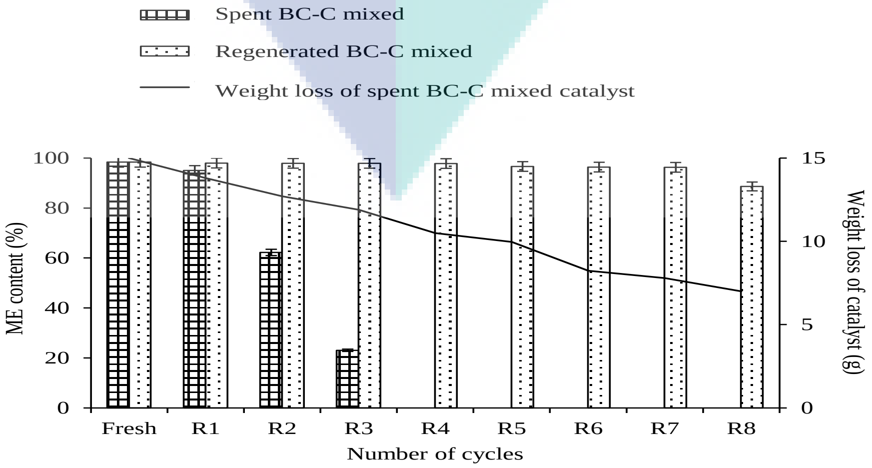
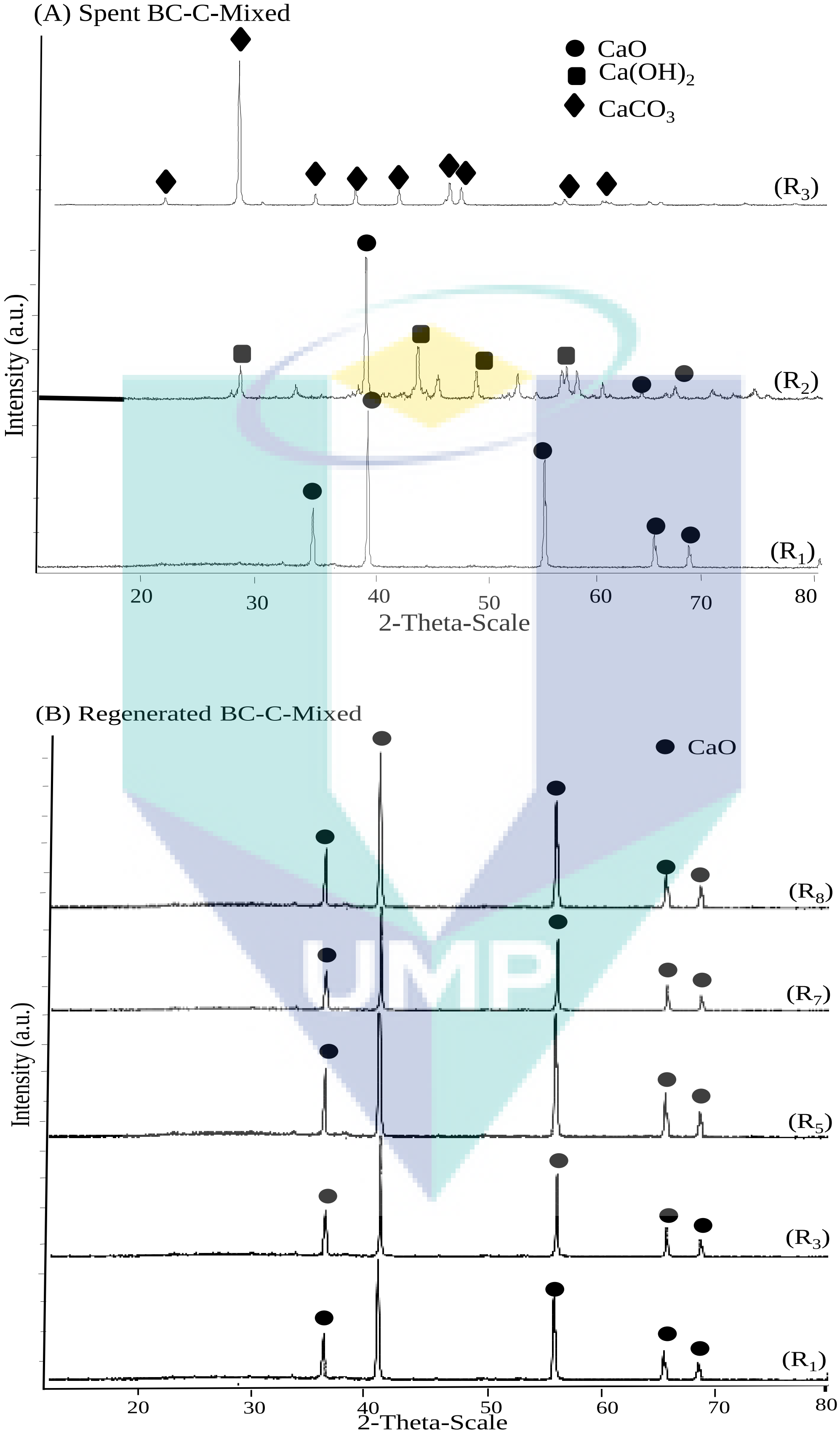


Figure 4.19: Methyl ester content from reused BC-C-Mixed-900



(A) Spent BC-C-Mixed

(B) Regenerated BC-C-Mixed

Figure 4.20: Powder XRD patterns of (A) Spent BC-C-mixed and (B) Regenerated BC-C-mixed

The leaching study on BC-C-mixed catalyst also investigated using treated methanol. The ME content was at only 5.3 %. It is assured that a very small amount of CaO leached in the reaction. The leaching activity of CaO was reported previous by Kouzu et al., 2009, where the large amount of leaching occurred when glycerol is present, and react with CaO to formed calcium diglyceroxide, a more soluble compound than CaO. In addition, the water formation in the transformation of calcium oxide to calcium diglyceride (Figure 4.21) may due to the serious leaching of CaO. The amount of the soluble CaO in the reaction reached 10.5 wt% for 2 h at the first transesterification, then decreased to 4% after second reaction. Hence, the shorter reaction time resulting lower soluble of CaO, where at 0.5 h the soluble substance amount was only 2.6 wt.%.

$$\underset{\text{Calcium oxide}}{CaO} \quad + \quad \underset{\text{Glycerol}}{2\,C_3H_8O_3} \longrightarrow \underset{\text{Calcium diglyceroxide}}{Ca(C_3H_7O_3)_2} \quad + \quad \underset{\text{Water}}{H_2O}$$

Figure 4.21: Transformation of calcium oxide to calcium diglyceroxide with presence of glycerol

4.7 TOLERANCE OF WASTE CATALYSTS TOWARDS FFA IN WPCO

Effects of FFA on transesterification of WPCO (acid value = 3.45 mgKOH/g) to methyl ester using BA-500 and BC-C-mixed-900 catalyst are shown in Figure 4.22. In this study, oleic acid was used to modify the FFA content. The tolerance of the BA-500 towards different levels of oleic acid is shown in Figure 4.22 (A) revealed that the effect FFA up to 1.75% level has very significant effect on methyl ester content. The methyl ester content dropped 20% at BA-500 catalyst 1 wt.%, in contrast for BA-500 catalyst of 5 wt.% and 7 wt.% has very little effect for them, where the methyl ester content still over 80%. While for BA-500 catalyst at 3 wt.% the methyl ester content reached 65% and the content continuous to decrease drastically as FFA content is increased. Much more drastic decrease in methyl ester content (to 5 wt.%) for transesterification using 5 and 7 wt.% BA-500 catalyst was noticed when the FFA content was increased to 2.5 wt.%. From the Figure 4.22 (A), it can be concluded that BA-500 catalyst has much higher tolerance towards FFA when high percentage of catalyst is used (5 and 7 wt.%).

In agreement with what was reported by Yan et al. (2009), the higher addition of catalysts could tolerate FFA content compared lower use of catalyst amount. This is because the higher catalyst concentration leads to the presence of relatively more active surface site. These sites make way for reactants to be adsorbed onto and perform the transesterification reaction.

As for the case of BC-C-mixed-900 catalyst, the increase of FFA content has reduced the content of methyl ester. From the Figure 4.22 (B), it shows that FFA content has considerable negative effects on the methyl ester content. For BC-C-mixed-900 catalyst, the FFA content varied using oleic acid up to 1.75 wt.% for catalyst amount 5 wt.% still gave methyl ester content over 80%. Different case for 7 wt.% BC-C-mixed-900 catalyst, the methyl ester content over 80 % was just produced with addition up to 1.25 wt.% FFA content. While for BC-C-mixed-900 catalyst at 8 and 3 wt.%, the methyl ester content has decreased below 80% at addition FFA content 0.25wt.%, this continuous to decrease with further addition of FFA. The significant decrease was at 2.5 wt.% FFA content for BC-C-mixed-900 catalyst amount at 8 wt.%. It is contrast with previous reported by Boey et al. (2012) to be able to withstand up 4 wt.% FFA, it is which allows the use of different high FFA content of feedstock.

