

**CATALYTIC BEHAVIOUR OF SULPHATED ZIRCONIA
SUPPORTED ON MCF AS CATALYST IN SELECTIVE
GLYCEROL ESTERIFICATION WITH PALMITIC ACID TO
MONOPALMITIN**

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GLYCEROL ESTERIFICATION WITH PALMITIC ACID TO
MONOPALMITIN**

by

KISHOR KUMAR A/L A MURUGAN

**Thesis submitted in partial fulfilment of the requirement
for the degree of Bachelor of Chemical Engineering**

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glycerol/palmitic acid = 4:1).

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LIST OF SYMBOLS

| Symbols | Description | Unit |
|------------|---|--|
| A | Pre-exponential factor | $L \cdot mol^{-1} g_{cat}^{-1} h^{-1}$ |
| A_i | Peak area of mono, di- or tripalmitin in the sample | Dimensionless |
| A_{IS} | Peak area of internal standard | Dimensionless |
| $A_{SD,i}$ | Peak area of mono, di- or tripalmitin in the standard reference | Dimensionless |
| C_G | Concentration of glycerol | mol/L |
| C_i | Concentration of mono-, di- or tripalmitin | mol/L |
| C_{PA} | Concentration of palmitic acid | mol/L |
| C_{PA0} | Initial concentration of palmitic acid | mol/L |
| $C_{SD,i}$ | Concentration of mono-, di- or tripalmitin for standard reference | mol/L |
| D_f | Dilution factor | Dimensionless |
| E_a | Activation energy | kJ/mol |
| R | Universal gas constant | Dimensionless |
| R_{SD} | Ratio of peak area of mono-, di- or tripalmitin in the standard reference to peak area of the internal standard | Dimensionless |
| S_{Mono} | Selectivity of monopalmitin | Dimensionless |
| S_{Di} | Selectivity of dipalmitin | Dimensionless |
| S_{Tri} | Selectivity of tripalmitin | Dimensionless |
| X_{G0} | Initial glycerol conversion | Dimensionless |
| X_{PA} | Conversion of palmitic acid | Dimensionless |
| X_{PA0} | Initial palmitic acid conversion | Dimensionless |
| Y_M | Monopalmitin yield | Dimensionless |

**SIFAT PEMAMNGKIN ZIRKONIA TERSULFAT BERPENYOKONG MCF
UNTUK PENGESTERAN TERPILIH GLISEROL DENGAN ASID
PALMITIK KEPADA MONOPALMITIN**

ABSTRAK

Dalam kajian ini, superacid zirkonia sulfat, disokong dengan *Mesocellular Foam* (MCF) telah disediakan oleh kaedah urea-hidrolisis. Pengesteran antara gliserol dan asid palmitik telah dijalankan dengan kehadiran pemangkin ini dan bekalan berterusan nitrogen untuk membuang air terbentuk. Muatan pemangkin dan suhu bahan tindak balas telah dimanipulasi untuk mendapat keadaan yang paling sesuai dan optimum untuk tindak balas pengesteran. Semua tindak balas pengesteran dikaji dalam proses kelompok dan aktiviti pemangkin SZMCF di bawah pelbagai parameter tindak balas seperti muatan pemangkin (1 – 3 wt%) berkenaan dengan bahan tindak balas yang menghad (asid palmitik) dan suhu tindak balas (160-180 °C) telah disiasat. Kesimpulannya, SZMCF pemangkin yang mempamerkan aktiviti yang baik adalah aktif dan sesuai untuk digunakan dalam tindak balas yang melibatkan molekul besar.

**CATALYTIC BEHAVIOUR OF SULPHATED ZIRCONIA SUPPORTED ON
MCF AS CATALYST IN SELECTIVE GLYCEROL ESTERIFICATION
WITH PALMITIC ACID TO MONOPALMITIN**

ABSTRACT

In this study, the sulphated zirconia superacid, supported on Mesocellular Foam (MCF) was prepared by urea-hydrolysis method. Glycerol and palmitic acid was esterified in the presence of this catalysts and continuous supply of nitrogen to remove water formed. Catalyst loading and temperature of reactants was manipulated to optimize the reaction condition for the esterification. All the esterification reactions were studied in a batch process and the activity of the SZMCF catalyst under various reaction parameters such as catalyst loadings (1 – 3 wt. %) with respect to limiting reactant (palmitic acid) and reaction temperatures (160 – 180 °C) was investigated. As a conclusion, SZMCF catalyst which exhibited good activity was as an active catalyst and suitable to be used in the reaction involving bulky molecules.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

In this era of globalisation, the biomass-derived fuel industry is getting attention worldwide due to the increasing prices of fossil fuels finite fossil fuel resources and its negative impact towards environment (Mahmudul et al. 2017; Ferretti et al. 2010). Specifically, biodiesel production capacity of Europe, USA, Brazil and Argentina in 2010 totals about 28 million tons per year (Ferretti et al. 2010).

Malaysia is one of the leading exporter of palm oil. This promotes downstream industries such as oleochemical, biodiesel, etc. The basic oleochemicals are fatty acids, methyl esters and fatty alcohols. The one of the main side product produced during the synthesis of biodiesel is glycerol about 10 to 20% of the total volume of biodiesel produced (Quispe et al. 2013).

