DEVELOPMENT OF CATALYSTS IN CHEMICAL INTERESTERIFICATION FOR GLYCEROL-FREE BIODIESEL PRODUCTION: CRITICAL ANALYSIS

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"DEVELOPMENT OF CATALYSTS IN CHEMICAL INTERESTERIFICATION FOR GLYCEROL-FREE BIODIESEL PRODUCTION: CRITICAL ANALYSIS"** was prepared by **CHOK WENG SHAN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Biodiesel production is commonly carried out via transesterification in which glycerol is produced as the by-product. Glycerol has a low market value and it is normally treated as waste product from the reaction. Separation process is also required to isolate the glycerol to obtain pure biodiesel. In fact, glycerol-free biodiesel production can be achieved through chemical interesterification which is an alternative route to the conventional transesterification reaction. Instead of glycerol, triacetin is produced as the by-product from chemical interesterification. Similar to conventional transesterification, chemical interesterification requires catalyst as well. This study analysed and compared the catalyst performance reported in the literature to find the best catalysts for the reaction. Different types of catalysts such as homogeneous acid (14%), homogeneous base (38%), heterogeneous acid (24%) and heterogeneous base (24%) catalysts were obtained from a total of 55 catalysts reported in 30 journals from year 2011 to 2020. Different aspects were analysed such as the biodiesel yields, reaction temperature, reaction time, catalyst amount and acyl acceptor to oil molar ratio. CH_3NaO (base) and CaO (base) were selected as the best homogeneous catalyst and heterogeneous catalyst, respectively based on their overall aspects. Based on the results reported, CH_3NaO was able to achieve 93% biodiesel yield with 20:1 methyl acetate to oil molar ratio (MAOMR) and 0.05:1 catalyst to oil molar ratio (COMR) at 60 °C for 0.2 hour (12 minutes). On the other hand, CaO was able to generate 90.5 wt.% of biodiesel with 30:1 ethyl acetate to oil molar ratio (EAOMR) and 4.0 wt.% catalyst at 80 °C for 5 hours. Potential catalysts to be used in chemical interesterification were also suggested such as tungsten phosphoric acid and sodium silicate. These are heterogeneous acid and base catalysts that were reported in transesterification with good performances. This analysis ultimately enables more efficient production of biodiesel through interesterification process in the future by selecting the suitable catalysts. This study also provides a direction for future catalyst development in chemical interesterification for biodiesel production.

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LIST OF SYMBOLS / ABBREVIATIONS

m_{actual}	actual ethyl ester mass, g
$m_{theoretical}$	theoretical ethyl ester mass, g
n	diluted multiple of ethyl ester
C_{ester}	ester mass concentration, g/mL
ρ_{oil}	oil density, g/mL
C	methyl oleate concentration, g/L
V_f	total product volume, L
m_i	total oleic acid mass, g
C_T^0	initial triglyceride concentration, M
C_T^t	triglyceride concentration at time ‘t’, M
C_{TA}^t	triacetin concentration at time ‘t’, M
C_{MADG}^t	MADG concentration at time ‘t’, M
C_{DAMG}^t	DAMG concentration at time ‘t’, M

BuMe	butyrate methyl ester
COMR	catalyst to oil molar ratio
DAMG	diacetinmonoglyceride
DBU	1,8-Diazo-bicyclo-[5.4.0]undec-7-ene
DMC	dimethyl carbonate
EAOMR	ethyl acetate to oil molar ratio
FAAE	fatty acid alkyl ester
FAEE	fatty acid ethyl ester
FAGC	fatty acid glycerol carbonate
FAME	fatty acid methyl ester
FFA	free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HMS	hexagonal mesoporous silica
HPA	heteropoly acid
HPLC	High Performance Liquid Chromatograph
KPEG	potassium polyethylene glycol

MADG	monoacetindiglyceride
MAOMR	methyl acetate to oil molar ratio
MNP	magnetic nanoparticle
MS	methanesulphonic
OPEFB	oil palm empty fruit bunch
PEG	polyethylene glycol
PGMA	poly-glycidylmethacrylate
SEM	Scanning Electron Microscopy
TA	triacetin
TBD	1,5,7-Triaza-bicyclo[4.4.0]dec-5-ene
TDA	1,2,3-Trizaole-4,5-dicarboxylic acid
TGA	Thermogravimetric Analysis
THF	tetrahydrofuran
TPA	tungsten phosphoric acid
TPD	temperature-programmed desorption
USY	ultrastable Y zeolite
WCO	waste cooking oil
XRD	X-ray Diffractometer

CHAPTER 1

INTRODUCTION

1.1 Global Energy Crisis

Undeniably, energy has now become a basic need in the human life. Human needs some forms of energy in order to accomplish nearly everything in our life, from a simple task like typing this paper that uses electrical energy for the laptop, to driving a vehicle that uses energy from the petroleum. It is known that energy will soon be depleted as everyone uses up so much energy in a single day. Looking at this fact, it is anticipating that energy crisis is going to happen soon in this planet. In fact, energy crisis had occurred during the 1970s. However, it is not as daunting as the one that is ahead of us, due to the developments and evolutions in the past decades.

There are sources for every energy and there are different types of sources due to their renewability, namely renewable energy source and non-renewable energy source. Renewable energy source is the source of energy that is unlimited in availability as it can regenerate promptly in a nearly limitless large amount. Examples for renewable energy source are solar energy, wind energy, hydro energy, tidal energy, geothermal energy and biomass energy. On the other hand, non-renewable source is an energy source with a very long regeneration time. Crude oil, coal and earth gas are the examples of this. Although some of these sources are available in a huge amount, they will eventually run out and not be replenished in our lifetimes due to the increase of the demand of these energies.

One of the energy crises that is believed to occur soon is the oil crisis. Oil crisis age would begin when there is a peak oil. The definition of peak oil is a point when the global extraction of petroleum reaches the maximum rate, the production rate after the point would enter a terminal decline. Based on the consumption rate of oil now, it would be gone and reaches the peak oil in about 30 years (Rhodes, 2009). Oil production is the main problem to cause oil crisis as there are very little oil being discovered for the past 30 years. Oil can be produced only if they were found, and there is only certain amount of oil in oil fields found. There were some peak oils happened in the history such as the

United State in 1971, the North Sea in 1999 and Mexico in 2006 (Kerr, 2011). The major oil production now includes the Russian Federation as well as the Middle East and both of them would reach the peak oil eventually. Figure 1.1 shows the past discoveries of oil and gas for the past decades as well as the exploration spending.