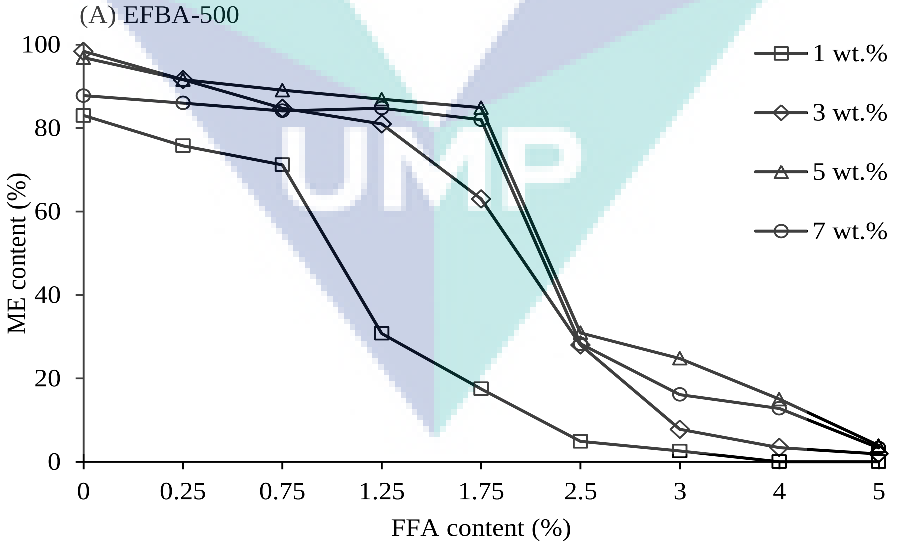


Figure 4.22: Methyl ester content using different catalyst amount with various FFA content (A) BA-500 and (B) BC-C-mixed-900

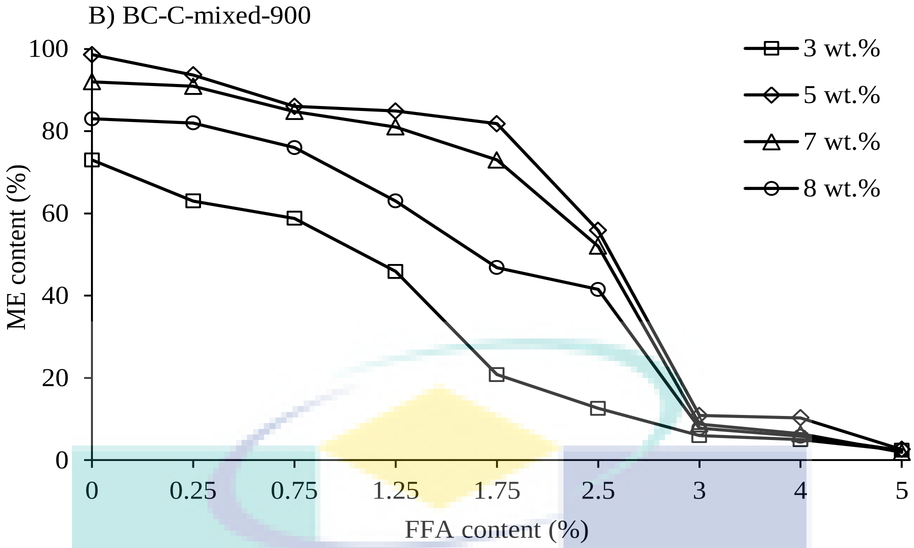


Figure 4.22: Continued

In this study, the effect of different MeOH:oil with variying FFA content onto methyl ester production was also been investigated. The results are presented in Figure 4.23 (A). The experiment with varying MeOH:oil mass rations (6:1 to 15:1) were performed at 3 wt.% of BA-500 catalyst. It can be seen from the result that the increasing FFA content gives a negative effect even with varied MeOH:oil molar ratio. However the increase in MeOH:oil molar ratio has shown that the BA-500 catalyst has developed resistance toward FFA content. From Figure 4.23 (A), when MeOH:oil molar ratio is 6:1, the ME content became collapse almost up to 40% with addition of 0.75 wt.% of FFA content. With increasing the MeOH:oil molar ratio to 9:1and with the addition of 1.25 wt.% of FFA, the ME content still reached over 80%. While for MeOH:oil molar ratio of 12:1 and 15:1 could be able to withstand up to 1.75 wt.% FFA content with producing ME over 80%.

The results of the effect of varying MeOH:oil molar ratio (9:1 to 18:1) with 5 wt.% of BC-C-mixed-900 catalyst amount are shown in Figure 4.23 (B). From the figure showed it seems there is a similar pattern with the BA-500, with increasing of MeOH:oil molar ratio, it could be increase of resistance with the FFA content. The use of lower MeOH:oil molar ratio (9:1) leads to saponification, causing in decreasing of ME content. While increasing MeOH:oil molar ratio (12:1 to 18:1) could increase the tolerance of catalyst up to 1.75 wt.%, with the production of methyl ester content over 75% for 3 h reaction duration.

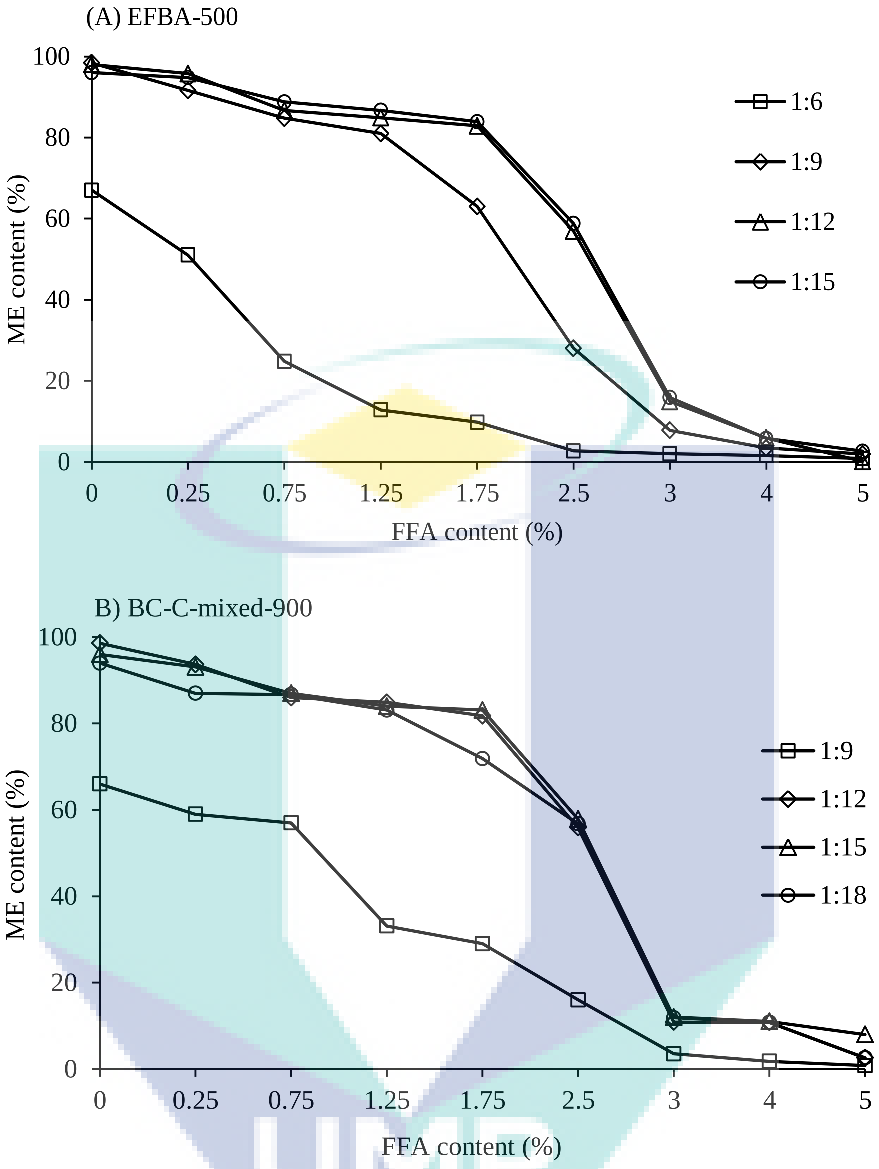


Figure 4.23: Methyl ester content using different MeOH:oil molar ratio with various FFA content (A) BA-500 and (B) BC-C-mixed-900

The addition too much of oleic acid into the reaction was decreased of methyl ester content. It is due to reacted of oleic acid with calcium oxide to form calcium oleate and lead soap in the reaction, the mechanism was given in Figure 4.24. In aqueous solution, calcium oleate anion that has sufficient hydrophilicity (through the carboxylate) as well as lipophilicity (through the carbon chain) to act as an emulsifier.