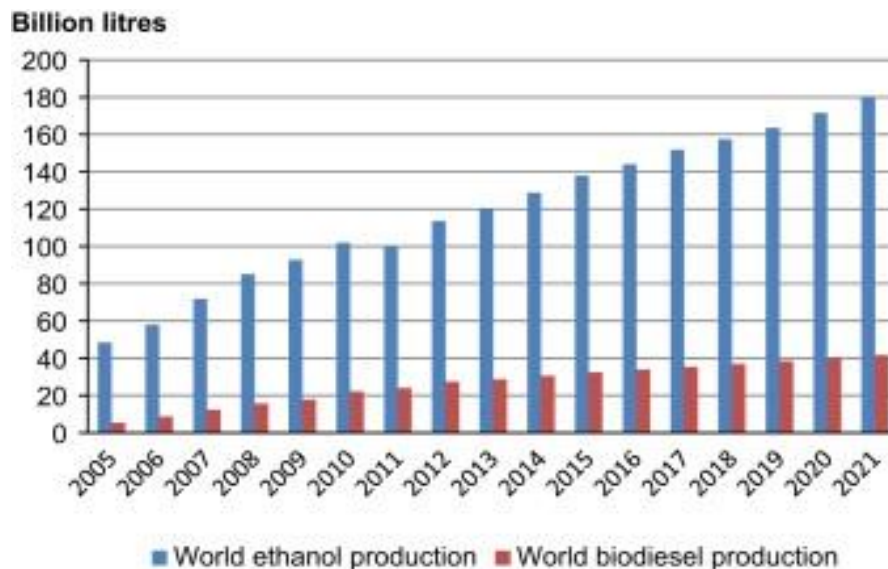


Figure 1.1 World ethanol and biodiesel production (Ashnani et al. 2014)

The estimated production of biodiesel from now until 2021 is shown in the Figure 1.1. From the figure, it can be seen biodiesel production is showing an increasing trend throughout the upcoming years. This will in turn increase the accumulation of glycerol that will be produced from the biodiesel production. The Global Glycerol Market is estimated to reach about USD 2.52 billion by 2020 and biodiesel is the main source of glycerol, accounting for over 1400 kt of glycerol production in 2013 (He et al. 2017). However, the glycerol produced during the reaction is crude glycerol which contains impurities. Due to the impurities that found in the crude glycerol such as methanol, fatty acid methyl esters and salts, makes the refining cost high. This makes the glycerol an inexpensive raw material which can be converted into value added products.

1.2 Glycerol

Glycerol also known as glycerin is an organic compound that has a chemical formula of $C_3H_8O_3$ and a chemical structure as shown in the figure 1.2. Glycerol has three hydroxyl groups which gives the compound some unique features such as soluble in water and hygroscopic properties. The main source of glycerol is from the biodiesel production and glycerol can be converted into value added products such as in the personal care, cosmetics, pharmaceutical, and food industries (He et al. 2017).

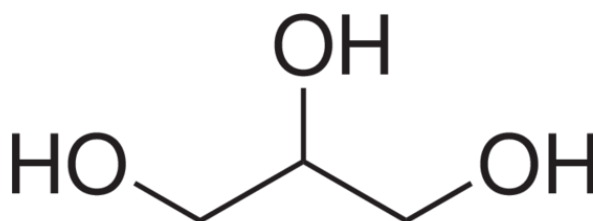


Figure 1.2 Chemical structure of glycerol

1.3 Monoglyceride

Monoglycerides are valuable chemical compound that commonly used in many industries such as food, pharmaceutical and cosmetics. This is because of the property that it carries that it can be used as surfactants (Yusoff and Abdullah 2016). Monoglycerides (MG) consist of a hydrophilic head and a hydrophobic tail as shown in the Figure 1.3, which give them detergency characteristics. Therefore, monoglycerides and their derivatives have a wide application as emulsifiers in food, pharmaceutical, and cosmetic industries. They increase skin permeability and thus facilitate percutaneous drug absorption. Currently, they are also being considered for use in low-calorie margarines. There are various kind of emulsifiers that are available in the market but monoglycerides is one of the commonly used type of food emulsifiers (Ghamgui et al. 2006). This is because monoglycerides are lipid molecule consist of a single fatty acid chain attached to the glycerol backbone. This molecular structure makes it amphiphilic because the glycerol head is polar and the fatty acid chain is nonpolar (Wang and Marangoni 2016). Emulsifiers are surface- active ingredients and can lower the interfacial tension by position itself in the interfaces and facilitate emulsion formation (Novales et al. 2005).

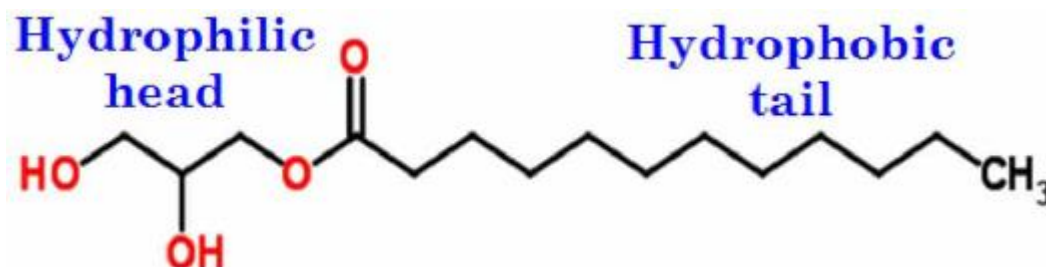


Figure 1.3 Chemical structure of monoglyceride

The monoglycerides are also known as esters that can be produced by three different methods: (a) the glycerolysis of vegetable oil, (b) the hydrolysis of triglycerides, and (c) the direct esterification of fatty acids with glycerol. The direct esterification of fatty acids with glycerol is most commonly used to produce monoglycerides (Kotwal et al. 2011). This is because the glycerolysis of vegetable oil is carried out with a strong base catalyst such as KOH, NaOH and this reactions conducted at temperature between 220 to 250 °C which means it has higher energy consumption (Yusoff and Abdullah 2016). Moreover the products obtained from this method have some drawbacks such as dark colour or burnt and low yield (Ghamgui et al. 2006). Direct esterification of glycerol with fatty acids in the presence of acidic catalyst can produce monoglyceride at relatively low temperature (Yusoff and Abdullah 2016).