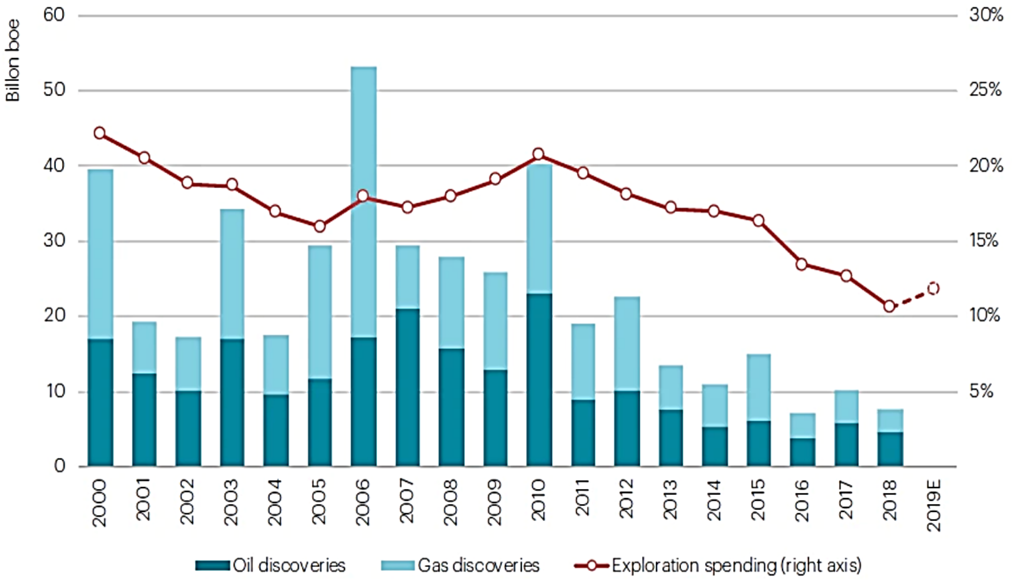


Figure 1.1: Past Discoveries of Oil and Gas from 2000 to 2018 (IEA, 2019)

Looking at Figure 1.1, it is shown that the oil discoveries are inconsistent and declining since the peak at the year 2006. In fact, the production of oil is increasing due to the rising demand of oil. With the current trend of oil discoveries, exploration requires acceleration or there will be not enough oil to meet the demand through 2050 (Rystad Energy, 2020). This is due to the cruel yet true fact that most of the oil in this planet has already been discovered and there is not much left to be found. The path that should be focused on to avoid the oil crisis is to start using renewable energy so that we are not totally relying on the non-renewable fossil fuel.

1.2 Biofuel

With concerns of rising oil prices and global warming that is mainly contributed by fossil fuels, biofuel has been the potential solver for all the problems as it is a source of renewable energy. Biofuel is basically any fuel derived from a living matter, which is called biomass (Lehman, 2020). Example of biomass are animal waste, plant and algae material. The purpose of biofuel is to replace the conventional fuels, also known as fossil fuels like petroleum, coal and natural gas that are considered as non-renewable energy source. However, expansion of biofuel production would require more farmlands to grow crops instead of food. Moreover, the cost to produce biofuel currently has not yet been able to compete with the cost to produce petroleum. According to the International Energy Agency, the target for global biofuel production is to triple it by 2030 in order to achieve the sustainable growth (Nunez, 2019).

Generally, there are multiple methods to produce biofuels such as fermentation, chemical reactions as well as using heat to break down sugars, starches and other molecules found in plants. After that, the products from these methods are refined to produce fuels that can be used in the vehicles, which is called liquid biofuels. Liquid biofuels are getting the most attention as they are mostly used in the transportations. Biodiesel is the second most popular liquid biofuel other than ethanol biofuel. It is generally made from oleaginous plants like oil palm and soybean. Other oil sources such as kitchen waste is also usable for biodiesel production. In Europe, biodiesel is very popular for diesel engines and it is commonly blended in different percentages with petroleum diesel fuel. Pure biodiesel can also be used in newer engines or modified engines. However, biodiesel has a higher freezing temperature than the conventional diesel. This makes high blends of biodiesel to freeze easily in cold weather.

In fact, biodiesel can also be made from algae and cyanobacteria known as the third-generation biodiesel. It is an improvement from previous generations of biodiesel as there is up to 40% of lipids by weight in algae that can be converted into biodiesel (Lehman, 2020). Scientists also found that the yield of biodiesel from algae and cyanobacteria was 10 to 100 times greater than the second-generation biofuels. However, the current production of biofuels is more expensive due to the high amount of energy required to produce them. Besides, some of the biofuel industrial productions actually emit more greenhouse gases that would offset the advantage by using renewable fuels. Due to the Covid-19 pandemic in 2020, the crisis has significantly impacted the energy used in the world. Global energy demand has declined in early 2020 but interestingly, the demand in renewable energy source is the only one that is currently growing (IEA, 2020).

1.3 Biodiesel in Malaysia

Biodiesel production is huge in Malaysia, due to the large availability of palm oil. It was forecasted to produce 1.56 billion litres of palm biodiesel in 2019, as the market demand was boosted since the launching of B10 blend which is a mixture of 90% petrol diesel with 10% palm biodiesel in 2018. Malaysia is also the second largest producer of palm oil after Indonesia (Chin, 2019).

Palm biodiesel is one of the liquid biofuels that is made from the renewable energy source. It can be blended with petrol diesel in any percentage or even fully replace petrol diesel in newer unmodified diesel engines. Besides, it can also be used in other transportations as well as the industrial applications. The government of Malaysia is currently expanding the markets of palm biodiesel to countries like the Middle East, Africa as well as Central Asia. By having a huge palm oil industry in Malaysia, this can boost the revenue and economy of Malaysia significantly. The development and researching of palm biodiesel in Malaysia actually began since 1981. It is also planning to introduce B20 blend which consists of 20% palm biodiesel in 2020. However, it is being delayed due to the outbreak of Covid-19 this year. Figure 1.2 shows the history of palm biodiesel developments in Malaysia.