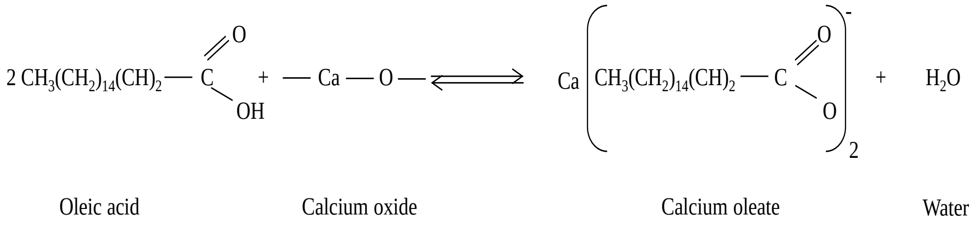


Figure 4.24: Saponification reaction of oleic acid

4.8 TOLERANCE OF CATALYSTS FROM WASTE SOURCES TOWARDS MOISTURE CONTENT IN WPCO

Effect of water addition using WPCO (moisture content = 0.11%) in transesterification process was studied. The presence of water content with addition 0.25 wt.%-5 wt.% using BA-500 and BC-C-mixed-900 as a catalyst and WPCO as a feedstock with different catalyst amount was presented in Figure 4.25 (A) and (B). However presence of water content in transesterification reaction involving BA-500 lowered the methyl ester in all variation of catalyst as showed in Figure 4.25 (A). At catalyst amount of 1 wt.%, the addition of water up to 0.75 wt.% decreased the methyl ester content as much as 50%. While for variation of catalyst amount at 3, 5 and 7 wt.% with addition of 0.75% water content still gave over 70% methyl ester content. The increasing water content in the reaction will decrease the methyl ester content steadily for all variations catalyst amount.

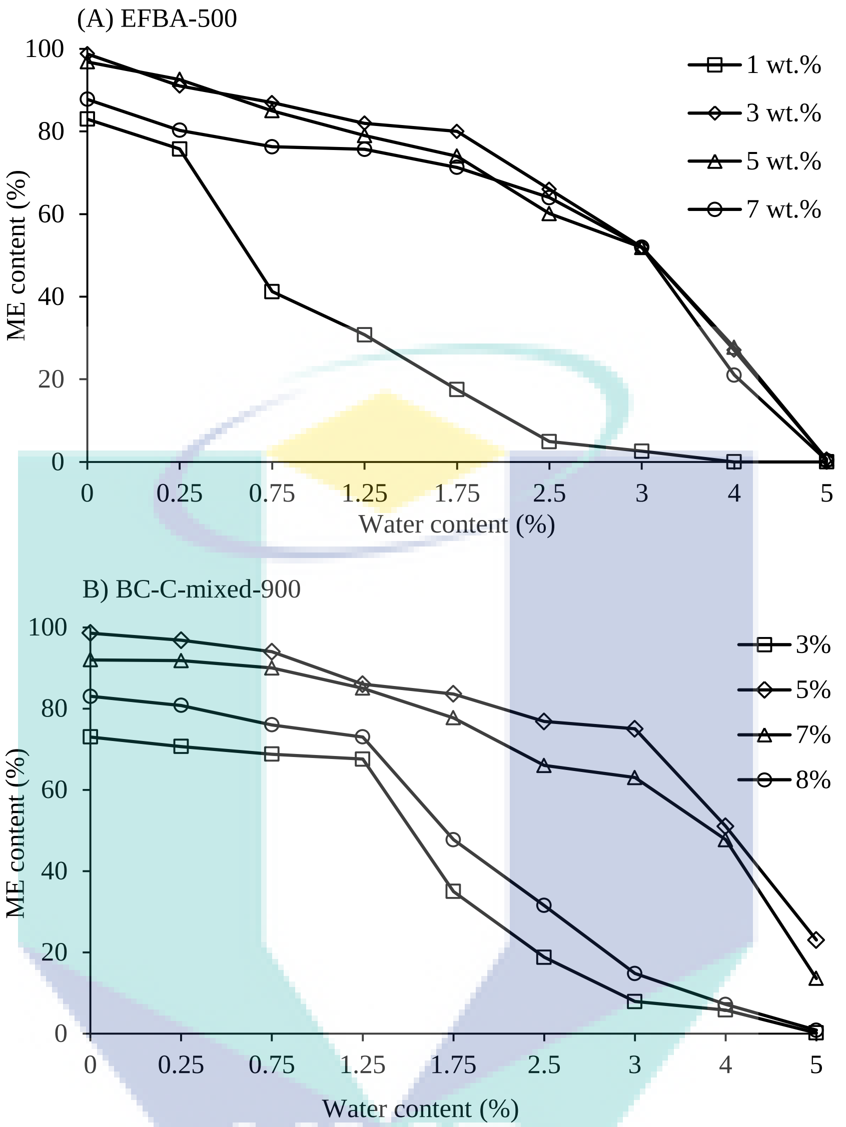


Figure 4.25: Methyl ester content using different catalyst amount with various water content (A) BA-500 and (B) BC-C-mixed-900

Excess methanol was used to study the catalyst’s tolerance towards water, and the results are present in Figure 4.26. Experiments with various MeOH:oil molar ratio was conducted with a catalyst amount of 3 wt.% of BA-500 and 5 wt.% of BC-C-mixed-900. However, the use of excess methanol did not bring any significant improvement to the water-tolerance property of the catalyst. As seen in Figure 4.26 (A), the increase of MeOH:oil at 12:1 and 15:1 made the catalyst more tolerant towards addition of water compared to MeOH:oil molar ratio 6:1 and 9:1. However, at 1.75 wt.% water content with MeOH:oil molar ratio 12:1 and 15:1, the methyl ester content reached below 80%. In contrast using BC-C-mixed-900 as a catalyst, when addition of water at 1.75 wt.%, the methyl ester content reached up to 80% with MeOH:oil molar ratio at 12:1 and 15:1.

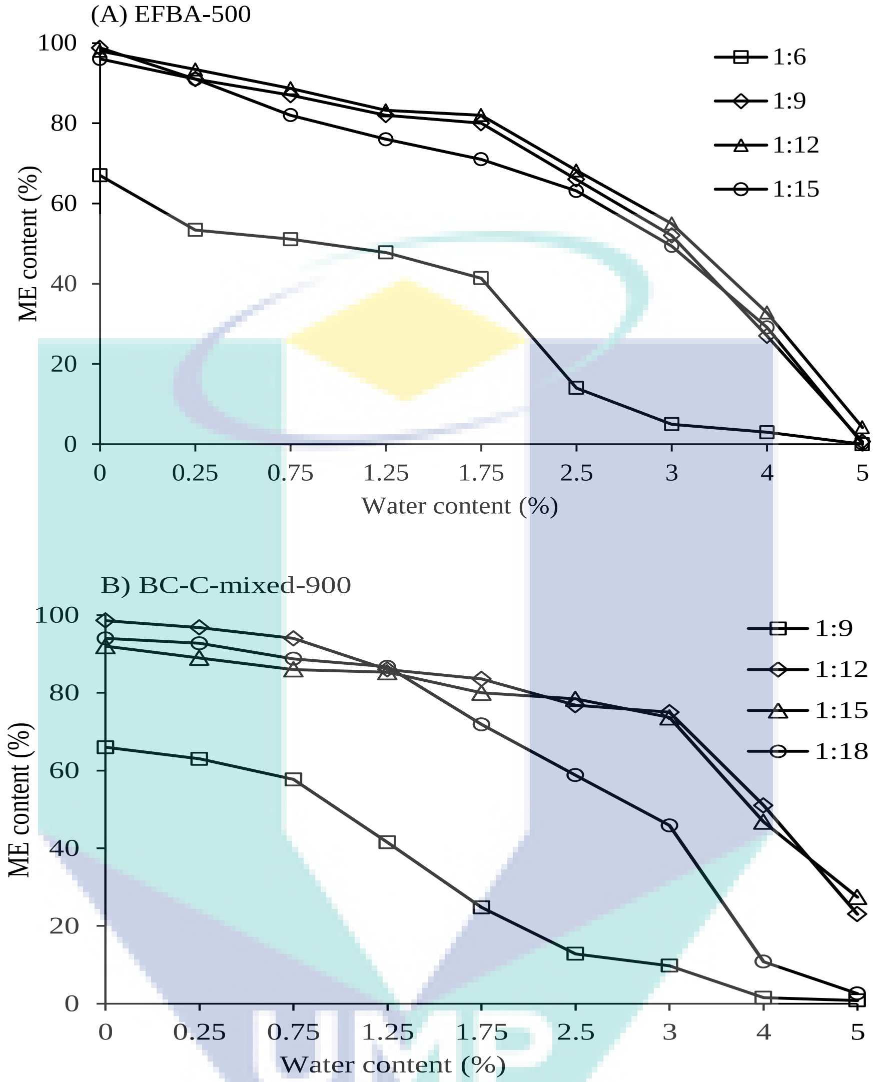


Figure 4.26: Methyl ester content using different MeOH/oil molar ratio with various water content (A) BA-500 and (B) BC-C-mixed-900

