FABRICATION OF POROUS CERAMIC FOAM AS CATALYST SUPPORT FOR HYDROTALCITE IN THE PRODUCTION OF FATTY ACID METHYL ESTERS (FAME)

by

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LIST OF ABBREVIATIONS

[MEpure] SD	concentration of the ester in the standard reference
ΔL	linear sintering shrinkage
3D	three dimensions
ASTM	American Society for Testing and Materials
BET	Brunauer, Emmet and Teller
CPO	commercial palm oil
DAG	diacylglycerol
DF	dilution factor of the sample
DG	diglycerides
EDX	energy dispersive X-ray
EN	European standard
FAAE	fatty acid alkyl esters
FAME	fatty acid methyl esters
FESEM	field emission scanning electron microscope
FFA	free fatty acid
GC-FID	gas chromatography flame ionization detector
IUPAC	International Union of Pure and Applied Chemistry
L	the length of the tubular catalyst support after sintering
L_o	the length of the tubular catalyst support before sintering
M	mullite
MAG	monoacylglycrol
MBA	Malaysian Biodiesel Association

M_D	mass of dry sample
MG	monoglycerides
ML	methyl linoleate
MM	methyl myristate
MO	methyl oleate
MP	methyl palmitate
MPOB	Malaysian Palm Oil Board
MS	methyl standard
MS	methyl stearate
M_W	mass of wet sample in air
M_W*	mass of wet sample in water
PO	palm oil
ppi	pores per inch
PSD	pore size distribution
PU	polyurethane
PVA	polyvinyl alcohol
PZT	plumbum zirconate titanate
Q	quartz
R	ratio of peak areas of ester to peak area of internal standard in the sample
RPC	reticulated porous ceramic
RSD	ratio of peak areas of ester to peak area internal standard in the standard reference
SSA	specific surface area per unit volume

TAG	triacylglycerol
TG	triglycerides
vol%	volume percent
wt%	weight percent
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	**Description**	**Unit**
ρ	density	gcm^{-3}
ρ_{bulk}	bulk density	gcm^{-3}
$(CH_3O)_2Mg$	magnesium methoxide	
2θ	scanning angle	°
Al	aluminium	
Al_2O_3	aluminium oxide	
AlO	aluminium oxide	
C	carbon	
$C_{12}H_{27}AlO_3$	aluminium tri-sec-butoxide	
$CaCO_3$	calcium carbonate	
CH_3ONa	sodium methoxide	
CO_2	carbon dioxide	
K_2CO_3	potassium carbonate	
KOH	potassium hydroxide	
Mg	magnesium	
MgO	magnesium oxide	
Na	natrium or sodium	
Na_2CO_3	sodium carbonate	

NaOH	sodium hydroxide	
NOx	nitrogen oxides	
O	oxygen	
Si	silicon	
SiC	silicon carbide	
SiO	silicon oxide	
T	temperature	°C
t	time	hour
TiO_2	titanium dioxide	

FABRIKASI SPAN SERAMIK POROS SEBAGAI PENYOKONG UNTUK MANGKIN HIDROTALSIT DALAM PENGELUARAN LEMAK ASID METIL ESTER (FAME)

ABSTRAK

Akibat permintaan untuk bahan api cecair petrol serta keluarganya yang tinggi, biodiesel telah menjadi semakin popular di seluruh dunia sebagai sumber tenaga alternatif. Penghasilan biodiesel mempunyai kesukaran dan kelemahan tertentu, maka para penyelidik mencari sumber penyelidikan baru untuk mencari teknologi alternatif untuk pengeluaran biodiesel melalui proses transesterifikasi. Oleh itu, teknologi menaik taraf pengeluaran biodiesel telah dicadangkan, yang bermula dengan pemangkin heterogen dalam proses transesterifikasi. Dalam kajian ini, pemangkin hidrotalsit yang bertindak sebagai pemangkin heterogen beserta porselin span berliang yang bertindak sebagai penyokong, telah disediakan melalui kaedah replikasi span polimer. Analisa telah dijalankan dengan mengenalpasti pencirian sifat mekanikal dan mikrostruktur seramik span berliang yang berbentuk tiub tersebut dan telah digunakan dalam proses transesterifikasi untuk menukarkan minyak masak sawit komersial kepada biodiesel. Kajian ke atas pencirian porselin span berliang dan pemangkin hidrotalsit sampel juga dijalankan melalui pembelauan sinar-x dan mikroskop imbasan elektron pancaran medan. Hasil keputusan menunjukkan bahawa kombinasi saiz liang 120/10 dengan 35 % berat muatan pepejal dan 55 % berat muatan pepejal, disinter pada 1250°C adalah gabungan yang paling sesuai untuk porselin span berliang berbentuk tiub sebagai sokongan pemangkin. menunjukkan bahawa 47.31% keliangan adalah peratusan yang sudah mencukupi untuk menyediakan ruang untuk pemangkin hidrotalsit ditempatkan manakala kekuatan mampatan sebanyak 3.7 MPa menjadikan tiub sokongan ini mampu menahan tekanan ke atas keseluruhan tiub. Hasil kajian ini juga menunjukkan bahawa pemangkin hidrotalsit telah berjaya dilekatkan kepada porselin span berliang berbentuk tiub yang bertindak sebagai sokongan pemangkin melalui proses pemendapan sol-gel. Pencirian hasil biodiesel daripada proses transesterifikasi telah berjaya mematuhi piawaian biodiesel yang telah ditetapkan oleh piawaian biodiesel Amerika dan Eropah dengan hasil tertinggi lemak asid metil ester (FAME) sebanyak 98.4 % pada suhu tindak balas pada 65°C, tempoh tindak balas selama 6 jam, nisbah metanol kepada minyak pada 6:1 dan kandungan pemangkin hidrotalsit disalut pada kadar 3 %. Keputusan yang dibentangkan ini boleh membantu teknologi pemangkin heterogen dalam proses transesterifikasi untuk meningkatkan pengeluaran biodiesel.