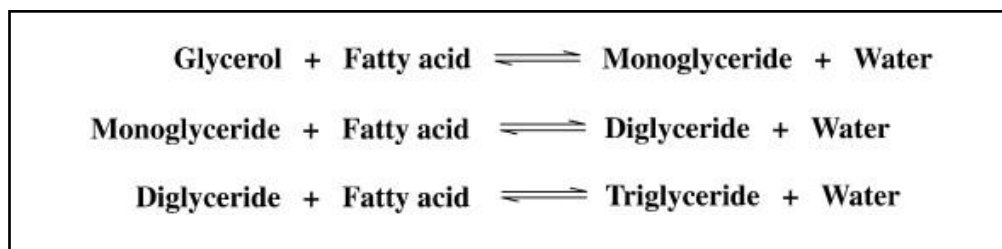


Figure 1.4 Reversible parallel reactions of glycerol esterification (Kotwal et al. 2011)

1.4 Direct Esterification of Glycerol with Fatty Acid

Esterification is a vital process in various industries such as pharmaceutical, food, cosmetics and biodiesel. Direct esterification of glycerol with fatty acid in the presence of acidic homogenous catalyst at low temperature around 363K to 393K is the common industrial way to produce monoglycerides. The common acid catalyst are, e.g., sulphuric acid, phosphoric acid or organic sulfonic acid (Bossaert et al. 1999). The yield that will be obtained from industrial production is usually around 40-60% monoglyceride, 35-45% diglycerides and triglycerides, with some salts and other by-products (Hoo and Abdullah 2014).

1.5 Palmitic Acid

Back then, the short-chain fatty acids were used for esterification reactions because long chains will take longer time to react. But now, the long-chain fatty acids are used for esterification reactions to produce monoglycerides with the aid of catalysts. There are various types of fatty acids used for esterification reaction such as lauric acid (Hoo and Abdullah 2014), stearic acid (Yang et al. 2003) and palmitic acid (Yusoff and Abdullah 2016). Palmitic acid also as known as hexadecenoic acid is saturated fatty acid which can be found in animal and plants. This palmitic acid is mainly produced from palm oil. It is a sustainable long term feedstock and cheap commodity in the oil field.

1.6 Problem Statement

The production of glycerol is increasing as the demand for biodiesel increases because the glycerol is the main by product from the production of biodiesel. This makes the accumulation of glycerol in the global market which in turn decreases its market price making it a cheaper raw material for other uses. At this situation, various

researches have been conducted to find a way to make a better use of glycerol to convert it into a value added chemical compound. Currently, producing emulsifier from monoglycerides getting a greater attention around the globe. Here, the glycerol plays a vital role as a raw material for the direct esterification process with fatty acids to produce monoglycerides. Emulsifiers are very important in industries that producing food, cosmetics and pharmaceutical. The emulsifiers are also responsible for reducing the overall fat and trans-fat levels in food such as chocolates and margarines (Hoo and Abdullah 2014; Hermida et al. 2010).

The direct esterification process requires acid catalyts to lower the operating temperature and to increase the selectivity towards the monoglycerides compared to diglycerides and triglycerides. There're many research conducted to replace the homogenous catalyts such as sulphuric acid, phosphoric acid and organic sulfonic acids. The catalyts that need to be used in the direct esterification process must have some criteria to label it as a good catalyts. The most important criteria that needed are such as high selectivity towards monoglycerides, high conversion of glycerol and fatty acid, reusability, environmental friendly and cost effective (Hoo and Abdullah 2014).

Recently, the discovery of catalyts supports and the active sites incorporated on the support become a potential heterogenous catalyts to be used in the esterification reaction. However, there are drawbacks in these catalyts such as small pore size, instability in hydrothermal treatment and poor reusability. Functionalised mesoporous silica based catalyts have been used in the selective synthesis of monoglyceride (Hoo and Abdullah 2014; Hermida et al. 2010). But, the application of the catalyts was limited to only for the esterification reaction using lauric acid. The direct esterification reaction using palmitic acid receives attention form the researchers because of its availability and one of the cheapest raw material in the oil market which makes it a

promising raw material to be converted into value added compounds. The palmitic acid is bulky molecule which will be hard to catalyse because of the mass transfer limitations and high activation energy barrier. Moreover, the long fatty acid chain of palmitic acid would make the activity lower which reduce the monoglyceride yield. To overcome these challenges stated above, a much highly active and stable mesoporous catalyst, highly selective towards monoglyceride and with large pore sizes is required.

Sulfated Zirconia supported on MCF (SZMCF) is a potential catalyst for the esterification reaction due to its superacidic properties, high surface area, large pore volume, uniform pore sizes and stable in hydrothermal treating which is highly required in the reaction involving bulky molecules and needs elevated temperature. The behaviour of SZMCF is not well studied yet in many reactions. However, there are researches conducted using sulphated zirconia supported on SBA-15. SBA-15 showed high activity in various reactions such as oxybromination (Chen et al. 2010), etherification (Barbera et al. 2015), hydrolysis (Degirmenci et al. 2011). The SBA-15 also showed high activity in the esterification reaction of glycerol with palmitic acid. The SZSBA-15 showed high selectivity towards monopalmitin (Yusoff and Abdullah 2016). As stated above, the behaviour of SZMCF is yet to identified as well as its role of acidity and pore characteristics. Therefore, there is general interest to explore the application of SZMCF catalyst in a reaction involving bulky molecules (i.e. esterification of palmitic acid with glycerol) and investigate the correlation between the catalyst characteristics and the catalytic activity. Since the catalyst is a mesoporous superacidic catalyst, the activity in this reaction is expected to be high and worth further investigation.

1.7 Research Objectives

The objectives of this study are:

- i. To synthesize sulphated zirconia supported on Mesoporous Cellular Foam (MCF) by varying the zirconia loadings.
- ii. To characterize physical, chemical and structural properties of the catalyst using several methods such as SEM, BET, etc.
- iii. To study the catalytic behaviours of the catalyst synthesised in direct esterification of glycerol with palmitic acid under different temperatures and the ratio of reactants to identify the best reaction conditions.