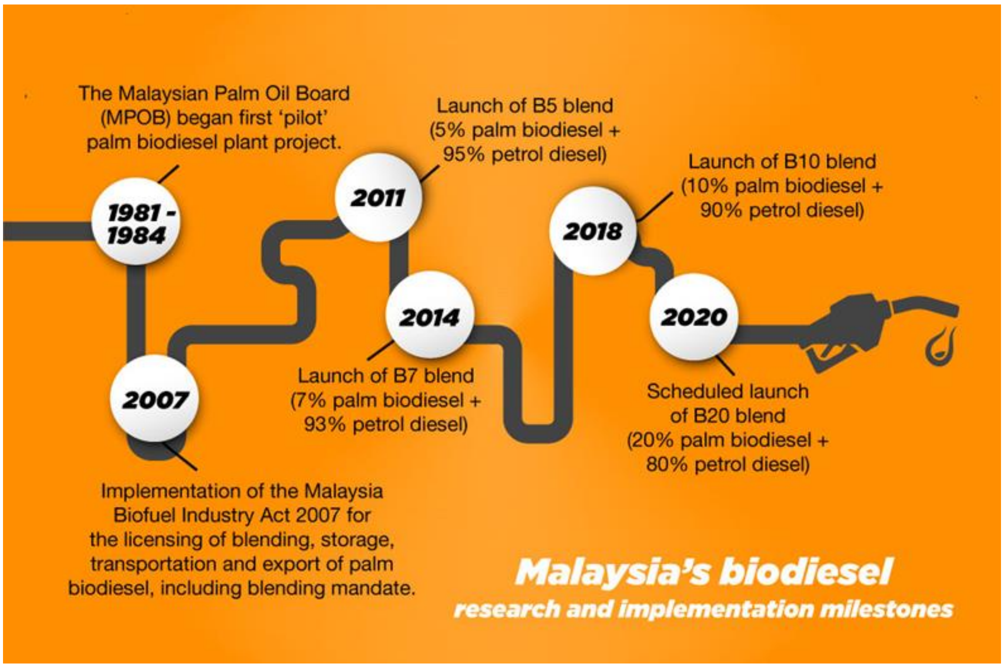


Figure 1.2: Malaysia's Palm Biodiesel Developments (Chin, 2019)

There are many benefits of using palm oil to produce biodiesel. In fact, the wastes made by palm oil industry can actually be recycled to become the feedstock of palm biodiesel production. This is viable due to the current innovative technologies, making palm oil a zero-waste crop for biodiesel production (Chin, 2019). Oil palm is also considered as the most productive crop among other oil crops. It is also economical friendly as it costs lesser than other vegetable oils used to produce biodiesel. As other crops may be vulnerable to weather changes, oil palm does not have this problem as it is less susceptible to weather changes. This makes it a more reliable source for the feedstock of biodiesel production (Chin, 2011).

1.4 Interesterification Process to Produce Biodiesel

There are several methods in the biodiesel production such as fermentation, micro-emulsification, pyrolysis and the most common method which is transesterification. Apart from these methods, there is also an alternative route to produce biodiesel called the interesterification process, which is said to be better than the transesterification process.

In the classical transesterification process, it is usually a reaction between a triglyceride which is the fatty acid with an alcohol like methanol or ethanol. However, there are several by-products in this reaction such as glycerol and water. Up to 10% of glycerol can be formed and it is considered as a waste product in biodiesel production through transesterification process (Sendzikiene and Makareviciene, 2019). This forms a problem when the biodiesel production keeps expanding, while the demand of glycerol remains low or none. Furthermore, separation process is needed to isolate the glycerol for a high purity biodiesel. This requires purification steps that make the process energy intensive and less cost effective.

In order to address the cons of transesterification process, interesterification process can be another alternative route. It is also a topic that scientists and researchers are focusing now as it brings several advantages compared to the conventional transesterification process. In interesterification process, triglyceride is being reacted with methyl acetate or ethyl acetate, which is a carboxylate ester instead of an alcohol. Figure 1.3 shows the chemical interesterification of triglyceride and methyl acetate.

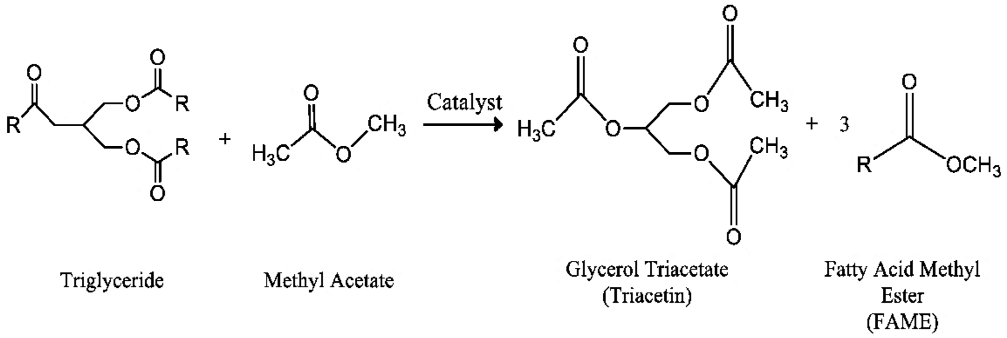


Figure 1.3: Interesterification Reaction (Estevez et al., 2019)

In this reaction, methyl ester or biodiesel will be formed with a by-product as well. However, instead of glycerol, the by-product from this reaction is triacylglycerol, also known as triacetin. In fact, triacetin is actually a useful by-product that can act as additive to biodiesel. Triacetin is found to be an anti-knocking agent in diesel engine that uses biodiesel. This is a huge advantage as the separation process could be eliminated to save cost and energy. Besides, triacetin also enhances the low-temperature characteristics of fuel (Sendzikiene and Makareviciene, 2019).

Interesterification process is currently not as popular as the transesterification process in biodiesel production because the catalyst used, parameters and other technical information are still under research. Researchers need to find the best operating condition for the reaction in order to maximize the yield of biodiesel, while making it cost effective at the same time. Undeniably, interesterification process has a huge potential to become the major pathway to produce biodiesel in the future.

1.5 Problem Statement

There are several types of interesterification pathways to produce biodiesel. This study will specifically focus on the chemical interesterification where catalyst is required in the process. There are different types of catalysts can be used in this reaction but the best one is yet to be discovered. Since this type of interesterification has not been investigated widely yet, the optimum operating conditions for this reaction still need to be determined. Researchers and scientists are trying their best to create a well-optimised process for this reaction, by considering the operating conditions such as the thermodynamic and kinetic reaction aspects as well as the types of catalyst used in the reaction. The catalysts are categorized into two types, homogeneous catalyst and heterogeneous catalyst. Besides, there are also acid catalyst as well as base catalyst. Both of the catalysts can be used in the chemical interesterification. Different types of catalyst have different effects on the reaction.

1.6 Importance of Study

Nowadays, researchers in the biodiesel production field are starting to shift towards chemical interesterification due to its benefits over the conventional transesterification as stated previously. Hence, it is important to study the development of chemical interesterification in biodiesel production. One of the most significant factors that affect the reaction is the catalyst. Hence, it is also important to study how different types of catalysts affect the reaction in terms of biodiesel yield and reaction parameters. Besides, more types of catalyst need to be tested in interesterification process to gauge their performances as it is still immature in the industry and not often being reported.