The presence of water has a greater negative effect than that of the free fatty acids. So, the water content should be kept below 0.06% (Ma et al., 1998), much lower than the allowable free fatty acids content. These problems may hinder the most efficient utilization of waste vegetable oils and crude oils since they generally contain water and free fatty acids. The present of water in the reaction system could change of the Lewis base site in BA-500 (metal –O– group) into Bronsted base sites (metal –OH group) (Yan et al., 2009). Although BC-C-mixed-900 showed better water tolerance than BA-500 with addition up to 1.25 wt.% of water, the addition amount of water caused CaO to form $Ca(OH)_2$ that is capable of extracting H^+ from methanol. Thus, generating additional methoxide anion which is strongly basic and promotes base catalyzed transesterification. While, on another site, a basic site of CaO solid base catalyst was reacted with H^+ from H_2O, then the fatty acid was lead of saponification in the reaction. As mechanism reaction was presented in section 2.10 Figure 2.9.

4.9 *IN SITU* TRANSESTERIFICATION OF O-DC USING ULTRASOUND IRRADIATION AND MECHANICAL STIRRING METHODS

In order to study the effect of different method in production of methyl ester content, *in situ* ultrasound irradiation and *in situ* mechanical stirring method were conducted. The quantity of methyl ester content produced using ultrasound and mechanical stirring method is effected by the amount of catalyst, MeOH:oil mass ratio and variation of solvent (presented in Figure 4.27).

In this study BA-500 is used as a catalyst with O-DC as a feedstock. The amount of catalyst (BA-500) was varied in the range of 4 – 28 wt.% (based on oil weight). As shown in Figure 4.27 (A), the efficiency of both *in situ* transesterification with ultrasound and mechanical stirring method are dependent on the amount of catalyst used. The ME content reached the highest value with ultrasound and mechanical stirring methods at 85.9 wt.% and 81.8 wt.% respectively with the catalyst amount of 20 wt.%. This is due to the contact opportunity between catalyst and the reactants. Hence, it propels the reaction kinetics. Based on the oil weight, the amount of catalyst used in this work seems to be higher due to several reasons; part of the catalyst could be entrapped in the clay matrix; this portion of the catalyst may not have contributed to catalytic activity. In addition, a part of the catalyst (basic nature) is also used to neutralize the acids in O-DC as a CPO (acid value = 13.8 mg KOH^{-1} g^{-1}).

As observed in Figure 4.27 (B), four different mass ratios of MeOH:oil were tested; 50:1, 100:1, 150:1, 200:1 and 250:1. The ME content increased as the MeOH:oil was raised from 50:1 to 150:1. A very sharp increase is observed between 50:1 and 100:1, which reached maximum performance at 150:1. However, further increase to 200:1 has negative effects on ME conversion. Too much methanol could dilute the oil and as a result, it slows the reaction rate (Gao et al., 2008), which in turn, lowers the conversions. Relatively larger amount of methanol was used in this work mainly to cater for the solvent-absorbing and solvent-retaining characteristics of the DC during reaction. Nevertheless, the excess methanol can be readily recovered at the end of the reaction. In this study, higher ME content is shown in ultrasound compare mechanical stirring method. Due to, the ultrasound radiation causes methanol to disperse into the oil, thus increasing the contact surface between reactants, consequently accelerating the reaction. The effect of cavitation (mechanical effects) created by ultrasound supplies sufficient energy into the immiscible medium and the continuous formations and collapsing of micro bubbles accelerate the miscibility of reactants in addition to chemical effects. In agreement with what was reported by (Gude et al., 2013), the ultrasound got higher conversion compare mechanical stirring method.

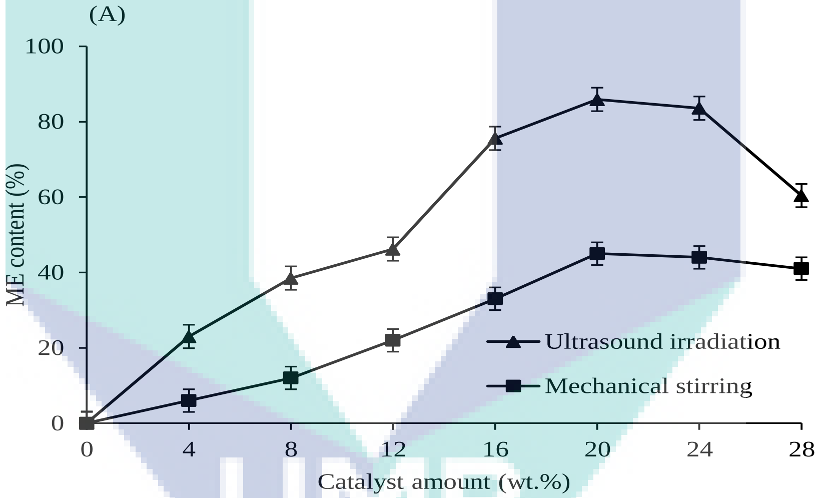


Figure 4.27: Effect of (A) catalyst amount; (B) methanol to oil molar ratio; and (C) co-solvents ratio on methyl ester content (reaction conditions: catalyst amount of 20%, MeOH:oil molar ratio 150:1, co-solvents (n-hexane:PE) 1:1, temperature 65 ˚C; reaction time for 1 h)