1.8 Scope of Study

In this work, the scope is limited to one type of mesoporous catalyst support and active material, the MCF with sulfated zirconia incorporated onto it. This catalyst has been used in the esterification reaction of glycerol with palmitic acid. The loading of the zirconia has been varied (10%, 20%, 30%, 40%) with respect to the total weight of the support. This catalyst SZMCF characterized using several methods such as SEM, EDX, BET, and surface acidity determination using titration. Then, the reaction conditions have been varied such as reaction temperature (160-180°C), catalyst loading (1-3 wt. %) and glycerol to palmitic ratio (2:1-5:1). The best reaction conditions that give highest conversion and yield have been identified.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Monoglyceride can be produced by direct esterification of glycerol with fatty acid in the presence of acidic catalyst. The catalyst must have criteria such as high selectivity towards monoglycerides, high conversion, cost effective as discussed earlier in Chapter 1. Back then the esterification of glycerol with fatty acid is carried out with the presence of an acidic homogenous catalysts such as sulphuric acid and phosphoric acid. This is because as a homogenous catalyst in liquid form in a liquid reaction, it can mix completely with the reactants which will increase the reaction rates and enhances mass transfer drastically. The use of acidic catalysts has advantages in the esterification reaction as the acidic catalyst can release H^+ ions which catalyzes the reaction. However, there's drawbacks with the homogenous catalysts. This is because as it completely mixed in the liquid reactants, it is very hard to separate it from the liquid phase and recover the catalyst (Jamalluddin and Abdullah 2014).

So, a better catalyst that will improve the monoglyceride synthesis process is needed to be explored. Recently, researches have been carried out and one of the best solution for this problem is an acidic heterogenous catalyst. Heterogenous catalysts are differ from the homogenous catalysts in term of phases. These catalysts usually exist in solid form as the esterification reaction occurs in liquid form. Because these catalysts exist in different phase from the reacting mixture it's easier to separate it and recover.

Following is the overview of the development of heterogenous catalyst, formation of MCF and its desirable textural properties that justifies the selection of

this catalyst support. It also reviews the sulfated zirconia applications in various reactions. The sulfated zirconia impregnated MCF could be a very potential acidic heterogenous catalyst because of the abundant pores. Here also reviews the effect of zirconia loading during the catalyst preparation. Following in this chapter will be the critical analysis of the catalysts that are used to produce monoglycerides.

2.2 Mesostructured Cellular Foam (MCF)

Mesoporous materials are highly versatile as a catalyst support and this has led to the researches of various silica based materials such as MCM, KIT, HSM, FSM, and SBA. Firstly, mesoporous molecular sieves such as Mobile Composition of Matter No.41 (MCM-41) had great attention from the researchers and widely used in applications as it possesses high surface area (up to $1000\text{m}^2/\text{g}$), large pore volume and uniform pore size. Because of these characteristics, MCM-41 is a potential catalyst to be used in reactions with bulky molecules (Díaz et al. 2003). However, MCM-41 has thin framework walls which might collapse if undergoes hydrothermal treatment. This makes the application of MCM-41 very limited especially in esterification reaction involving long chain fatty acids which requires high temperature. Zeolites also were tested for the esterification reaction but due to its relatively small pore size they could not be used for the bulky molecules (Stawicka et al. 2013).

Among these mesoporous materials, SBA-15 is one of the most potential support as it has high specific surface area ($600\text{-}1000\text{ m}^2/\text{g}$) and better hydrothermal stability (Tang et al. 2016). However, the SBA-15 has small pores to cause mass transfer restrictions due to long diffusion paths during the liquid reactions (Jamalluddin and Abdullah 2014).

Many research works have been conducted to develop a highly stable mesoporous material which eventually leads to the successful alteration of the SBA-15 structure to form a so-called mesocellular foam (MCF) which is considered as promising material to overcome the drawbacks of SBA-15 and MCM-41. Mesocellular foam is aerogel-like mesoporous material composed of large uniform spherical cells that are easily accessible via large openings which is known as windows (5-20nm) interconnected with uniformly sized windows featuring a continuous three dimensional (3D) mesopore system. This allows large molecules to pass through easier as in like esterification reaction which enhances the mass transfer and allow faster diffusion of reactive particles (Jamalluddin and Abdullah 2014; Widyaningrum et al. 2012).

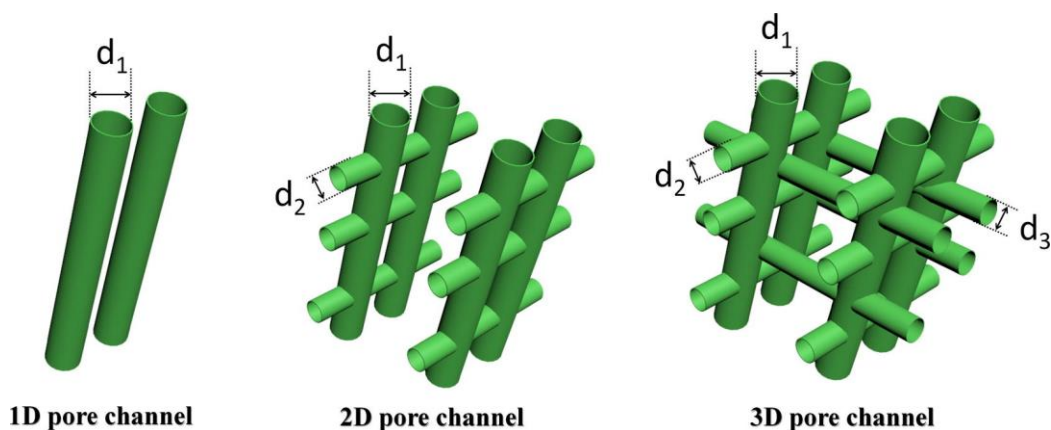


Figure 2.1: The schematic of 1-D, 2-D, and 3-D pore channel (Wei et al. 2016)