FABRICATION OF POROUS CERAMIC FOAM AS CATALYST SUPPORT FOR HYDROTALCITE IN THE PRODUCTION OF FATTY ACID METHYL ESTERS (FAME)

ABSTRACT

The increasing demand for liquid petrol fuels, as well as their higher price, biodiesel has been gaining worldwide popularity as an alternative energy source. The classic ways of producing biodiesel have certain difficulties and disadvantages such as that determined researchers for finding alternative technologies for its production. Thus, in this study an upgraded technology of biodiesel production has been proposed. The tubular porcelain catalyst as the catalyst support and hydrotalcite as the heterogeneous catalyst were prepared. Analyses have been done including the methods of preparation of the tubular ceramic support with the replication polymeric sponge method, characterization of mechanical and microstructure properties of tubular ceramic support and the application on the transesterification of commercial palm cooking oil to biodiesel. The characterization of tubular ceramic support with hydrotalcite catalyst has been done using X-ray diffraction and field emission scanning electron microscope. The results reveal that the combinations of pore size 120/10 ppi with 35 wt % and 55 wt % of solid loading, sintered at 1250°C is the most suitable combination of tubular porcelain catalyst support. Results were found that 47.31% of porosity are the sufficient enough to provide the space for the hydrotalsite catalyst to deposit while the value of compression strength 3.7 MPa can withstand the stress induced by the pressure applied over the whole support. The results of this research also shown that the hydrotalcite catalyst is successfully coated to the tubular porcelain catalyst support by sol–gel deposition process. Characterization of the biodiesel from the transesterification process was successfully met the American and European Biodiesel Standards with the highest yield of fatty acid methyl esters (FAME) about 98.4 % under the following reaction conditions: reaction temperature at 65°C, reaction time of 6 hours, ratio methanol to oil molar ratio of 6:1 and catalyst loading 3 wt %. The results presented here may facilitate improvements in the technology of heterogeneous catalytic in the transesterification process for biodiesel production.

CHAPTER 1

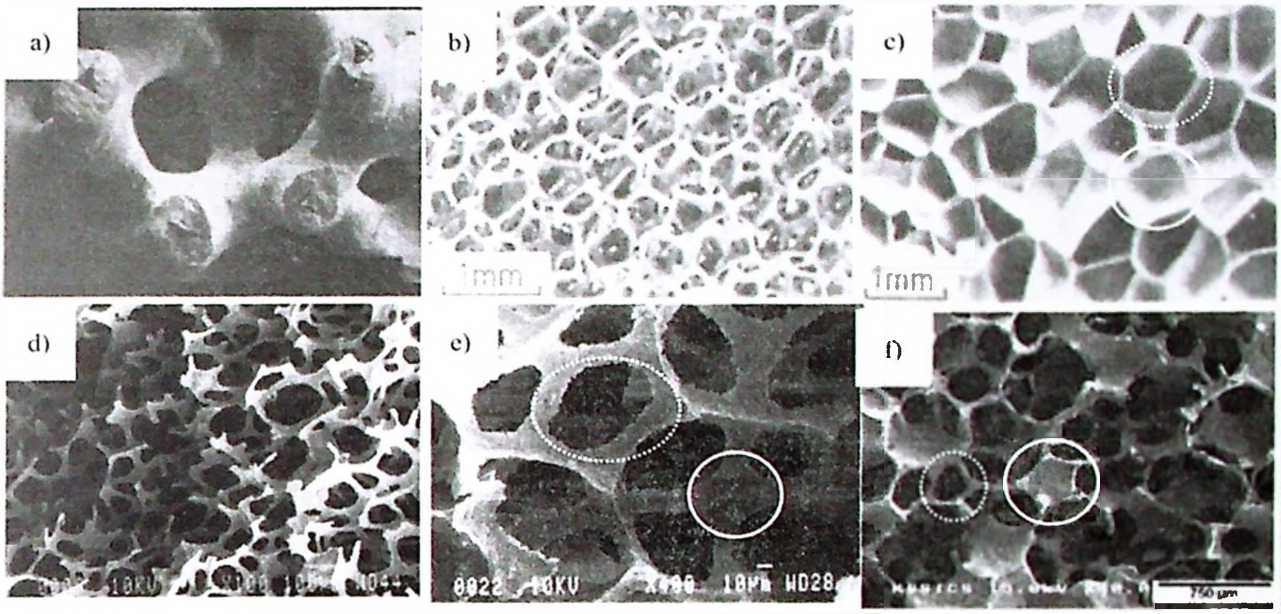
INTRODUCTION

This chapter starts with the overview of ceramic foams that leads to the development of alternative catalyst support for transesterification process. This chapter also gives a brief overview of biodiesel production, which leads to the development of heterogeneous transesterification process. The problem statement, scope of research and objectives of this research project are also stated clearly in this chapter.