1.7 Aims and Objectives

In this study, different types of catalysts used in chemical interesterification to produce biodiesel will be analysed. There are a total of three main objectives in this project:

1. To compare different types of homogeneous and heterogeneous catalysts (acid and base) used in chemical interesterification on the yields, reaction parameters (temperature, time, catalyst loading, acyl acceptor to oil molar ratio) and reusability of catalyst.
2. To conduct analysis on different catalysts used in chemical interesterification based on journals to find out the most suitable catalysts in terms of yields, reaction parameters, catalyst reusability and overall aspects.

3. To suggest potential catalysts from conventional transesterification that can be used in chemical interesterification for biodiesel production.

1.8 Outline of the Report

The report consists of five chapters which includes the introduction, literature review, methodology and workplans, results and discussions, and conclusions. In the first chapter which is the introduction, global energy crisis is explained along with the reasons that cause it to happen. To solve this, biofuel is introduced to replace fossil fuel which is a non-renewable source. Biodiesel is one of the liquid biofuels, the current market and history of biodiesel in Malaysia are also stated in the first chapter of the report. Besides, interesterification process in biodiesel production is also explained briefly. Problem statement and the objectives of this project are included as well.

The second part of the report is regarding to the literature reviews done in this research. This includes the studies of different type of catalysts used in transesterification as well as chemical interesterification reactions. This section also compares homogeneous catalysis and heterogeneous catalysis reactions. Reaction parameters in interesterification are also discussed briefly.

The third chapter includes the methodology of this report. This section focuses on the analysis methodology which includes all the steps involved in completing the paper. There are a total of five steps and every step is explained briefly in this section.

The fourth chapter includes the journals collected with different catalyst used in chemical interesterification. This section categorises the catalysts into different categories and compares their biodiesel yields, reaction parameters and reusability of catalyst. This part also includes analyzation to find out the best homogeneous and heterogeneous catalysts in each aspect and also overall aspects. The last part of this chapter suggests two potential catalysts from transesterification reaction to be used in the chemical interesterification for biodiesel production.

The last chapter in the report is the conclusions and recommendations for future research. This section provides a summary on the report and also some insights for the development of catalysts in chemical interesterification.

CHAPTER 2

LITERATURE REVIEW

2.1 Production of Biodiesel

There are different ways to produce biodiesel which consist of different types of raw materials such as frying, refine and crude oils. Most of the methods like transesterification and chemical interesterification require catalyst and different types of catalyst can be used for different pathways. There are acidic catalysts as well as basic catalysts. Examples for bases are potassium or sodium hydroxides while for acids are sulphuric acid. Besides, lipase, supercritical fluid and ion exchange resins are also the choices of the catalyst to be used in biodiesel production.

Biodiesel is produced by natural and renewable raw materials which are the oils from animal fat and vegetables. The benefits of these raw materials are the fact that they are biodegradable and non-toxic. Vegetable oils can be extracted from different types of plants such as soybean, cottonseed, palm and coconut, as well as lard and tallow from animals. Table 2.1 shows the typical composition of different types of fatty acid found in these oils.

Table 2.1: Fatty Acid Composition for Different Oils (Marchetti, Miguel and Errazu, 2007)

Fatty acid	Soybean	Cottonseed	Palm	Coconut	Lard	Tallow
Lauric	0.1	0.1	0.1	46.5	0.1	0.1
Linoleic	53.7	55.2	10.1	2.2	10.7	2.9
Linolenic	8.6	0.6	0.2	0.0	0.4	0.9
Myristic	0.1	0.7	1.0	19.2	1.4	2.8
Oleic	22.8	19.2	40.5	6.9	44.2	42.4
Palmitic	10.2	20.1	42.8	9.8	23.6	23.3
Stearic	3.7	2.6	4.5	3.0	14.2	19.4

Biodiesel production starts from vegetable oils, and reacted with different chemicals to produce biodiesel, resulting to different pathways of production. One of the most common methods is the transesterification method which has been used in the industry for a long time. The alternative pathway to produce biodiesel is interesterification method which is less well-known and carries a huge potential in future.

2.1.1 Transesterification

Production of biodiesel from transesterification is the most popular method in the industry. In transesterification, triglycerides from different types of oils react with an alcohol to form esters and glycerol, where catalyst is required in this reaction. The overall chemical equation is shown in Figure 2.1. The esters produced from the reaction is the final product, which is biodiesel. The common esters synthesised are methyl esters and ethyl esters, as methanol and ethanol are the general alcohols for the reaction. Methyl esters are the common fuel in most of the places due to the lower cost of methanol. However, in Brazil, ethyl esters are being used as fuel as ethanol is less expensive there.

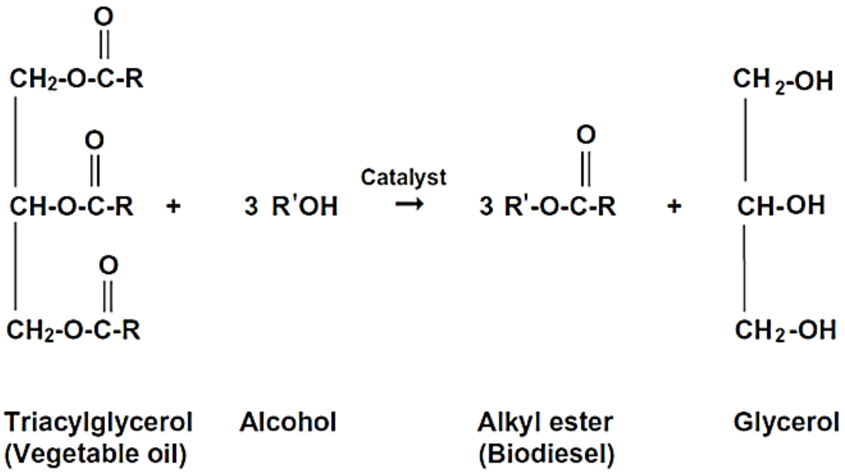


Figure 2.1: Catalytic Transesterification (Van Gerpen et al., 2010)

Transesterification is the conventional method to produce biodiesel and it has existed in the industry for a long time. However, the drawback in this method is the by-product glycerol being a waste product and purification is needed to yield pure biodiesel.