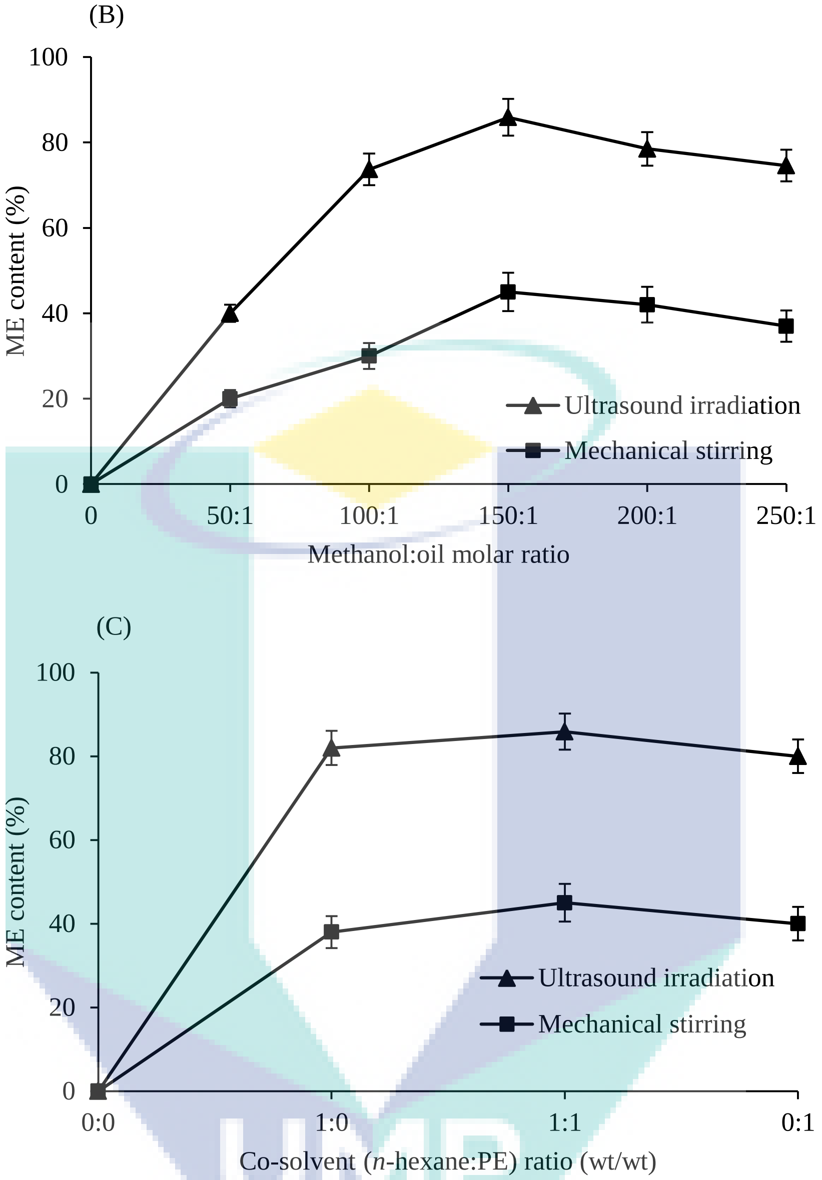


Figure 4.27 : Continued

In this work, co-solvents (*n*-hexane:PE mixture) were used to aid *in situ* oil extraction as well as oil solubility in the reaction media. Figure 4.27 (C) shows the influence of the co-solvents in the transesterification of the DC where the content of ME approximately 80% and 84% were achieved by using PE or hexane alone, respectively. Higher conversion value for hexane is understandable as hexane (dielectric constant, 1.89) is less polar than PE (dielectric constant, 2.0–2.2), thus hexane is easily soluble in oil. On the other hand, the higher polar PE has better methanol solubility characteristic. This implies that by combining these two solvents, a better solubility between oil and methanol can be achieved as evident of highest ME content (86%) was achieved in the combination ratio of 1:1 *n*-hexane:PE mixture. The reduction of energy consumption is one of the advantages of the ultrasound technique in methyl ester production. A study on the energy requirement for transesterification using ultrasound and hotplate (mechanical stirring) methods revealed that transesterification using hotplate requires much more energy than ultrasonic process (Gude et al., 2013). This shows that with appropriate reactor design, non-mechanical stirring techniques have potential to reduce the process energy requirement significantly.

Moisture content test was investigated of DC before and after dry. The DC before and after dry contents of 72.88% and 4.44% water, respectively. Drying process of DC is one of the important process in *in situ* transesterification process.

4.10 PROPERTIES OF METHYL ESTER

4.10.1 Chemical Properties of Methyl Ester

GC chromatogram proves that methyl ester from transesterification of RBD-PO, WPCO and O-DC using BA-500 as a catalyst, shown in Figure 4.28. In RBD-PO and WPCO mainly consists of methyl ester of oleate ((C18:1) 45.2% and 42.3 %), palmitate ((C16:0) 37.0% and 28.2%), linoleate ((C18:2) 12.2 and 18.1%), respectively. The minor constituents such as stearate (C18:0), stearic (C18:3), myristate (C14:0), laurate (C12:0). From the Figure shown, the presence of palmitoleate (C16:1) 4.8 % in the chromatogram of WPCO, while not present in RBD-PO, it is was explained in section 4.1.1 and the methyl heptadecanoate (C17:0) as an internal standard also shown in all chromatogram. From GC chromatogram methyl ester content was calculated using formula in section 3.7.2 and was found that methyl ester content of RBD-PO and WPCO was achieved 99.0% and 98.8, respectively. While, for GC chromatogram of methyl ester from transesterification of O-DC, shows the methyl ester of palmitate (C16:0) 43.9% is the major methyl ester fatty acid followed by oleate (C18:1) 41.6% and linoleate (C18:2) 11.5%. Stearic (C18:3), palmitoleate (C16:1), myristate (C14:0), and laurate (C12:0) are minor constituents. The methyl ester content was calculated of 85.9% using GC analysis.

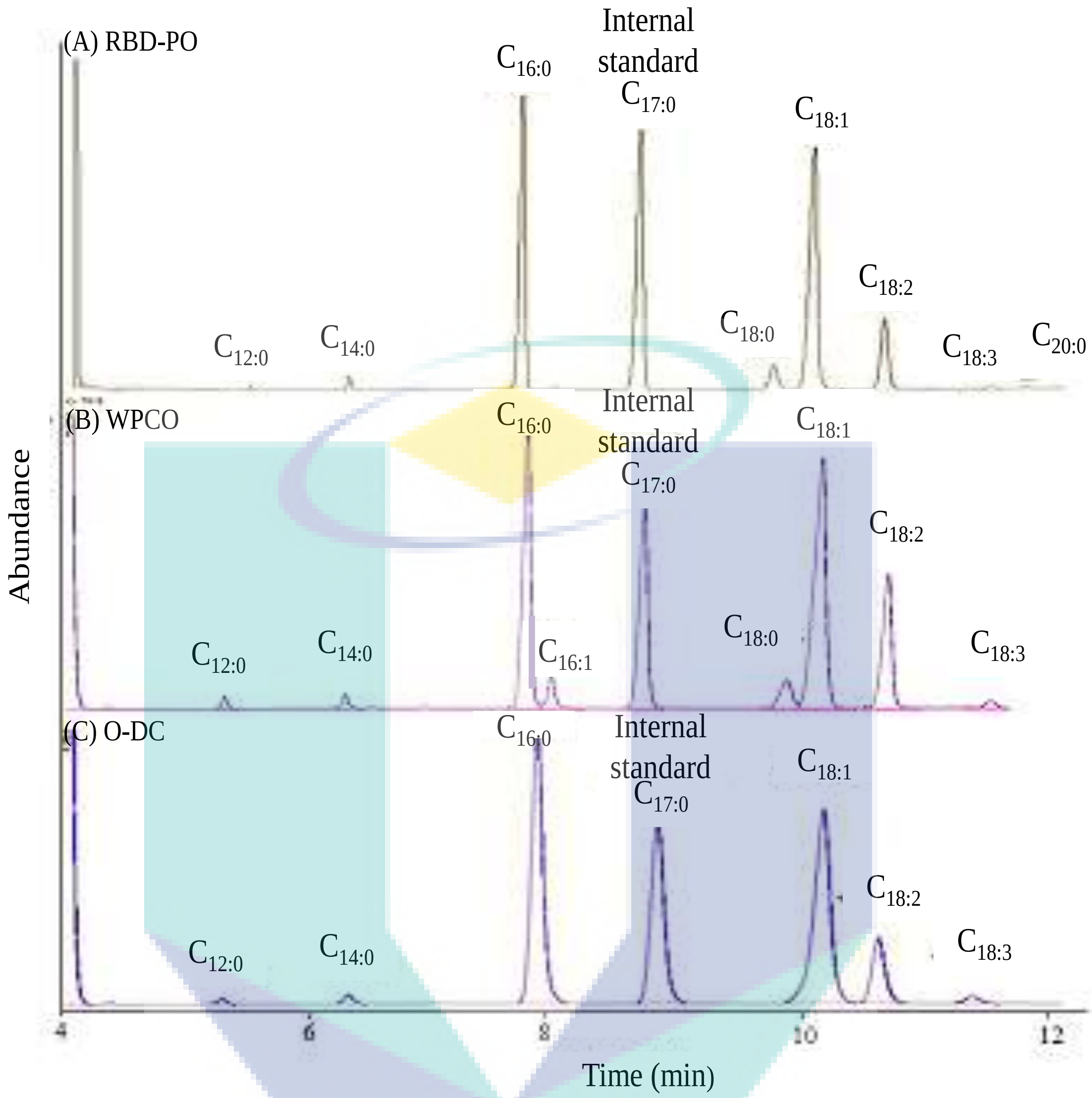


Figure 4.28: Gas chromatogram methyl ester with BA-500 as a catalyst

For comparison, the integration of methyl ester content from transesterification of RBD-PO, WPCO and O-DC using ^{1}H NMR was observed, shown in Figure 4.29. The ^{1}H NMR spectrum was found A_{ME} appears at 3.7 ppm, while $A_{\alpha\text{-CH2}}$ appears at 2.3 ppm. The conversion calculated by equation in section 3.7.2 was found the methyl ester content was achieved at 98.0%, 98.0% and 86.4% for RBD-PO, WPCO and O-DC, respectively. The results of ^{1}H NMR most similar with results of GC analysis with relative error ≤ 1 % are presented in Table 4.12.