1.1 Ceramic foam

Ceramic foam is a very interesting area of research due to its wide applicability. Ceramic foams can be described as highly porous brittle materials with large voids (cells) (Sifontes et al., 2009) or ceramics containing pores. Ceramic foam also known as ceramic sponge (Dietrich et al., 2010; Dressler et al., 2009; Grosse et al., 2009; Senguttuvan et al., 2001) or reticulated porous ceramic (RPC) (Zhu et al., 2002; Jun et al., 2006; Akpinar et al., 2010) or cellular ceramic (Acchar et al., 2009; Barg et al., 2009; Bhaduri, 1994; Colombo & Bernardo, 2003; Oliveira et al., 2006; Sharafat et al., 2004) is a special class of porous materials comprised of cells with size ranging from a few microns to a few millimeters, where the cells can be surrounded by ceramic walls or contain solid material at only cell edges (struts), thus creating an interconnected structure (open cell foam) (Sifontes et al., 2009). There are several descriptions of ceramic foams in such as cellular structures composed of a three-dimensional network of struts (Luyten et al., 2009) or ceramic foams are a class of highly porous materials that is used for a wide range of technological applications (Nor et al., 2008).

Ceramic foams with either closed-cell or open-cell characteristic as presented in Figure 1.1 different properties.



Remark

Open pore ◌

Closed pore ○

Figure 1.1 Different sizes of pore in ceramic foam (Leonov, 1997; Peng et al., 2000; Yang et al., 2010).

Closed-cell foams are composed of polyhedral like cells connected via solid faces, with no interconnectivity between them, whereas open-cell structures have solid edges and open faces, with fluid flow possible from one cell to another (Twigg & Richardson, 2007). This kind of materials are highly porous ceramics (70-95%) with an open, network and dodecahedral internal structure with a continuous void volume connecting adjacent pores (Zhu et al., 2002) and typically have open accessible in the range of 10 to 100 pores per inch (ppi) (Twigg, 2002).

Generally, porous ceramic materials such as ceramic foams are classified into three classes depending on the pore diameter; microporous with the pore size less than 2 nm, mesoporous with the pore size is between 2–50 nm, and macroporous with the pore size more than 50 nm, accordingly by the International Union of Pure and Applied Chemistry (IUPAC). Their properties such as low density, low thermal conductivity, high temperature stability and high chemical resistance are particularly important to meet the requirement with their applications. For examples, specific surface area of 150 m^2/g, which is still in the range as shown in Table 1.1 and applicable for catalysis and for filtration, the specific surface area is depends on the application (Ishizaki & Komarneni, 1998).

For applications as sensors in engineering field, the specific surface area of more than 1 m^2/g is required. In many applications of ceramic foams, high number or volume of total open porosity is desirable to increase the specific surface area. An increase in porosity will decrease the mechanical strength. Low mechanical strength limits the operating conditions for ceramic foams, and consequently increases the required dimensions of ceramic foams. Both high open porosity and high mechanical strength may be required simultaneously in order to use the ceramic foams under severe operating conditions. In general, as observed from prior studies on porous materials, a clear understanding of the properties of ceramic foam is very essential for for different applications (Carty & Lednor, 1996; Gonzenbach et al., 2007; Peng et al., 2000; van Setten et al., 1999). In order to develop the high-quality of supports, the properties of pore size distribution, total porosity ratio, surface quality with the absence of large defects or large pores, mechanical properties and chemical stability are important (Bouzerara et al., 2006).

Ceramic foams have been used in many ways from common applications to high-tech processing. For example, ceramic foams with open pores commonly used as molten metal filters (Dhara & Bhargava, 2006; Dietrich et al., 2010; Twigg & Richardson, 2007), gas sensors (Zhu et al., 2003; Dhara, 2006), catalyst supports (Montanaro et al., 1998; Richardson et al., 2003; Twigg & Richardson, 1995) and combustion burners (Grosse et al., 2009; Twigg & Richardson, 1995; Zhu et al., 2002). While ceramic foams with closed pores are used as load bearing (Dhara & Bhargava, 2006; Luyten et al., 2010; Montanaro et al., 1998), acoustic and thermal insulation (Ishizaki & Komarneni, 1998). Ceramic foam with a gradient in percent porosity, pore size or pore connectivity are useful for biomedical implants such as artificial bone and supports for membranes in catalysis (Dhara & Bhargava, 2003; Ohji, 2013).

Table 1.1 Porous materials and their requirements for different applications (Ishizaki & Komarneni, 1998).

	Filter	**Catalyst**	**Bioreactor**	**Gas distributor**	**Sensor**	**Oil-containing bearing**
Open porosity (%)	>30	>30	>30	>30	>30	20-40
Pore size	Appropriate size, depending on applications	Appropriate size, depending on applications	For bacteria: 5-30 μm For enzymes: 10-100 nm	>μm	Depending on the applications	>μm
PSD[a]	Narrow	Narrow (depending on application bimodal)	Narrow (depending on application bimodal)	Narrow	Narrow	Insensitive
SSA[b]	Depending on the applications	1-2000 m^2/g	>1 m^2/g	Depending on pore size	>1 m^2/g	Insensitive
Permeability	High	Depending on the applications	Depending on the applications	High	Depending on the applications	Insensitive
Mechanical strength	High	Depending on the applications	High	High, depending on applications	Depending on the applications	High
Other	Chemical resistance	Catalysis function	Appropriate surface potential		Sensing function, appropriate surface condition	Chemical and wear resistance

[a] PSD = pore size distribution
[b] SSA = specific surface area per unit mass

1.1.1 Architecture of ceramic foam

Ceramic foams are one type of porous materials with remarkably high volume of total open porosity (≈ 90%). One of the production methods for ceramic foams by coating the slurry on the polyethylene foam. Ceramic foam with large pores of 50 µm to 1 mm in diameter can be obtained by this method (Ishizaki & Komarneni, 1998).