The Figure 2.2 shows the SEM images of MCF which shows the large spherical cell interconnected by windows. The formation of sponge or aerogel-like foam of MCF is because of the alteration of SBA-15 synthesis by adding a swelling agent (Aktas et al. 2011). The swelling agent that will be added is usually non-polar substance which starts the formation of MCF structures with its presence in the hydrophobic core of the micelles and expands them (Jamalluddin and Abdullah 2014). This makes the hexagonal structure of the SBA-15 to change into a foam-like structure (Kim et al. 2012). The Figure 2.3 shows the difference between the MCF before adding the swelling agent which is 1,3,5-trimethylbenzene (TMB) and also after adding it (CAT-0 without TMB, CAT-1 1g TMB and followed by 2 and 3)

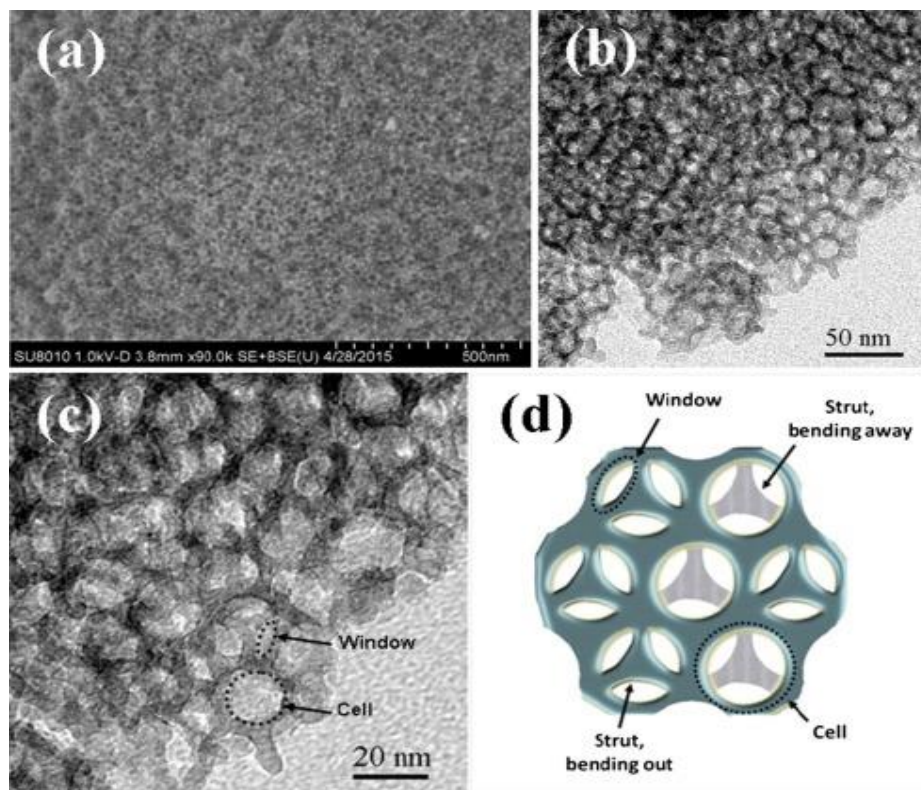


Figure 2.2: Representative SEM/TEM images (a–c) and a model illustration of MCF support showing 3D pore structures (d) (Wei et al. 2016)

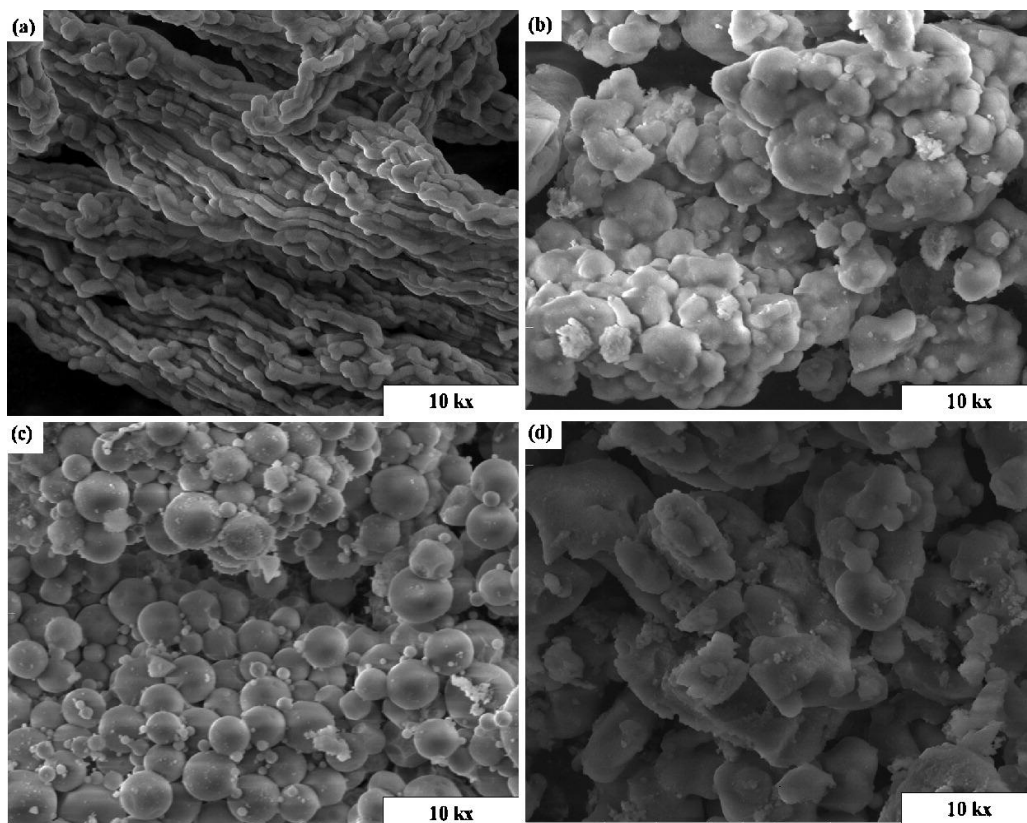


Figure 2.3: SEM images of MCF materials prepared with different TMB dosages and subsequently incorporated with Fe. (a) CAT-0, (b) CAT-1, (c) CAT-2 and (d) CAT-3.