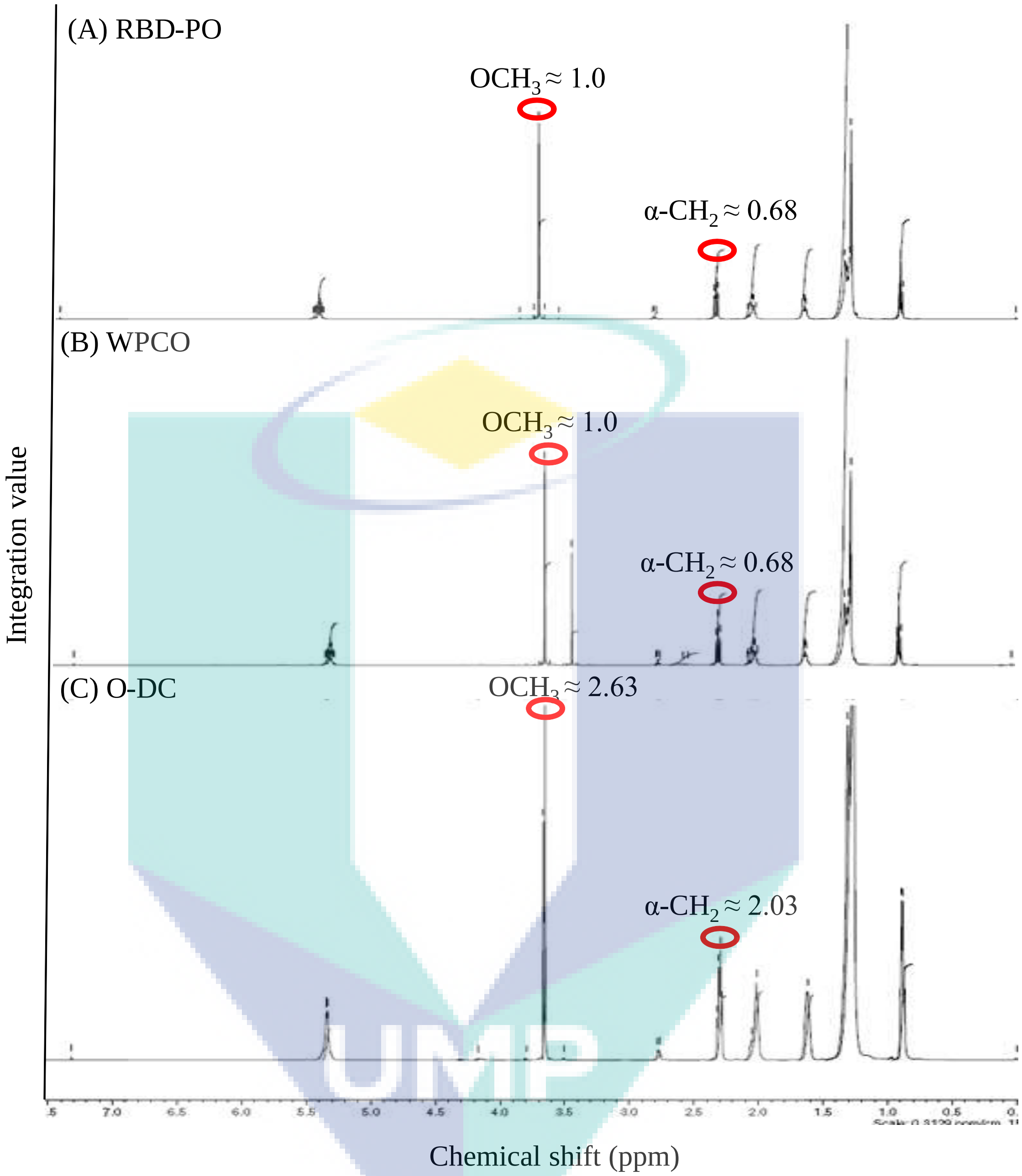


Figure 4.29: ^{1}H NMR spectrum methyl ester with BA-500 as a catalyst

Table 4.12: Methyl ester content of different feedstock using GC and ^{1}H NMR using BA-500 as a catalyst

Feedstock	ME content (%)		Relative error
	GC	^{1}H NMR	
RBD-PO	99.0	98.0	1.0
WPCO	98.8	98.0	0.8
O-DC	85.9	86.4	0.6

4.10.2 Physical Properties of Methyl Ester

Properties of biodiesel from BA-500, BC-CaO-900 and C-CaO-900 using WPCO as a feedstock are tabulated in Table 4.13. It shows that the ester content of the final products was determined following EN 14103 standard. The density and viscosity of the fuels affect the start of injection, the injection pressure, and the fuel spray characteristic, so that they influence the engine performance, combustion and exhaust emissions. Many performance characteristics such as cetane number and high heating value (HHV), are related to the density. In addition, since the diesel fuel injection systems measure the fuel by volume, the fuel density will influence engine output power due to a different mass of fuel injected (Bahadur et al., 2005). Viscosity is also of among the important properties of methyl ester, as viscosity gives effect to the fuel atomization and engine deposits (Knothe, 2001). By transesterification process, the viscosity can be reduced drastically, so it could be suitable for diesel engine. The biodiesel has flash point greater than petroleum diesel, makes biodiesel as much safer substance than petroleum diesel. The could point is the temperature, when crystals form in the fuel, the could point biodiesel higher than petro diesel. The HHV is one of the important analysis in the production biodiesel, measured using bomb calorimeter. The cold point and HHV is among the physical important parameters in ignition of biodiesel.

Table 4.13: Properties of the prepared biodiesel with different catalysts

Property	(Specification)	BA-500	BC-CaO-900	C-CaO-900	Method
Ester content (% m/m)	96.5 Min.	98.8 ± 0.4	97.8 ± 0.4	98.0 ± 0.3	EN 14103
Density (15 ˚C) (kg/m^3)	860 – 900	882	880	887	EN ISO 3675
Viscosity (25 ˚C) (cP)	3.5 – 5.0	4.3	4.2	4.0	EN ISO 3104
Flash Point (˚C)	>130 °C	156	156	168	ASTM D93
Cold Point (˚C)	Report	10	8	8	ASTM D2500
HHV (MJ/kg)	Report	38.0	38.6	39.2	ASTM D240
Sulfur content (mg/kg ppm)	10 Max.	4	4.5	4.5	EN ISO 20846

Reaction conditions BA-500: Catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1 for 1 h. Reaction conditions BC-CaO-900 and C-CaO-900: Catalyst amount, 5 wt.%; MeOH:oil molar ratio, 12:1 for 3 h.

4.11 COMBUSTION AND EMISSION ANALYSIS

4.11.1 Combustion Analysis

Engine performance for WPCO B10 blend using BA-500 as a catalyst on horizontal single cylinder 4 stroke diesel engine (YANMAR NF19-SK) was investigated. Then the crank angle degree (˚CA) and the regulated emission such as NO_x (nitrogen oxides), CO (carbon monoxide) and CO_2, are listed to survey detailed. The previous work was reported, increasing proportion of biodiesel blending causes the decreased NOx emissions (Aydin and Bayindir, 2010). Figure 4.30 shows that the peak in-cylinder pressure curve diesel and WPCO B10 an engine load of 5.5 MPa at 1200 rpm. It can be seen from the figure that, there was significant point at 8 CAD to 20 CAD where WPCO B10 show higher-pressure release when the peak cylinder in maximum point. While the diesel, shows lower pressure release during in this point, it is due to the presence of a small percentage of methanol additive in the fuel, more power stroke can be achieved for better combustion.

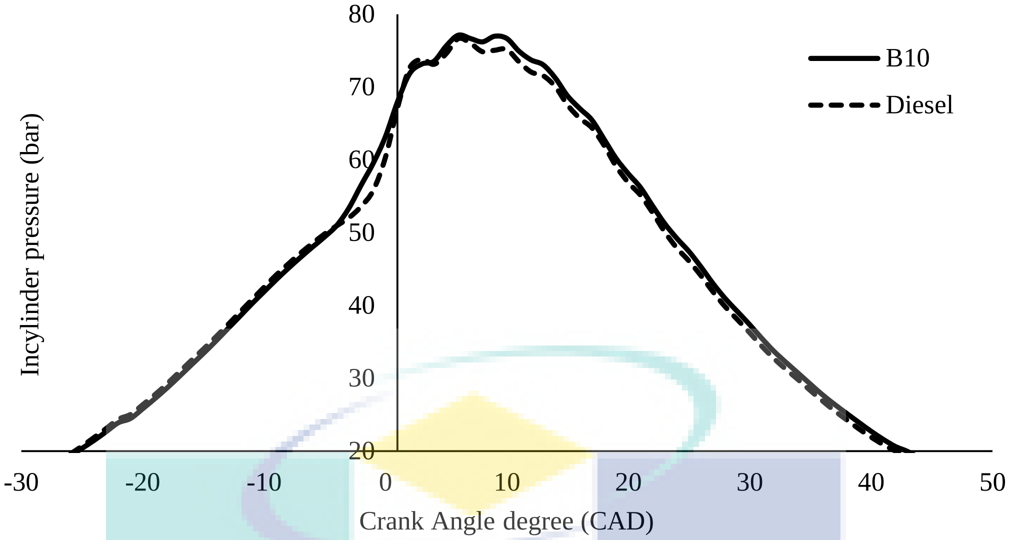


Figure 4.30: Peak in-cylinder pressure curve with engine load, 5.5 MPa at 1200 rpm.