There are two different structures for the foam: closed-cell (Bhaduri, 1994) or closed pore structure (Taguchi & Schüth, 2005) and open-cell (Colombo, 1999) or open pore structure (Ishizaki & Komarneni, 1998; Twigg & Richardson, 2007). The open pores connect to the outside of the materials and closed pores which are isolated from the outside and may contain a fluid. Penetrating pores are a kind of open pores; these have at least two openings located on the two sides of a porous material. Figure 1.2 shows the different type of pores. For most industrial applications of ceramic materials, open pores are required. The open-cell structure has high porosity (> 75%) with solid edges and open faces. Fluid can readily flow through the open faces with low resistance but with high turbulence due to its highly tortuous paths. By introducing open pores in ceramic, it will affect the ceramic properties. There are involved two important changes which is the decreased of density and increased the specific area. However, these changes will generate useful properties such as fluid permeability and filtration.

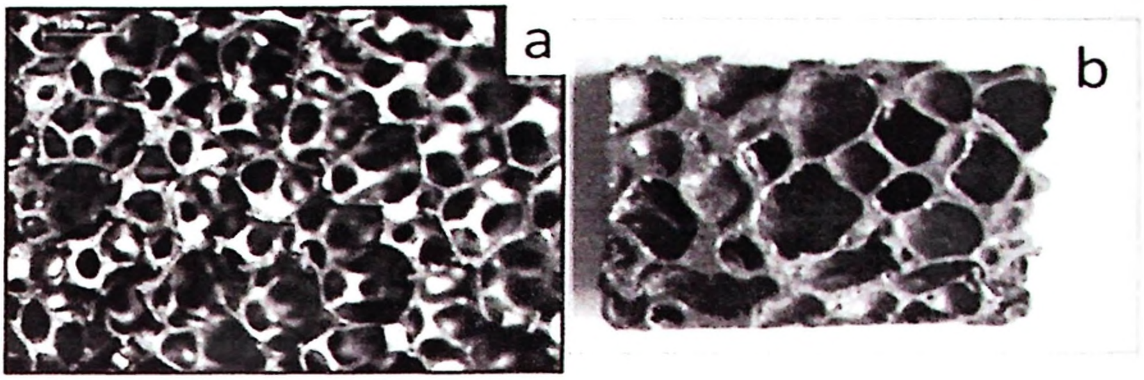


Figure 1.2 Different morphology of pores. Pores are classified into two major types: a) open pores and b) closed pores (Banús & Ulla, 2013).

Large specific surface area is necessary for catalysis. In many applications of porous materials, high open porosity is desirable to increase the specific surface area or fluid permeability. An increase in porosity decreases the mechanical strength. Low mechanical strength limits the operating conditions for porous materials and consequently increases the required dimensions of porous materials. The pore density is an estimation based on the properties of the commercial polymer foam from which the ceramic was formed (Richardson et al., 2000; Twigg & Richardson, 2007).

1.1.2 Advantages of ceramic foam as structured catalyst supports

In general, as observed from prior studies, many industrial catalysts are made into pellets. However, ceramic foams have attracted considerable attention as potential catalyst supports. The application of ceramic foam in certain industrial catalytic processes could be a great benefit. Twigg & Richardson (2007) reviewed the advantages of ceramic foams as structured catalyst supports compared to pellet in three major benefits:

a) Conventional pellet packing usually require longer reactor tube with small diameter to give the necessary heat transfer surface. This in turn may result of increasing the heat transfer but having a long narrow tube of pellets may cause a significant pressure drop penalty, the effectiveness factor decrease and more catalyst volume required. With the fabrication of ceramic foam to precisely fit the tube, such narrow, long tube is not necessary. Furthermore, the radial heat transfer is excellent, the pressure drop is much lower and much more effective.

b) The catalyst pellet using smaller particles to increase the outer surface area to volume ratio, reducing diffusion limitation regimes but leads to a higher pressure drop. While the ceramic foam structures can give both improved effectiveness and lower the pressure drop.

c) There are many processes where the intermediate compound is the desired product, such as partial oxidation reactions. Residence time and exposure of the gas becomes very important. Thus, high flow rates are sometimes necessary, which increases the pressure drop. If diffusion is limited in the catalyst, the intermediate compound may also be trapped within the catalyst particle, increasing the time exposure of the compound to interact with the catalyst and react further. The ceramic foam, with its high porosity and open structure, limits the exposure time of the reactant to the catalyst. Furthermore, since there are limited micropores on the ceramic foam, diffusion limitation which may trap the intermediate reactant within the catalyst particle is negligible.

1.2 Overview of biodiesel

Recent developments in the fields of fuel have led to a renewed interest in biodiesel. Biodiesel is a substitute for diesel fuel, which is similar to petroleum diesel in combustion properties, but free from sulphur as well as cleaner burning fuel than petroleum diesel. Over the past century, there has been a limitation of traditional fossil resources and increasing of crude oil prices. Therefore, previous studies were done to explore the potential of biodiesel from renewable energy sources such as vegetable oils or animal fats. Biodiesel has similar physical and chemical properties with petrodiesel fuel. Biodiesel is more environmentally friendly than their fossil alternatives. It has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression–ignition (diesel) engines. Biodiesel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultra-low sulfur diesel fuel such as inherent lubricity and low toxicity (Leung et al., 2010), derived from a renewable and domestic feedstock, superior flash point (Asakuma et al., 2009) and biodegradability (Zabeti et al., 2009), negligible sulfur content, and lower overall exhaust emissions (Lim & Teong, 2010). Important disadvantages of biodiesel include high feedstock cost (Baroutian et al., 2009; Sinha et al., 2008; Zabeti et al., 2009), inferior storage and oxidative stability (Gerpen & Knothe, 2005; Leung et al., 2010; Lim & Teong, 2010), lower volumetric energy content (Hossain & Mazen, 2010; Leung et al., 2010; Singh & Singh, 2010), inferior low-temperature operability versus petrodiesel and in some cases, higher NOx exhaust emissions (Georgogianni et al., 2009). The standards for biodiesel and petroleum based diesel are provided in Table 1.2.