2.1.2 Interesterification

Researchers have found a promising alternative pathway to produce biodiesel, which is the interesterification of triglycerides and methyl acetate. Unlike transesterification which is an exchange of an alkoxy group when an ester is reacted with an alcohol, interesterification is the exchange of alkyl groups when two different esters are being reacted together. The chemical equation of a general interesterification is shown in Equation (2.1):

$$R_1CO - OR_2 + R_3CO - OR_4 \leftrightharpoons R_1CO - OR_4 + R_2CO - OR_2 \qquad (2.1)$$

Interesterification is said to be better than transesterification due to the different by-product formed in the production of biodiesel. Generally, triglycerides are reacted with methyl acetate to form fatty acid methyl esters (FAME) which is the biodiesel as well as a by-product called triacetin. Triacetin is a more valuable by-product as compared to glycerol that is formed from transesterification process. Triacetin has a variety of applications such as a gelatinizing agent or plasticizer for polymers and explosives (Bonet et al., 2009). Besides, it is also soluble in biodiesel itself and it can even act as a fuel additive (García et al., 2008). Interesterification has been known as the solution to various problems found in the conventional transesterification in biodiesel production.

During the interesterification, methyl acetate is used instead of an alcohol which is used in transesterification. This changes the polarity of the reaction mixture from polar to non-polar, due to the absence of alcohol as the reactant (Casas, Ramos and Pérez, 2011b). In the case where catalyst is used, catalyst will become partial insoluble. In the production of biodiesel, there are three consecutive reversible reactions involved in the interesterification reaction. As illustrated in Figure 2.2, when reacted with methyl acetate, the triglycerides from vegetable oils are first converted into monoacetindiglyceride (MADG). After that, MADG is converted into diacetinmonoglyceride (DAMG) in the presence of methyl acetate. In the final step, DAMG is converted into the final by-product which is triacetin, where a molecule of FAME is released in each step. These reactions are highly reversible due to the high miscibility of both reactants and products.

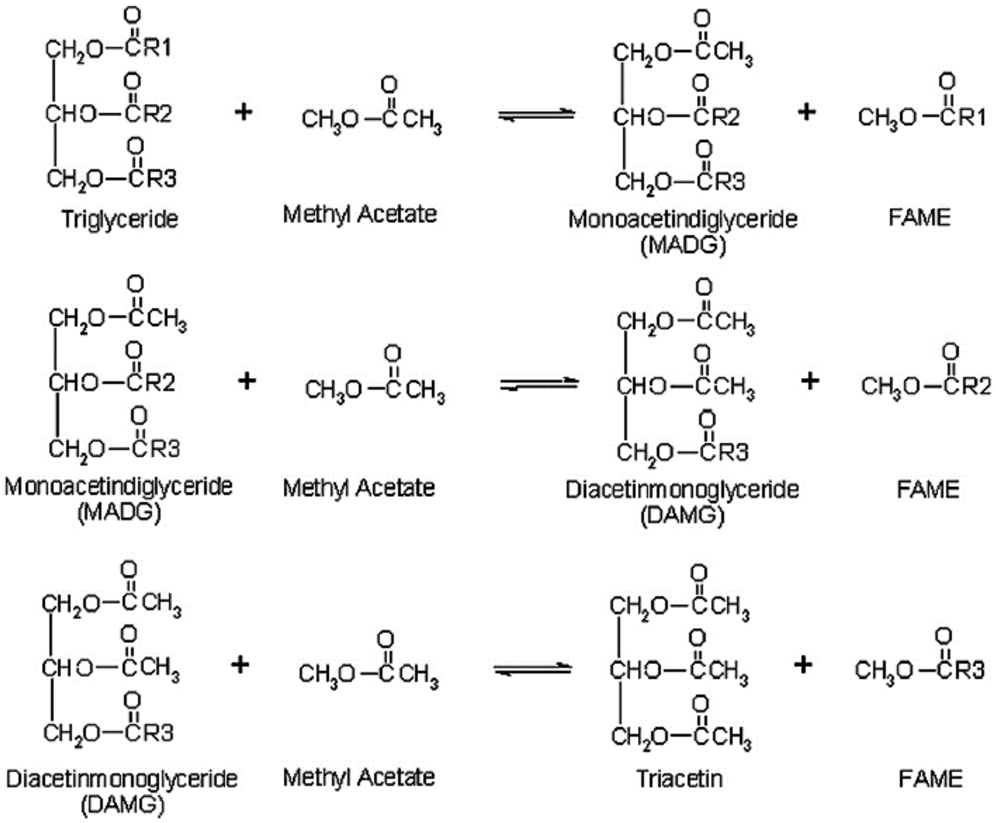


Figure 2.2: Consecutive Interesterification Reactions (Casas, Ramos and Pérez, 2011b)

2.2 Chemical Interesterification

There are three types of interesterification which are chemical interesterification, enzymatic interesterification as well as supercritical interesterification. In the production of biodiesel, interesterification has been mostly investigated under supercritical condition or using enzymes. Chemical interesterification that uses catalyst is rarely being studied and it has only been investigated based on the transesterification, where alkali methoxide catalyst is used for interesterification of vegetable oils. Chemical interesterification has the most potential among all the processes as it has the lowest operation costs and the fact that it can be carried out under mild reaction conditions (Casas, Ramos and Pérez, 2011a).

Unlike enzymatic interesterification and supercritical interesterification, chemical interesterification has not been widely investigated yet. In the past, the ester interchange reaction of triglycerides in chemical interesterification is being focused the most. It is usually employed to enhance the properties such as microstructure, thermal behaviour, crystallization properties and polymorphism of the oils and fats (Casas, Ramos and Pérez, 2011b). In the history, this type of interesterification of oils was first introduced by Normann, Grün and Van Loon during the 1920's. Various types of catalyst were used such as alkaline earth metals and alkali metals compounds, sulfonic acid and compounds of cadmium, lead, tin and zinc. The temperature is different for different types of catalyst, for instances, alkali metals are used at lower temperature below 130 ℃ whereas sulfonic acid as well as other metal compounds are used at higher temperatures from 130 ℃ to 260 ℃ (Going, 1967).

Since the catalyst for interesterification is studied based on transesterification, the catalyst like alkali hydroxides that are typically used in transesterification are being tested in interesterification. Alkali methoxides are also used in transesterification as it reduces the formation of soap and provides higher yield (Bautista et al., 2009). However, in the case of interesterification that involves esters, these catalysts have a limited solubility, hence limiting the application of these catalysts in interesterification reaction. There is a way to increase the solubility of these catalyst by using polyethylene glycol (PEG) with potassium (KPEG). PEG is a phase transfer catalyst that can be used in the case where the catalyst is not miscible with the reagents. KPEG complex can be formed to improve the solubility of nucleophiles like potassium hydroxide and potassium methoxide (Casas, Ramos and Pérez, 2011b).