4.11.2 Emission Analysis

a) Nitrogen Oxide Emissions

Nitrogen oxide (NO_x) emission tests were conducted with fuel blend of WPCO B10 compared with diesel is presented in Figure 4.31. The data indicated that the WPCO B10 had higher NO_x emission levels than diesel fuel. The NOx variation of the blend with respect to engine speed showed similar trends with that of the diesel fuel. The highest NO_x emissions was found at 1200 to 1500 speed rpm and a decrease at 2400 speed rpm level. NOx emissions are a function of temperature. In the case of biodiesel, NOx emissions are a function of combustion temperature. The higher the heat of combustion, the greater the NOx emissions. Because biodiesel contains more oxygen than diesel fuel, the heat of combustion is slightly higher.

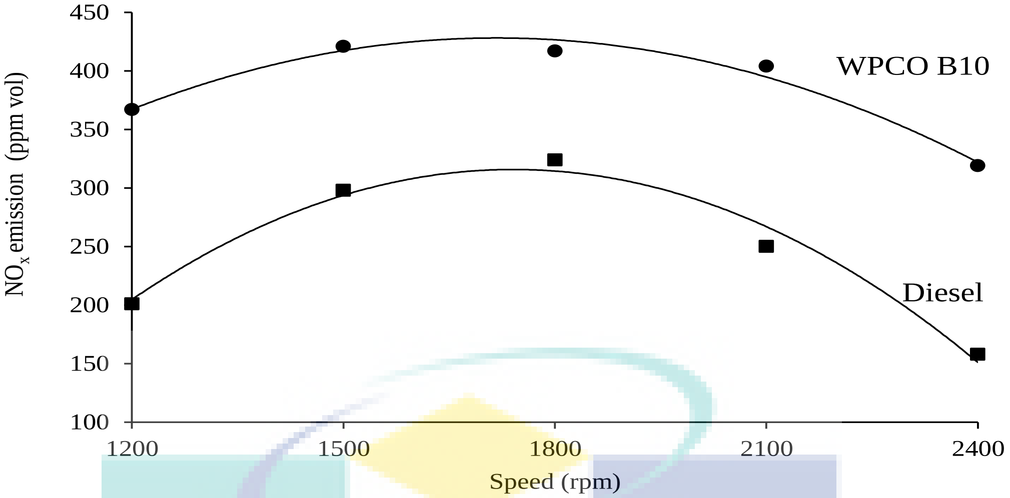


Figure 4.31: The NO_x emission of various engine speeds for different test fuels

b) *Carbon Monoxide Emissions*

The variation of CO emissions with respect to speed for WPCO B10 and diesel are presented in Figure 4.32. CO usually formed in diesel engine due to lack of oxygen molecules. Blending of WPCO B10 decreases the emission of CO, it is due to increasing in oxygen content. The additional oxygen content in the fuel, which enhances more complete oxidation compared with the diesel fuel, thus reducing CO emissions (Godiganur et al., 2009). This trend also was reporter by Sahoo et al. (2007), the increasing variation of blends of biodiesel content will decrease CO emission.

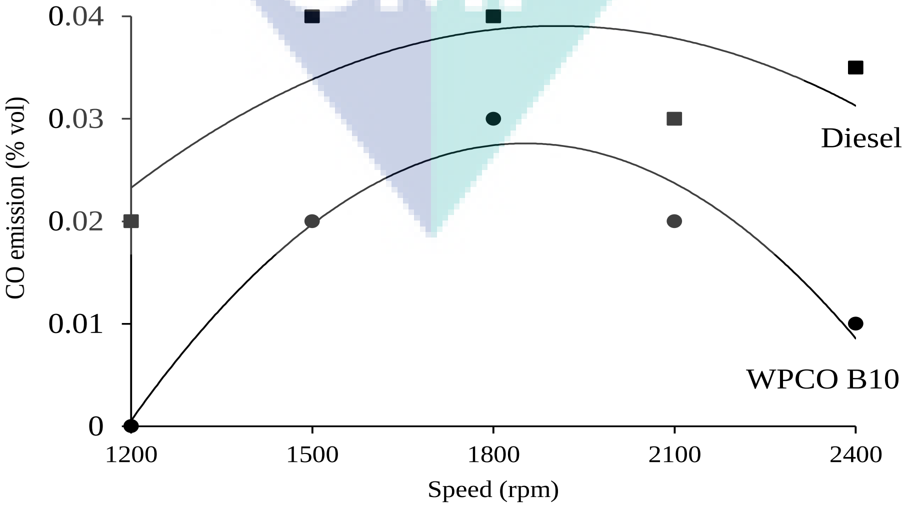


Figure 4.32: The CO emission of various engine speeds for different test fuels

c) *Carbon Dioxide Emissions*

In order to study the effect of engine loads from WPCO B10 and diesel with respect to speed was presented in Figure 4.33. It can be seen, the WPCO has fewer of CO_2 emissions than diesel fuel during complete combustion it is due to the lower carbon to hydrogen ratio in biodiesel. In fact, the biodiesel is a low carbon fuel and has a lower elemental carbon to hydrogen ratio than diesel fuel. It is in line was previous work by Ozsezen et al. (2009) and Utlu and Koçak (2008), they found fewer CO_2 emissions of biodiesel than diesel during complete combustion.

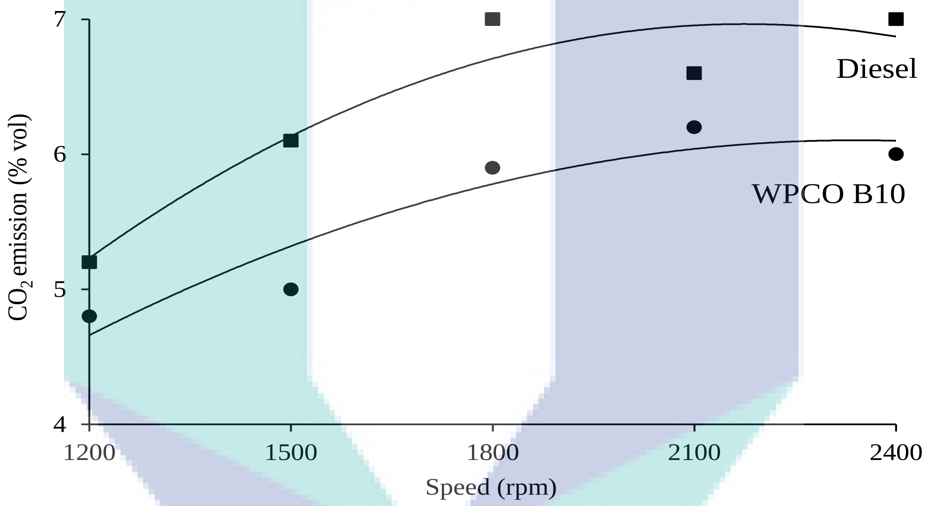


Figure 4.33: The CO_2 emission of various engine speeds for different test fuels

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The experiments have produced many outcomes that can be concluded as listed below:

i. The transesterification using WPCO and RBD-PO with optimum conditions using BA-500, BC-CaO-900 and C-CaO-900 catalyst resulting ME content over 96.5%.

ii. The regenerated of BA-500 reuse up to two cycles , while for BC-C-Mixed-900 reuse up to seven cycles when maintaining methyl esters content above 90%. The tolerance towards FFA and water was studied. BA-500 could tolerate FFA until 1.25 wt.% and water 1.75 wt.%. While BC-C-Mixed-900could tolerate FFA until 1.75 wt.% and water 2 wt.%, with ME content over 80% for both catalysts.

iii. The ME contents of O-DC via *in situ* transesterification using ultrasound irradiation and mechanical stirring were 85% and 45%, respectively.

Waste source as a feedstock and catalyst are the best options for decreasing the cost of biodiesel production. As a note concerning the use of waste/used oils, it is worth recalling the success of Kyoto city, Japan. The city has recorded a remarkable success in utilizing a fraction of biodiesel prepared from used cooking oil to run their 215 municipal trucks as well as 81 municipal buses at B20 composition (20% biodiesel blend). As such, the use of oils and catalysts from waste sources is not an unachievable effort, which not only adds value to the waste materials but also assists in preserving a relatively greener environment. Furthermore, the utilization of waste sources has a positive impact on the environment. As the second world's largest palm oil producer and exporter, Malaysia is now looked upon as the pioneer of a new and exciting palm biodiesel industry. The benefits of biodiesel from waste sources encompassing economical and environmental components are well in line with the Malaysian government's efforts in developing the Malaysian Biofuel Policy for the country. In addition, the Malaysian government is fully committed to a clean and healthy environment. The selecting of catalyst from waste sources is the best option. However, the choice of catalysts that are able to resist the presence of FFA and moisture in feedstocks as well as the catalysts ability to be reused is another consideration to lower the biodiesel production cost. The tolerance of the catalyst towards FFA and moisture is an important aspect to be considered if waste/used oils are to be used as feedstocks.