Conventionally, the biodiesel production is performed by converting vegetable oil using an alcohol in the presence of a catalyst, to chemically break the molecule of the raw renewable oil into methyl or ethyl esters of the renewable oil with glycerol as a by-product. This process is called transesterification. There are different varieties of vegetable oils such as canola (Baroutian et al., 2009; Gerpen & Knothe, 2005; Singh & Singh, 2010), palm (Baroutian et al., 2009; Noiroj et al., 2009), jatropha (Achten et al., 2008; Hawash et al., 2009), sunflower (Hossain, 2009; Sun et al., 2010) and coconut (Kawashima et al., 2009; Zabeti et al., 2010) as precursors for biodiesel production. The choices of alcohols used are methanol (Silva, et al., 2010) and ethanol (Xie & Li, 2006). The catalysts used in the transesterification include sodium hydroxide (Hossain & Mazen, 2010), potassium hydroxide (Xie & Li, 2006), sulphuric acids (Kolaczkowski et al., 2009), supercritical fluids (Singh & Singh, 2010) and enzymes such as lipase (Yagiz et al., 2007). In the experimental studies, the final product is either called as fatty acid alkyl esters (FAAE) or fatty acid methyl esters (FAME) instead of biodiesel, unless it meets the specification of ASTM D6751.

Table 1.2 Comparison for the standard diesel based on American Society for Testing and Materials (ASTM) (Helwani et al., 2009).

Property	**Diesel**	**Biodiesel**
Standard number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C10–C21)	Fatty acid metyl ester (C12-C22)
Specific gravity (g/ml)	0.85	0.88
Flash point (K)	333 – 353	373 – 443
Cloud point (K)	258 – 278	270 – 285
Pour point (K)	243 – 258	258 – 289
Water (vol %)	0.03	0.05
Carbon (wt. %)	87	77
Hydrogen (wt. %)	13	12
Oxygen (wt. %)	0	11
Sulfur (wt. %)	0.05	0.05
Cetane number	40 – 55	48 – 60

Biodiesel production has become an interesting area for many researchers due to its potential as an alternative fuel that offers a complementary strategy for sustainability. Transesterification of vegetable oils has become the most common approach of biodiesel production. Vegetable oils have the chemical structure as shown in Figure 1.3, comprise of 98 % triglycerides (TG) and small amounts of monoglycerides (MG) and diglycerides (DG) (Helwani et al., 2009). Triglycerides are esters of three fatty acids and one glycerol containing substantial amounts of oxygen in its structure and the fatty acids vary in their carbon chain length and in the number of double bonds (Helwani et al., 2009).

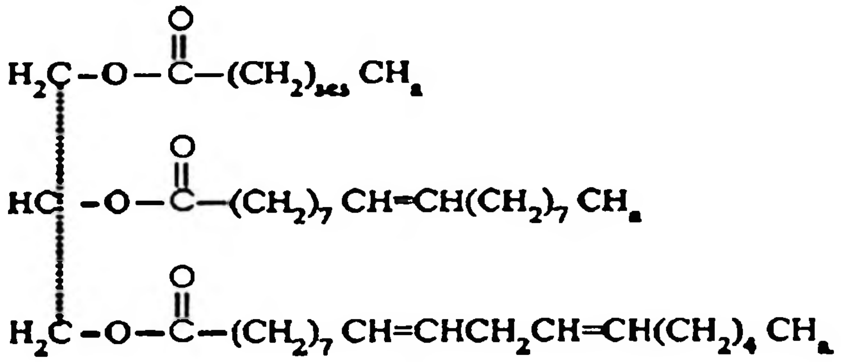


Figure 1.3 Chemical structure of triglyceride (Singh & Singh, 2010).

Each vegetable oil has different type of fatty acids. There are some advantage of vegetable oils such as available in almost every part of the world, renewable source since the vegetables can be planted and harvested continuously and potential to become the environmental friendly fuel because the fuel derived from the oils contains no or the least sulphur element (Helwani et al., 2009).

1.2.1 Transesterification

Transesterification is the reaction of vegetable oil or animal fat with an alcohol to form esters and glycerol. A catalyst is used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Alcohols are the primary and secondary monohydric aliphatic compounds having 1–8 carbon atoms. Methanol and ethanol are used most frequently in the transesterification process. Methanol is preferred because of its lower cost and its physical and chemical advantages (polar and shortest chain alcohol) over ethanol. The former reacts immediately with TG and dissolves easily in NaOH. In order to complete a transesterification stoichiometrically, a 3:1

molar ratio of the alcohol to TG is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Rashid et al., 2008).

The transesterification reaction as shown in Figure 1.4, which involves a triglyceride (TG) reaction with a short-chain monohydric alcohol normally in the presence of a catalyst at elevated temperature to form FAAE and glycerol (Figure 1.4). The conversion of TAG to biodiesel is a stepwise process whereby the alcohol initially reacts with TAG as the alkoxide anion to produce FAAE and diacylglycerols (DAG); reaction [1] as shown in Figure 1.4, which react further with alcohol (alkoxide) to liberate another molecule of FAAE and generate monoacylglyerols (MAG); reaction [2], (Figure 1.4). Lastly, MAG undergo alcoholysis to yield glycerol and FAAE; reaction [3], (Figure 1.4), with the combined FAAE collectively known as biodiesel. Three moles of biodiesel and one mole of glycerol are produced for every mole of TAG that undergoes a complete conversion.