Typically, methyl acetate is being used as the acyl acceptor in interesterification with triglycerides. Methyl acetate is not the only acyl acceptor that can be used as ethyl acetate can also be used in the production of biodiesel. By reacting ethyl acetate and triglyceride, fatty acid ethyl esters (FAEE) will be formed as the biodiesel product. However, it has not been investigated widely yet as researchers focus more on methyl acetate. Nevertheless, ethyl acetate is still a potential acyl acceptor due to its renewable characteristic (Chuepeng and Komintarachat, 2018). Other than ethyl acetate, dimethyl carbonate (DMC) is also a good option of acyl acceptor in interesterification reaction. This is also a glycerol-free production of biodiesel as DMC reacts with triglyceride to form two moles of FAME and fatty acid glycerol carbonate (FAGC) as the by-product. The reaction is shown in Figure 2.3.

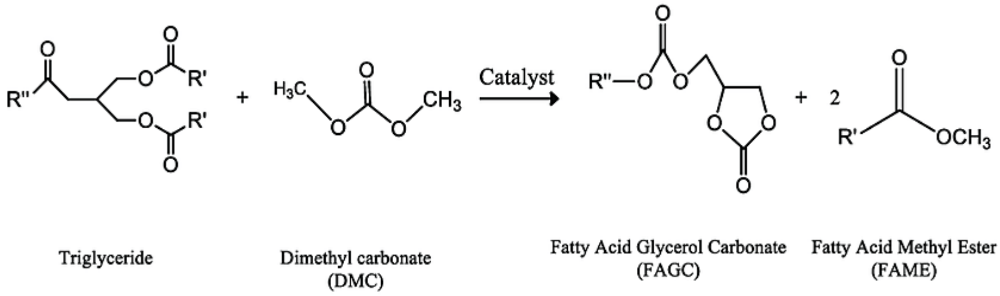


Figure 2.3: Interesterification of Triglyceride and DMC (Estevez et al., 2019)

The replacement of typical methyl acetate with DMC is attractive and beneficial due to the characteristics of DMC. It is also known as a green reagent prototype because of its environmental friendly properties and contains no harm to humans. DMC is less toxic than methanol and it is one of the safest chemicals as it is non-flammable, non-corrosive and non-toxic (Choi et al., 2002). In fact, DMC can be produced by methanol and carbon monoxide, where these raw materials can both be obtained from the synthesis gas of the thermochemical conversion of biomass (Choi et al., 2002).

2.2.1 Homogeneous and Heterogeneous Catalysis

Chemical interesterification is a reaction that requires catalyst and it can be categorized into two types which are homogeneous catalyst and heterogeneous catalyst. A homogeneous catalyst represents a catalyst that is in the same phase as the reactant. On the other hand, a heterogeneous catalyst is a catalyst that is in a different phase with the reactant. This can be referred to the catalyst used in transesterification in biodiesel production as interesterification has not been widely investigated yet. In the alcoholysis of transesterification, homogeneous catalyst is typically used and there are also acid and basic catalysts. In the conventional biodiesel production, basic catalysts are the most common catalyst in the industry for a long time. This is because a base catalysed reaction offers advantages such as higher yield of fatty acid alky esters. Besides, the reaction is much faster than an acid catalysed reaction and it can occur in milder reaction conditions. However, it can be affected by the amount of free fatty acids (FFA) and also the moisture concentration of the raw materials (Avhad and Marchetti, 2016).

In fact, a homogeneous catalysis reaction has a lot of disadvantages in the production of biodiesel. For example in the transesterification, the isolation of the glycerine from the catalyst is very difficult as they are in the same phase. To purify the biodiesel, large amount of water is required and by doing so, tons of wastewater will be generated as the consequence (Ferreira et al., 2019). Taking consideration to the cost of production, homogeneous catalyst is not able to be reused after a reaction. Certain equipment is also required to perform the separation process as the catalyst is dissolved in the reagents. Hence, the main problem in homogeneous catalysis system is the high process cost (Da Costa Evangelista et al., 2016).

Taking account of the drawbacks brought by homogeneous catalyst in biodiesel production, heterogeneous catalyst becomes a viable alternative. Since heterogeneous catalyst is not in the same phase as the reactant and not being dissolved in the medium, separation of the catalyst from the mixture is fairly easy. There will be less impurities in the products and it reduces the purification cost of biodiesel (Da Costa Evangelista et al., 2016). Moreover, heterogeneous catalysts can be reused and regenerated easily. Hence, it is good for both the industry as well as the environment. Not only it can reduce the production cost by reusing and regenerating, water treatment in the separation process is also unnecessary (Dossin et al., 2006). Besides, by using heterogeneous catalyst, it will not form soap in the process (Da Costa Evangelista et al., 2016). However, heterogeneous catalyst in biodiesel production is still immature at the moment.

Heterogeneous catalysts are good alternatives as they can solve the problems faced by using homogeneous catalysts. Most of the studies in biodiesel production nowadays have turned into using heterogeneous catalysts to replace acid and base homogeneous catalysts. This is due to the great characteristics of the heterogeneous catalysts in the economic aspects as they are non-corrosive and their ability to be regenerated and reused in continuous process, as well as the easy separation from the product. Most importantly, they are not sensitive to the FFA concentrations in the oils and therefore the raw materials are not restricted. Besides, the fact that they does not produce any soap eliminates the washing step that requires extra cost (Sani, Daud and Abdul Aziz, 2014). Several studies have reported the usage of heterogeneous solid catalysts in the yield of transesterification such as calcium oxide, magnesium oxide, hydrotalcites, ion exchange resins and so on, as shown in Table 2.2 with different types of oils.

2.2.2 Acid and Base Catalysts used in Interesterification

Homogeneous catalysis in the production of biodiesel is the major pathway and it has been reported through many studies. There are both acid and base homogeneous catalysts. Examples of acid catalyst are hydrochloric acid and sulphuric acid. Acid catalysts are mainly used for oil with high percentages of FFA which is normally above 1% by the mass. These catalysts are able to esterify and transesterify the triglycerides simultaneously (Zabeti, Wan Daud and Aroua, 2009). However in transesterification, high molar ratio of alcohol to oil and a longer reaction time are required (Zabeti, Wan Daud and Aroua, 2009). By using an acid catalyst, it may corrode the equipment and reduce the lifetime of the equipment.