5.2 RECOMMENDATION

Through the research, it was successfully investigated a series of experiments on transesterification, a number of recommendations are proposed to enhance the whole research as listed below:

i. For the further research, different sizes of the catalysts should be tested to study their effectiveness in transesterification.

ii. The study the tolerance of the catalyst towards a specific saturated and unsaturated fatty acid.

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PUBLICATIONS

PUBLISHED PAPERS

Journals

[1] Maniam, G. P., Hindryawati, N., **Nurfitri, I**., Manaf, I.S.A., Ramachandran, N., and Rahim, M.H.A. (2014). *Utilization of waste fat from catfish (Pangasius) in methyl esters preparation using CaO derived from waste marine barnacle and bivalve clam as solid catalysts. Journal of the Taiwan Institute of Chemical Engineers*. *In Press*, available from: *doi:10.1016/j.jtice.2014.11.010*

[2] Maniam, G.P., Hindryawati, N., **Nurfitri, I**., Jose, R., Rahim, M.H.A., Dahalan, F.A., and Yusoff, M.M. (2013). Decanter cake as a feedstock for biodiesel production: A first report. *Energy Conversion and Management*, *76*, 527-532.

[3] **Nurfitri, I**., Maniam, G.P., Hindryawati, N., Yusoff, M.M., and Ganesan, S. (2013). Potential of feedstock and catalysts from waste in biodiesel preparation: A review. *Energy Conversion and Management*, *74*, 395-402.

Proceeding

[1] Maniam, G.P., Hindryawati, N., **Nurfitri, I.**, Jose, R., Rahim, M.H.A., and Yusoff, M.M. (2014). Ultrasound-aided in situ transesterification of oil adsorbed on decanter cake using EFBA and Na_2SiO_3 as catalysts. Proceedings *Fifth International Symposium on Energy from Biomass and Waste*, San Servolo, Venice, Italy; 17 - 20 November 2014. ISBN 9788862650854.

CONFERENCE PRESENTATIONS

Oral presentation

[1] Maniam, G.P., Hindryawati, N., **Nurfitri, I.,** Jose, R., Rahim, M.H.A., and Yusoff, M.M. *Ultrasound-aided in situ transesterification of oil adsorbed on decanter cake using EFBA and* Na_2SiO_3 *as catalysts*. Presented at Fifth International Symposium on Energy from Biomass and Waste, 17-20 November, 2014, San Servolo, Venice, Italy.

[2] Maniam, G.P., Hindryawati, N., **Nurfitri, I.,** and Manaf, I.S.A. *Methyl esters preparation from waste fat of catfish (Pangasius) using CaO derived from bivalve clam shell as solid catalyst*. Conference on Industry-Academia Joint

Initiatives in Biotechnology (CIA: Biotech 13), 5-7 December, 2013, Equatorial hotel, Cameron highland

[3] Maniam, G.P., **Nurfitri, I.,** Hindryawati, N., Jose, R., Yusoff, M.M., and Ibrahim, D.N. *Economic viability of biodiesel production from waste sources: A case study*. Presented at the 5th AUN/SEED-Net Regional Conference on Materials Engineering & the 5th Regional Conference on Natural Resources and Materials, 22-23 January, 2013, Parkroyal Penang Resort Hotel, Batu Feringhi, Penang, Malaysia.

[4] **Nurfitri, I.,** and Maniam, G.P. *Potential of palm empty fruit bunch (EFB) ash as a catalyst in the production of biodiesel.* Presented at the Malaysian International Conference on Trends in Bioprocess Engineering (MICOTriBE) 2012 Universiti Malaysia Perlis, 3-5 July, 2012, Meritus Pelangi Beach Resort & Spa, Langkawi, Malaysia.

[5] Maniam, G.P., Boey, P.-L., Ganesan, S., and **Nurfitri, I.** *Nano CaO from waste shells as a catalyst in tranesterification of palm olein.* Presented at the International Conference for Nanotechnology 2012, 30 May-1 June, 2012, Universiti Malaysia Pahang, MS Garden Hotel, Kuantan, Pahang, Malaysia.

Poster presentation

[1] **Nurfitri, I.,** and Maniam, G.P. *Biodiesel production via transesterification of waste cooking oil using waste baby clam (Paphia undulata) shell as a heterogeneous base catalyst.* Presented at the 5th International Conference on Postgraduate Education (ICPE-5 2012), 18-19 December, 2012, Current and Future Trends in Postgraduate Education, Universiti Teknologi Malaysia (UTM), Johor Bahru, Malaysia.

[2] Maniam, G.P., and **Nurfitri, I.** *Optimization of palm empty fruit bunch (EFB) ash as a catalyst in the production of biodiesel*. Presented at National Conference on Postgraduate Research 2012 (NCON-PGR2012), 7-9 September, 2012, Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia.

EXHIBITION

[1] **Gold Medal (2014)**

Gaanty Pragas Maniam, Noor Hindryawati**, Irma Nurfitri,** Nurul Hajar Embong, Jose Rajan, Mohd Hasbi Ab. Rahim, Mashitah M. Yusoff. Renewable green fuel from biowaste. Presented at The Invention & New Product Exposition (INPEX), 18th-20th June 2014. David L. Lawrence Convention Center, Pittsburgh, Pennsylvania.

[2] **Gold Medal (2014)**

Gaanty Pragas Maniam, Neshabran Ramachandran, Noor Hindryawati, **Irma Nurfitri,** Nurul Hajar Binti Embong, Intan Shafinaz Binti Abd. Manaf, Mashitah M. Yusoff, Mohd Hasbi Ab. Rahim. Calcium oxide derived from waste gypsum as a new heterogeneous catalyst for methyl esters production. Presented at Creation, Innovation, Technology & Research Exposition (Citrex 2014) Exhibition. Universiti Malaysia Pahang. 5th-6th March 2014. Complex Sukan Universiti Malaysia Pahang, Kuantan, Pahang. Malaysia

[3] **Silver Medal (2014)**

Gaanty Pragas Maniam, Neshabran Ramachandran, Noor Hindryawati, **Irma Nurfitri,** Nurul Hajar Binti Embong, Intan Shafinaz Binti Abd. Manaf, Mashitah M. Yusoff, Mohd Hasbi Ab. Rahim. Calcium oxide derived from waste gypsum as a new heterogeneous catalyst for methyl esters production. Presented at 25th International Invention, Innovation & Technology Exhibition (ITEX 2014). 8th-10th 2014. Kuala Lumpur Convention Center, Kuala Lumpur. Malaysia

[4] **Silver Medal (2014)**

Gaanty Pragas Maniam, Nurul Hajar Binti Embong, Intan Shafinaz Binti Abd. Manaf, Noor Hindryawati, **Irma Nurfitri,** Neshabran Ramachandran, Mashitah M. Yusoff, Mohd Hasbi Ab. Rahim. Methyl esters preparation from potential oil palm industry waste. Presented at Creation, Innovation, Technology & Research Exposition (Citrex 2014) Exhibition. Universiti Malaysia Pahang. 5th-6th March 2014. Complex Sukan Universiti Malaysia Pahang, Kuantan, Pahang. Malaysia

[5] **Gold Medal (2013)**

Gaanty Pragas Maniam, Noor Hindryawati, **Irma Nurfitri,** Mohd Hasbi Ab. Rahim, Jose Rajan and Mashitah M. Yusoff. *Novel Utilization of Decanter Cake as a Feedstock for Biodiesel Production*. Presented at (BioMalaysia), 21th-23th August, 2013, Persada Johor International Convention Centre, Johor,, Malaysia.

[6] **Silver Medal (2013)**

Gaanty Pragas Maniam, Noor Hindryawati, **Irma Nurfitri,** Mohd Hasbi Ab. Rahim, Jose Rajan and Mashitah M. Yusoff. *Novel Utilization of Decanter Cake as a Feedstock for Biodiesel Production*. Presented at Creation, Innovation, Technology & Research Exposition (Citrex 2013) Exhibition. Universiti Malaysia Pahang. 28th-29th March, 2013, Complex Sukan Universiti Malaysia Pahang, Kuantan, Pahang. Malaysia