2.3 Sulfated Zirconia

Recently, the alternative for the conventional homogenous catalysts are being researched and the promising replacement is the superacidic catalysts. These superacidic catalysts are very acidic as it called superacidic and it also has some other advantages such as high stability at elevated temperatures, resistance to deactivation and higher regeneration capability (Martins and Schmal 2006; Yadav and Yadav 2014). These superacidic catalysts are also a breakthrough towards an environmentally friendly processes. These superacidic catalysts can be prepared by following three simple steps which are; (1) preparation of metal oxide gels using metal salts, (2) impregnation with sulfating agents (H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$) and (3) calcination of the sulphated materials at high temperature (Yadav et al. 2012).

There various sulphated oxide catalysts have been researched for their application in many reactions. Among them sulphated zirconia received much attention due to its some unique characteristics such as its high thermal stability and superacidic properties. This sulphated zirconia also shows a high activity in various hydrocarbon reactions at mild temperature such as alkane isomerisation and cracking. Sulfated zirconia has demonstrated high activity in the esterification reaction of acetic acid with n-butanol at 75⁰C. According to the author, sulphated zirconia can be completely regenerated after a simple calcination at 550⁰C. For the esterification of dodecanoic acid with 2-ethyl-hexanol at 160⁰C, the catalyst activity only dropped to 90% of its original value after five continuous runs. The transesterification of crude palm kernel oil with methanol in the presence of sulphated zirconia showed a high yield (Suwannakarn et al. 2008).

2.4 Sulfated Zirconia in MCM-41 and SBA-15

Further investigation on the MCM-41 catalyst has been done and new functional groups such as sulfonic acids have been incorporated on to the MCM-41 using co-condensation method (Mohino et al. 2002). The synthesised catalyst has been used in the esterification reaction, a maximum conversion of 98% with selectivity of monoglyceride of 35% after 24 hours of reaction.

Recently, studies showed potential of SBA-15 catalysts usage in direct esterification of glycerol and lauric acid with high selectivity towards monoglyceride. SBA-15 incorporated with sulphated zirconia are being studied under different temperatures (413K-433K). It is found that the conversion increased with increasing temperature. This shows that the at higher temperature the kinetic energy of the

glycerol and lauric acid was higher which leads to the chemisorption of reactants onto the active sites. The higher kinetic energy of the reactants makes the reactants collide more often which increases the effective collision rate, thus increasing the lauric acid conversion. The continuous removal of water from the reactor using the nitrogen purge shifted the equilibrium to form more monoglyceride. The increase in temperature also increased the yield of monoglyceride drastically. This observation shows that the glycerol esterification is mainly occurs inside the mesoporous catalyst, which favoured the formation of monoglyceride compared to di- and triglyceride. Bulkier molecules of di- and triglyceride restricts it to react in the internal mesoporous pores (Hoo and Abdullah 2014).

2.5 Direct Esterification of Glycerol with Fatty Acid

The esterification reaction has been receiving much attention from industries because of the product form the reaction which is organic esters. These organic esters are applied in variety of application (Nagendramma and Kaul 2012; Kong et al. 2016). Esterification is a chemical reaction that occurs with the presence of alcohol and carboxylic acid. The overall conversion in this reaction is slow. With the addition of an acidic catalyst the conversion can be increased significantly in much lesser time. This is because the reaction is alkali and the presence of acidic catalyst has strong acid sites for the reaction to occur and provides more surface area (Testa et al. 2013).

Table 2.1: Glycerol conversion over different solid catalysts (Testa et al. 2013)

| Catalyst | Conversion (%) | |
|---------------------|-----------------------|-----|
| | 1 h | 3 h |
| Blank | 36 | 85 |
| p-TSA | 100 | 100 |
| Amberlyst-15 | 97 | 100 |
| SSBA | 100 | 100 |

Reaction condition: glycerol:acetic acid 1:3; catalyst amount 50 mg; $T = 105\text{ }^{\circ}\text{C}$.

p-TSA: Ptoluensulfonic acid

Esterification of glycerol with fatty acid produces a mixture of mono-, di- and triglycerides with different compositions as shown in Figure 2.4. Among these monoglycerides has an important characteristic as the emulsifier in many industries (Wang and Marangoni 2016).

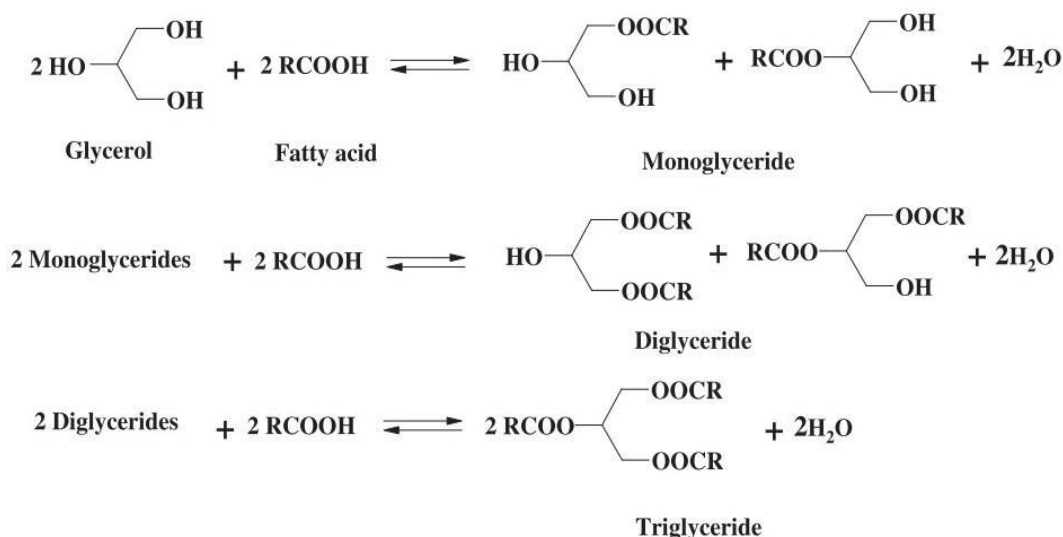


Figure 2.4: Esterification of glycerol with fatty acid (Kotwal et al. 2011)