Apart from acid catalyst, alkaline catalyst is also used in transesterification such as potassium hydroxide and sodium hydroxide. Reaction using this kind of catalysts have reported high conversion and fast reaction rate with mild reaction conditions (Atabani et al., 2012). However, as mentioned at the previous section, separation and purification processes as well as the non-reusable catalysts are still the major drawbacks of the process in production of biodiesel. There are also several limitations of using alkaline catalyst in the reaction such as the percentages of FFA in the oils. In alkali catalysis, soap and excess water will be produced when dealing with oils with high FFA content. This can lead to difficulty on the separation of biodiesel and glycerol when soap is formed, if there is more than 5% of FFA in the oil. Emulsion formation may also occur and this requires washing to become the final product. This will increase the cost of process due to the water treatment and huge water consumption. Moreover, hydrolysis of triglycerides may occur due to the presence of water, yielding new FFAs with diglycerides (Sani, Daud and Abdul Aziz, 2014).

Table 2.2: Reaction Conditions using Different Heterogeneous Catalysts in Transesterification Reaction

Catalyst	**Oil**	**Methanol to Oil Molar Ratio**	**Catalyst to Oil Ratio (w/w)**	**Temperature (℃)**	**Time (h)**	**Conversion (%)**	**Reference**
CH_3CO_2K/CaO	Bitter almond oil	9:1	2.0%	60	2.0	91.22	(Fadhil, Al-Tikrity and Khalaf, 2018)
CaO/SiO_2	Cooking oil	14:1	8.0%	60	1.5	91.00	(Putra, Nata and Irawan, 2020)
MgO supported on $\boldsymbol{\gamma}$-Al_2O_3	Soybean oil	6:1	5.0%	60	6.0	60.00	(Navas et al., 2018)
Potassium methoxide	Soybean oil	6:1	2.0%	80	0.25	91.00	(Celante, Schenkel and de Castilhos, 2018)
$Zn/Ca/Al_2O_3$	Cooking oil	24:1	6.0%	65	3.0	97.80	(Mohd Kamal, Wan Abu Bakar and Ali, 2017)
Na_2ZrO_3	*Ricinus communis* oil	15:1	5.0%	65	3.0	99.90	(Martínez et al., 2018)

Table 2.2 (Continued)

Catalyst	**Oil**	**Methanol to Oil Molar Ratio**	**Catalyst to Oil Ratio (w/w)**	**Temperature (℃)**	**Time (h)**	**Conversion (%)**	**Reference**
Hydrotalcite-hydroxyapatite	Soybean oil	12:1	5.0%	240	4.0	80.40	(Brasil et al., 2017)
Diaion PA306S resin	Cooking oil	3.5:1	50.0%	50	10	>90.00	(Shibasaki-Kitakawa et al., 2011)
	Acid rice bran oil	-	33.0%	50	40	97.10	(Shibasaki-Kitakawa et al., 2015)

In order to use alkaline catalysts, it is required to use refined raw materials that consist of not more than 0.5% FFA concentration and 0.06% water, by mass (Atabani et al., 2012). Therefore, the raw materials to be used in homogeneous process with alkaline catalysts are limited. Cheap raw materials like acid oils and cooking oil are not able to be used unless they undergo pre-treatment. Addition to the wastewater treatment from biodiesel purification process and also the loss of homogeneous catalyst can impact the financial negatively and it may not be able to compete with the petroleum diesel (Sani, Daud and Abdul Aziz, 2013).

In the chemical interesterification of triglycerides with methyl acetate to produce biodiesel, both acid and base catalysts can be used. Casas, Ramos and Pérez (2011a) have been focusing on using base catalysts in the interesterification to yield FAME by using methyl acetate. They have tested catalysts such as potassium hydroxide (KOH), potassium methoxide (CH_3OK) and potassium polyethylene glycol (KPEG). Details of the experiments are stated in Table 2.3. Solid KOH was also used in homogeneous form when it was mixed with other chemicals to dissolve the catalyst in the reaction mixture during interesterification to produce biodiesel.

It was reported that there was zero formation of FAME during the potassium hydroxide-catalysed interesterification reaction. This is because unlike transesterification, alkoxide is not formed in an ester medium without alcohol in interesterification. In transesterification, alkoxide is formed when alcohol is present and reacts with the hydroxide. Hence, potassium hydroxide in interesterification reacts irreversibly with esters instead, which yields potassium acetate as well as potassium soaps (Casas, Ramos and Pérez, 2011a). Besides, hydroxide serves as a catalyst when there is water during the interesterification of oils and fats. This reaction is called hydroxide interesterification that happens when triglyceride saponification occurs and its by-product, glycerol is formed and reacts with the hydroxide. An alkoxide called glycerolate anion is the product of this reaction (Burgers, Mott and Seiden, 1965).

Table 2.3: Different Types of Base Catalysts Used in Interesterification Reaction

Catalyst	**Lipid Source**	**Reaction Conditions**				**FAME Content (wt. %)**	**Reference**
		Methyl Acetate to Oil Molar Ratio	**Catalyst to Oil Molar Ratio**	**Temperature (°C)**	**Time (h)**		
Homogeneous							
CH_3OK (Mixed with Oil)	Sunflower oil	12:1	0.2:1	50	0.25-0.5	73	(Casas, Ramos and Pérez, 2011a; b)
CH_3OK (+PEG200)	Sunflower oil	12:1	0.2:1	50	0.25-0.5	60	(Casas, Ramos and Pérez, 2011a; b)
CH_3OK (Methanolic Solution)	Sunflower oil	12:1	0.2:1	50	0.25-0.5	78	(Casas, Ramos and Pérez, 2011a; b)
KPEG	Sunflower oil	12:1	0.2:1	50	0.25-0.5	73	(Casas, Ramos and Pérez, 2011a; b)

Table 2.3 (Continued)

Catalyst	**Lipid Source**	**Reaction Conditions**				**FAME Content (wt. %)**	**Reference**
		Methyl Acetate to Oil Molar Ratio	**Catalyst to Oil Molar Ratio**	**Temperature (°C)**	**Time (h)**		
CH_3ONa	Tributyrin	21:1	0.05:1	60-80	0.1-0.2	93*	(Battistel et al., 2011)
Heterogeneous							
KOH	Sunflower oil	12:1	0.2:1	50	0.25-0.5	0	(Casas, Ramos and Pérez, 2011a)
CH_3OK (Solid)	Sunflower oil	12:1	0.2:1	50	0.25-0.5	55	(Casas, Ramos and Pérez, 2011a; b)
Mixed oxide MgAl 3:1	Tributyrin	21:1	0.05:1-0.1:1	80-140	8	24*	(Battistel et al., 2011)

* Butyrate Methyl Ester Yield (%)

In fact, Casas, Ramos and Pérez (2011a) have tried different forms of potassium methoxide apart from solid powder, such as premixing it with vegetable oil, adding polyethylene glycol (PEG) and creating a methanolic solution. All the other forms help to curb the induction period that occurs when dealing with solid potassium methoxide. PEG is a type of phase transfer catalysts that is added to the potassium methoxide to form KPEG complex like crown ethers. This complex is able to enhance the solubility of methoxide anion in the reactants. However, there are some difficulties in removing the PEG from the oil and methyl acetate. PEG can only be extracted from the mixture by using water due to its high miscibility in the solvent. The additional extraction step may increase the overall process cost as water and other equipment are required. Besides, high molecular weight PEG esters can be formed when PEG reacts with methyl acetate and triglycerides through transesterification as it has two terminal hydroxyl groups (Gallardo et al., 1998).