The transesterification reaction is reversible, although the reverse reaction (production of MAG from FAAE and glycerol, for instance) is negligible largely because glycerol is not miscible with FAAE, especially FAME when using methanol as the alcohol component. The reaction system is biphasic at the beginning and the end of biodiesel production, as methanol and vegetable oil and glycerol and FAME are not miscible. Methanol is most commonly used in the commercial production of biodiesel, since it is generally less expensive than other alcohols. Other alcohols aside from methanol and ethanol are also of interest for biodiesel production because FAAE produced from higher alcohols may have different fuel properties in comparison to methyl or ethyl esters (Gerpen & Knothe, 2005).

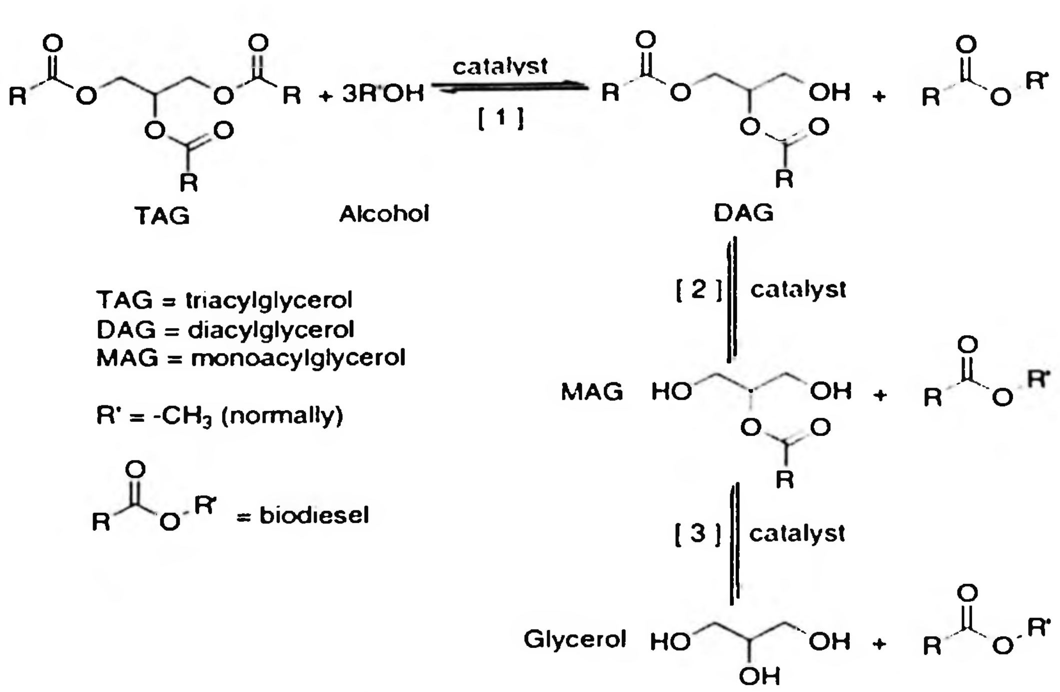


Figure 1.4 Overall scheme of transesterification process (Rashid et al., 2008).

The catalytic transesterification of vegetable oils with methanol to produce biodiesel is known as methanolysis (Helwani et al., 2009). This process used of acids or bases, such as sulphuric acids or sodium hydroxides (Park et al., 2010) as catalysts to facilitate the reaction. Generally, in transesterification of vegetable oils, all the catalysts can be fitted into three classifications as known as homogeneous (Arzamendi et al., 2007), enzyme (Yagiz et al., 2007) or heterogeneous catalysts (Fei & Teong, 2008). Enzyme can fall into either homogeneous or heterogeneous categories depending on its mobility. Homogeneous base catalysts are an alkaline liquid such as sodium hydroxide, sodium methoxide, potassium hydroxide or potassium methoxide (Sinha et al., 2008). Homogeneous acid catalysts are an acidic liquid such as sulphuric acid, hydrochloric acid or sulphonic acid (Zabeti et al., 2009) whereas, heterogeneous catalysts are acid or base solids that include immobilized enzymes, titanium-silicates, alkaline-earth metal compounds, anion exchange resins on organic polymers (Helwani et al., 2009). The application of homogeneous catalysts such as sodium or potassium hydroxide, sodium or potassium methoxide is still common in industries because they are relatively cheap and quite active for this reaction, but heterogeneous catalysts appears as a promising and growing biodiesel catalyst area.

1.3 Problem statement

In the Malaysian scenario, the main constraint is the rising petroleum prices and new strategies will have to emerge which will have possible social consequences. There may have to be practical and economic solutions, with the inevitable use of biodiesel. Biodiesel offers similar power to diesel fuel in existing engines and fuel injection equipment with little impact to operating performance. The only limiting factors of biodiesel are feedstock prices and production costs.