In the industries, the esterification reactions are carried out in the presence of an acidic catalyst. Back then, the usage of acidic homogenous catalyst is common such as sulphuric acid, phosphoric acid or organic sulfonic acid (Bossaert et al. 1999). These homogenous catalysts have some drawbacks such as large energy consumption, difficult separation or recovery of catalyst, toxic and corrosive. So, the acidic heterogenous catalyst is needed in this reaction to increase the rate of reaction, conversion and the selectivity towards monoglycerides. This heterogenous catalyst also easier to separate and cost effective.

Heterogenous catalyst is very promising candidate for this reaction because it carries many advantages such as reusable, low corrosion, environment friendly and easy separation. This catalyst has also capability to limit the di- and triglyceride formation because the esterification reaction mainly occurs inside the pores of the mesoporous catalyst where the di- and triglyceride cannot form because of narrower space compared to their molecule sizes.

2.6 Factors Influencing the Esterification Reaction

Apart from the type of catalysts, reaction conditions also play an important role influencing the rate of reaction, conversion and selectivity of monoglyceride in the esterification reaction. In order to find the optimum reaction condition for this reaction, some operating conditions are varied during the reaction such as the reaction temperature, catalyst loading and glycerol to fatty acid molar ratio.

2.6.1 Effect of reaction temperature

Reaction temperature is one of the important parameters which affects the rate of the overall reaction and conversion. High reaction temperature is required for the esterification reaction of glycerol with long chain fatty acids to break the molecules and increase the mutual solubility. This statement is further proved by the results from (Hoo and Abdullah 2014). They investigated the effect of reaction temperature in esterification of glycerol and lauric acid. They used 20 wt.%-HPW/DS catalyst which increased the conversion of lauric acid from 50% to 86% when the temperature increased from 150 to 170°C after 3 h of reaction. This is because when the temperature increased the kinetic energy of the reacting particles also increased which increases the number of collisions among them. This increases the rate of effective collisions which in turn increases the rate of reaction significantly.

The effect of reaction temperature is also studied by (Hermida et al. 2011) on the esterification reaction between glycerol and lauric acid to selectively produce monolaurin with the presence of an acidic catalyst HSO₃SBA-15. It is found that the conversion increases as the reaction temperature increases.

2.6.2 Effect of catalyst loading

The catalyst loading also plays an important role in the esterification reaction. It is vital to know the amount of catalyst loading needed because lower amount would actually prolong the time of the reaction whereas the overloading of the catalyst would actually won't have any effect on the conversion and it would be waste of cost. (Hermida et al. 2011) have tested the effect of catalyst loading using HSO₃SBA-15 catalyst loading of 1wt%, 3wt%, and 5wt% with respect to the reactant at reaction temperature of 433K and glycerol/lauric acid molar ratio of 4:1. After the 6 h of reaction time the results showed that the lairoc acid conversion increased when the catalyst loading increased from 1wt% to 3wt%. This increase in conversion is because of the more acidic sites available when the catalyst loading increased. However, the conversion does not increase much when the catalyst loading increased from 3wt% to 5wt%. This is because there are actually more active sites available compared to the actual active sites needed for the reactant to occupy. Then, the monoglyceride yield is remained stable with the increase amount of catalyst loading which further proved the statement that the formation of monoglyceride is indeed occurs in internal mesoporous of the catalyst.

The effect of catalyst loading also investigated by (Hoo and Abdullah 2014) with (1wt% to 5wt%) in the esterification reaction of glycerol and lauric acid using 20wt%HPW/DS catalyst. The reaction rate increased with the increasing catalyst loading which is because of the availability of more acidic sites. However, the highest conversion was at 2wt% catalyst loading.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

In this chapter, the materials and methods used throughout this study are described in detail. Following will be the experimental procedures involved in this study such as the preparation of catalyst, characterization, direct esterification and product analysis.

3.2 List of Chemicals

For the synthesis of catalysts, testing of the catalysts, and direct esterification of glycerol and fatty acid into monoglycerides, a number of chemicals and materials are needed. The chemical needed are listed in Table 3.1, along with their purity, usage and supplier.

Table 3.1: List of chemical used throughout the study

| Chemical | Purity | Purpose of Use | Supplier |
|---|---------------|-----------------------|-----------------|
| Plunoric 123 | | Preparation of MCF | Aldrich |
| Tetraethyl Orthosilicate (TEOS) | 99% | Preparation of MCF | Merck |
| Hydrochloric Acid (HCL) | 37% | Preparation of MCF | Fischer |
| 1,3,5-trimethylbenzene (TMB) | 99% | Preparation of MCF | Aldrich |
| Urea | 99% | Preparation of SZMCF | Fischer |
| Sulphuric Acid (H ₂ SO ₄) | 97% | Preparation of SZMCF | Fischer |
| Zirconyl chloride octahydrate (ZrOCl ₂ ·8H ₂ O) | 98% | Preparation of SZMCF | Acros Organic |

| Chemical | Purity | Purpose of Use | Supplier |
|-----------------|---------------|---------------------------------------|-----------------------|
| Glycerol | 99.8% | Esterification reaction | R&M Chemical |
| Palmitic Acid | 98% | Esterification reaction | Merck |
| Monopalmitin | 99.9% | GC standard for calibration | Supelco Analytical |
| Dipalmitin | 99.9% | GC standard for calibration | Supelco Analytical |
| Tripalmitin | 99.9% | GC standard for calibration | Supelco Analytical |
| Acetone | 99.5% | Product Analysis | R&M Chemical |
| Methyl Acetate | 99% | Product Analysis | R&M Chemical |
| n-tetradecane | 99% | Internal standard in product analysis | Merck |
| Methanol | 99.9% | Solvent for catalyst recovery | Merck |