Biodiesel is produced from transesterification of vegetables oils or animal fats with the addition of methanol as a catalyst, after the glycerol is removed. There are two methods of transesterification; homogeneous and heterogeneous transesterification. Homogeneous transesterification has been well accepted and commercialized in a big scale. Unfortunately, homogeneous transesterification has problems associated with the complexity of the product separation and purification processes due to the homogeneous nature of its mixture (reactants, catalyst and product in a similar phase, i.e. liquid). Homogeneous transesterification produces soap which requires much water to wash and also the formulation of emulsion in the mixture. The formation of emulsion in the mixture can worsen the complexity of the separation and purification. Furthermore, it could contribute to the loss of triglycerides. The high price of biodiesel is largely due to these factors. The cost can be reduced if non-edible oil feedstock is used and heterogeneous catalysis for biodiesel production is improved considerably (Demirbas, 2009). Another problem using the homogeneous catalysis is difficulty in removing the basic catalysts after the reaction, production of large amount of waste water and emulsification. Furthermore, the growing concern about the environment prompts the chemical industry to develop less polluting and more selective chemical processes. In this context, solid catalysts as known as a heterogeneous catalyst appear promising to replace the liquid homogeneous catalysts because they are less corrosive, easier to handle and separate, reusable and generating less amount of toxic wastes. The use of heterogeneous catalysis in transesterification reactions prevents the undesirable saponification, allows process simplification and offers reduction in the processing costs by eliminating the additional steps required by the liquid homogeneous catalysts.

Heterogeneous transesterification is easier and simpler to operate because the catalyst is in a different phase from the product or reactants. However, the reactivity of heterogeneous (solid) catalyst has always become a great concern. Preparation of solid catalyst that is highly reactive and selective has become a challenge and because of that, hydrotalcite has been chosen based on its performance as heterogeneous catalyst in the previous researchs (Barakos, Pasias, & Papayannakos, 2008; Othman, Rasid, & Fernando, 2006; Trakarnpruk & Porntangjitlikit, 2008). This research is focused on the development of solid catalyst support in order to produce biodiesel from vegetable oils. For an application as solid catalyst support, ceramic foam has been chosen due to its potential application in a wide range of porous materials. Ceramic foams as porous membranes are typically used because they offer a higher permeability than dense membranes, but the membrane itself is inert with respect to the catalytic reaction and the catalyst is physically separated from the membrane. In this research, hydrotalcite catalyst is immobilized in the ceramic foam. The ceramic foam in a tubular shape has been chosen because it provides mechanical strength to intermediate layer and membrane layer to withstand the stress induced by the pressure applied over the whole membrane support. Hydrotalcite is prepared by using sol-gel techniques so that it can easily deposited to the tubular ceramic support whereas, the tubular ceramic support is prepared by polymeric sponge method using porcelain as a raw macrials because of porcelains have great potential, including long term stability at high temperatures, resistance to harsh environments, resistance to high pressure drops, inertness to microbiological degradation (Carbajal, Rubio-Marcos, Bengochea, & Fernandez, 2007; Kamseu et al., 2007). The parameters of concern in this study are methods of preparation tubular ceramic support with polymeric sponge method, characterization of mechanical and microstructure properties of tubular ceramic support and application on the heterogeneous transesterification of commercial palm cooking oil to biodiesel.

1.4 Project objectives

The present research study has the following objectives:

i. To produce and characterize porcelain foams with different pore sizes as tubular catalyst support for transesterification of biodiesel.

ii. To deposite and characterize hydrotalcite on porcelain tubular catalyst support via sol-gel method.

iii. To apply the hydrotalcite/porcelain tubular catalyst support as a solid catalyst in the heterogeneous transesterification of commercial palm cooking oil to a biodiesel.

iv. To characterize the FAME products of commercial palm cooking oil as a diesel substitute.

1.5 Research scope

This research focuses on the preparation of hydrotalcite/porcelain tubular catalyst support as a solid catalyst in heterogeneous transesterification for biodiesel production from commercial palm cooking oil with methanol. The effect of tubular catalyst support preparation condition such as pore size, sintering temperature and percentage of solid loading was investigated. The characterization of the tubular catalyst support was performed using field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), compressive strength using a universal testing machine and sintered density and porosity were measured by the water immersion method or Archimedes method. The transesterification of commercial palm cooking oil was also investigated by studying the effect of reaction time on the easter yield. Additionally, the characterization of biodiesel obtained from transesterification of commercial palm cooking oil with methanol was performed following the ASTM D6751 standard specifications.

1.6 Organization of the thesis

There are five chapters (including introduction) in this thesis and each chapter gives specific information about this research project.

Chapter 1 gives the introduction of this research project. This chapter starts with the overview of ceramic foams that leads to the development of alternative catalyst support for transesterification process. This chapter also gives a brief overview of biodiesel production which leads to the development of heterogeneous transesterification process. The problem statement, scope of research and objectives of this research project are also stated clearly in this chapter.

Chapter 2 gives literature review of this research project background. This chapter provides the literature review of ceramic foam in terms of its preparation and properties. Further in this chapter are the reviews of the transesterification processes. Other sub-sections covered in this chapter are the reviews of hydrotalcite as heterogeneous catalyst. Finally, literature review on the biodiesel in terms of its composition, properties and performance as diesel fuel.

Chapter 3 describes the materials and methodology used in this research project. The first part of this chapter gives the part design of this research project. The subsequent sub-sections describe clearly the methodology of this research project - the part design, material and chemicals, equipment and facilities, fabrication and characterization of tubular ceramic foam, preparation and characterization of hydrotalcite, transesterification process using a hydrotalcite solid catalyst and characterization of the product of this research project.

Chapter 4 presents the results and discussions of this research project. The sequence of topics in this chapter follows the sequence of sub-sections in Chapter 3. This first part of this chapter contains the result and discussion obtained from the characterization of porcelain tubular catalyst supports followed by the results and discussion obtained from the hydrotalcite catalyst. Subsequent sub-sections on this chapter contain the characterization of product (biodiesel).

Chapter 5 concludes the research project. Recommendations for future work related to this research project are also given.

CHAPTER 2

LITERATURE REVIEW

This chapter provides the literature review of ceramic foam in terms of its preparation and properties. Further in this chapter are the reviews of the transesterification processes. Other sub-sections covered in this chapter are the reviews of hydrotalcite as heterogeneous catalyst.

2.1 Biodisel

In the past few years, biodiesel has been one of the major interesting research subjects due to the increase in consumption of this renewable fuel worldwide. Biodiesel is the first and only alternative fuel to commercial diesel to have a complete evaluation of emission results (Demirbas, 2009). The name biodiesel was introduced in the United States during 1992 by the National Soy Development Board (Singh & Singh, 2010). Biodiesel meant life in Greek, while the word diesel was come from the name of a German inventor and mechanical engineer, Rudolf Diesel. Biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources and are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. As an alternative fuel for internal combustion engines, biodiesel is defined as a mixture of monoalkyl esters of long chain FAME derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C14 – C22) esters of short-chain alcohols, primarily, methanol or ethanol (Demirbas, 2009).

There have been several studies in the literature reporting that biodiesel has better properties than that of petroleum diesel such as renewable, biodegradable, non-toxic (Murugesan et al., 2009; Singh & Singh, 2010), essentially free of sulfur and is generally suitable to match the future European regulations which limit the sulphur content to 0.2 % in weight in 1994 and 0.0 5% in 1996 (Cantrell et al., 2005; Kim et al., 2004; Leung et al., 2010), aromatics (Kansedo, 2009; Kawashima et al., 2008), biodiesel degrades four times faster than diesel, blending of biodiesel with diesel fuel increases engine efficiency (Ahmad et al., 2009; Murugesan et al., 2009), does not produce greenhouse effects because the balance between the amount of CO_2 emissions and the amount of CO_2 absorbed by the plants producing vegetable oil is equal (Lim & Teong, 2010; Murugesan et al., 2009), biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine (Sharma & Singh, 2009; Sinha et al., 2008) and chemical characteristics revealed lower levels of some toxic and reactive hydrocarbon species when biodiesel fuels were used (Murugesan et al., 2009).

2.1.1 Development of biodiesel in Malaysia

Malaysian government had realized the importance of developing biofuel and in particular, biodiesel in the long term since early 1980s. As the world's largest exporter of palm oil, Malaysia needs to be the pioneers in the palm biodiesel industry. In 1982, the project of developing palm biodiesel was initiated at laboratory scale by Malaysian Palm Oil Board (MPOB). Later, in 1984 with collaboration from a local oil company, Petronas, the palm oil biodiesel pilot plant was built and successfully commissioned to produce 3000 metric tonnes of palm oil methyl ester annually. Palm oil biodiesel had been invariably subjected to various systematic evaluations as petroleum derived diesel fuel replacement during the following year. Recent developments in the field of palm oil biodiesel have led to develop inter-grade biodiesel production technology, which solved the gelling issue when biodiesel is used under cold condition near freezing temperatures in 1992. However, no major development had been achieved mostly due to weak industrial demand and inconsistent political support even though extensive laboratory research and field trials had been conducted from time to time. Stagnation in Malaysia's biodiesel industry continued until the Fifth Fuel Policy was announced under the Eighth Malaysia Plan (2001–2005). The Fifth Fuel Policy was revised from the earlier Four Fuel Diversification Policy in 1981 where its aim was to prevent over dependence on oil as the main energy resource. The renewable energy was declared as the fifth fuel in the energy supply mix in Malaysia under this new policy. In 2005, the Government of Malaysia had drafted the National Biofuel Policy to carve out a comprehensive framework and concrete initiatives for the use of biofuels in Malaysia to gain more momentum for the development of biodiesel. The National Biofuel Policy entailed a strategy which was aimed to reduce Malaysia's petroleum-derived fuel import bill, further promoting the demand for palm oil, which was expected to be the primary commodity for biofuels production in Malaysia, as well as to shore up the price of palm oil especially during the period of low export. Since that, the development of biodiesel in Malaysia had been growing by leaps and bounds. There are 10 active biodiesel plants in the country with a total annual biodiesel installed capacity of 1.2 million tonnes as according to Malaysian Biodiesel Association (MBA). Until now, 91 biodiesel licenses have been issued by Malaysia's Ministry of Plantation Industries and Commodities (Lim & Teong, 2010).

2.1.2 Raw materials for biodiesel production

Recent developments in biodiesel have heightened the need for raw materials in the biodiesel production mainly on its availability and cost. Countries such as USA and those belonging to European community are self-dependent in production of edible oils such as soybean and rapeseed (Leung et al., 2010; Marchetti et al., 2007). Malaysia, Indonesia and other similarly countries with coastal area have coconut, palm and jatropha for the synthesis of biodiesel (Fei & Teong, 2008; Gerpen & Knothe, 2005; Zabeti et al., 2009). Being the largest sugarcane producer in the world, Brazil used sugarcane for the synthesis of biodiesel (Sharma & Singh, 2009). The raw materials used in India for development of biodiesel are jatropha curcas (jatropha) and pongamia pinnata (karanja) (Helwani et al., 2009; Samios et al., 2009).

The raw material for biodiesel production is not restricted to vegetable oils only. Researchers in United States have tried algae as a raw material for biodiesel production because they believed that that even vegetable oils will not be enough to meet the future demand of biodiesel. For example, they used algae, microalgae Chlorella protothecoides and lipid content for the synthesis of biodiesel (Hossain, 2010; Lim & Teong, 2010).

2.1.3 Synthesis of biodiesel from vegetable oil

Transesterification also known as alcoholysis is a chemical process to produce biodiesel. Transesterification is the displacement of alcohol group from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is