3.3 Experimental Flow Chart

The flow diagram of the methodology involved throughout this study is shown in Figure 3.1. There are four stages involved in this study which are catalyst preparation, catalyst characterization, active study in glycerol esterification with palmitic acid and reaction kinetic study. First the MCF support is synthesised which was then incorporated with zirconia to obtain ZrMCF which was then impregnated in sulphuric acid to obtain SZMCF. The prepared MCF, ZrMCF, SZMCF was then characterized using XRD. The performance and catalytic behaviour of SZMCF was compared with MCF in glycerol esterification with palmitic acid.

The activity of the catalyst was studied and the best catalyst was chosen with high conversion and high selectivity towards monopalmitin. The catalyst is then selected for further study to investigate the effects of reaction conditions towards the conversion of palmitic acid and monopalmitin yield.

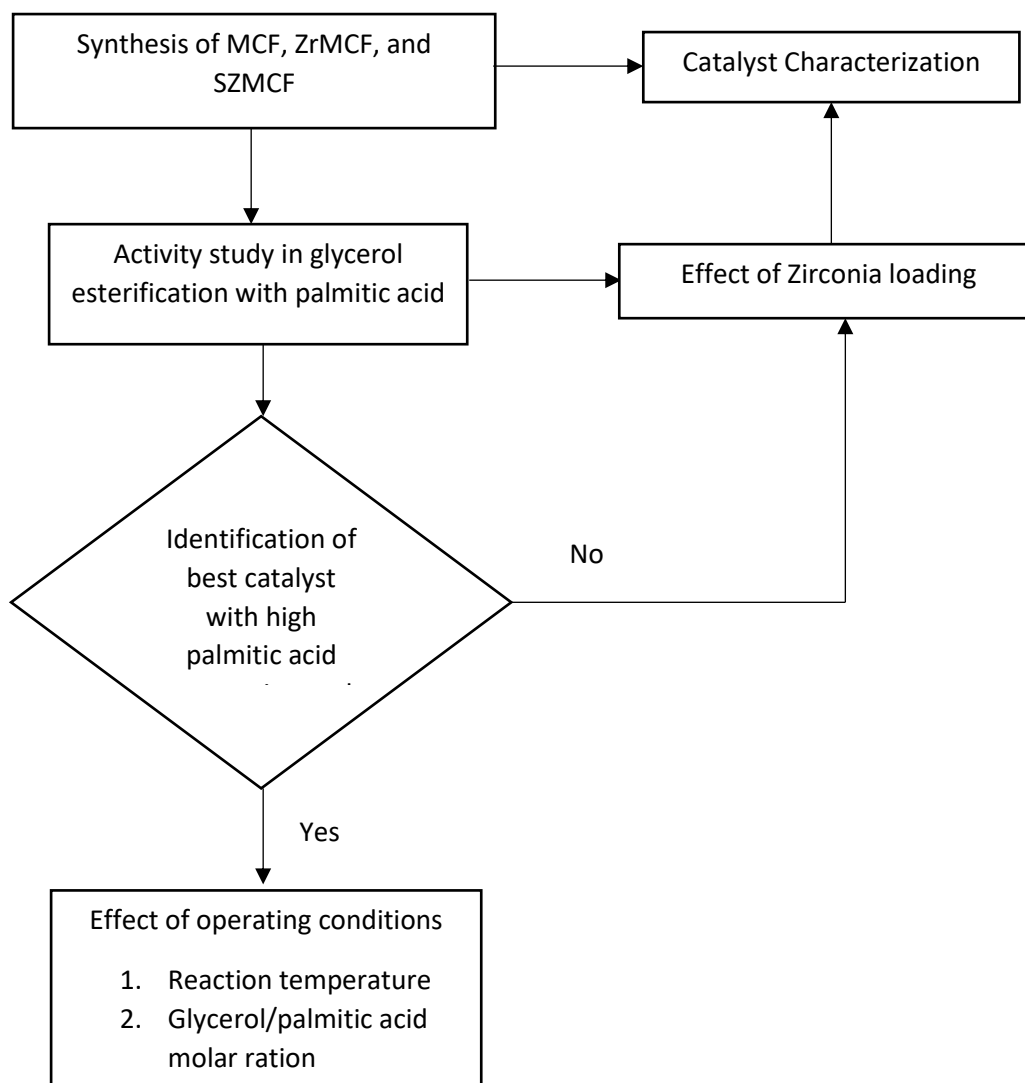


Figure 3.1: Flowchart of overall experimental works

3.4 Equipment

There are several equipment used in this study. The main equipments used are listed in the Table 3.2.

Table 3.2: List of equipment used

| Equipment | Brand | Purpose of use |
|------------------------|-----------------------------------|--|
| Analytical balance | Shimadzu | Weight measurement |
| Stirring hot plate | IKA [®] RET basic | Sol-gel preparation |
| Oven | Memmert | Hydrothermal treatment of sol-gel solution Drying of sample |
| Heating mantle | Favorit | Incorporation of zirconia via urea hydrolysis |
| Furnace | Carbolite | Calcination of MCF and catalysts |
| Micro centrifuge | Profuge 6K | To separate product mixture |
| Gas chromatography FID | Agilent Technologies 7820A system | To determine the product (mono-, di- and tripalmitin) |