The second method to eliminate the induction period is to premix the potassium methoxide with the oil. This method possesses a similar reaction rate to the KPEG-catalysed interesterification. This also indicates that the interesterification reaction itself is actually faster than the transfer of potassium methoxide in the mixing reaction (Casas, Ramos and Pérez, 2011a). The third method to solve the induction period is to use potassium methoxide as a methanolic solution. It was reported that the reaction rate can be improved significantly by using methanolic potassium methoxide as the catalyst. This is because the catalyst is fully dissolved in the reaction mixture of oil and methyl acetate in the beginning stage of reaction. Comparing to potassium methoxide in powder form, methanolic potassium methoxide has less security issues. Figure 2.4 and Figure 2.5 show the catalytic activities of different catalysts in different forms. The reaction conditions of these tests were temperature of 50 ℃ with methyl acetate to oil molar ratio of 12 and catalyst to oil molar ratio of 0.5.

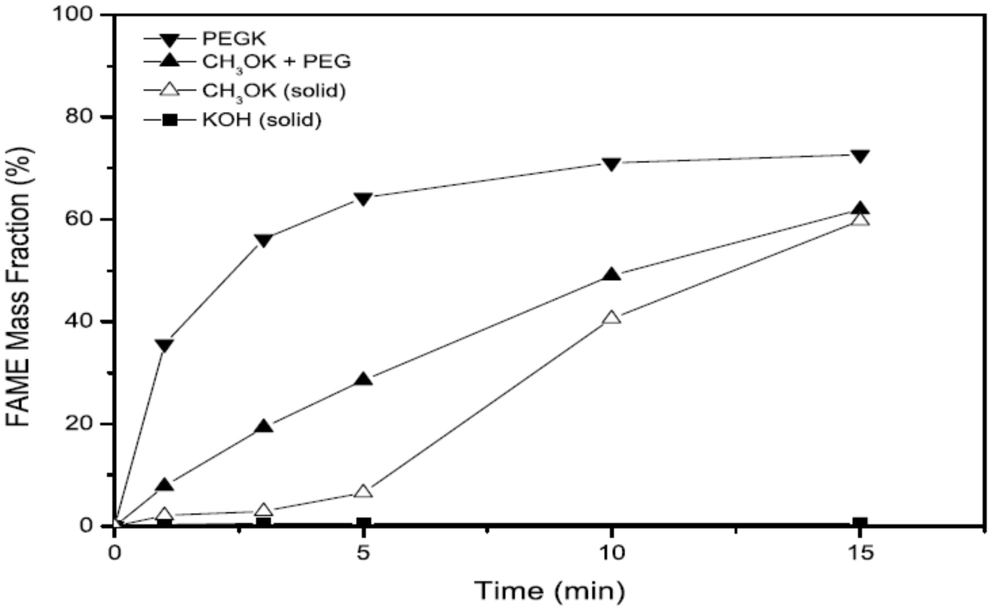


Figure 2.4: Catalytic Activities of KOH, CH_3OK and KPEG in Interesterification Reaction (Casas, Ramos and Pérez, 2011a; b)

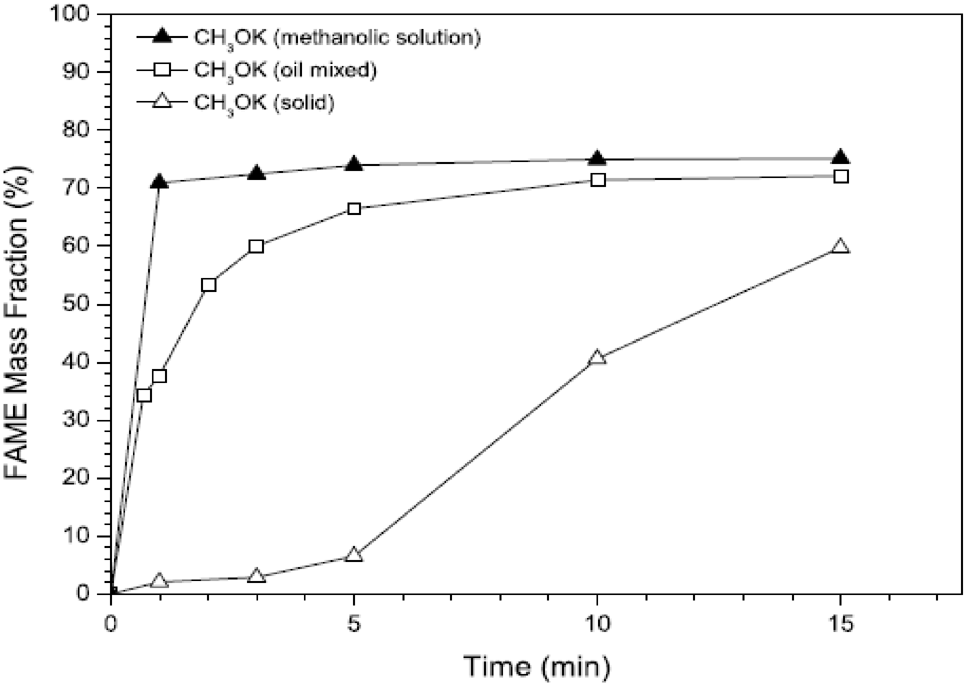


Figure 2.5: Catalytic Activities of Different Forms of CH_3OK in Interesterification Reaction (Casas, Ramos and Pérez, 2011a; b)

Battistel et al. (2011) have also done interesterification of tributyrin by using some acid and base catalysts. Different types of base and acid catalysts used in interesterification are shown in Table 2.3 and Table 2.4, respectively.

Table 2.4: Different Types of Acid Catalysts Used in Interesterification Reaction

Catalyst	**Lipid Source**	**Reaction Conditions**				**Butyrate Methyl Ester Yield (%)**	**Reference**
		Methyl Acetate to Oil Molar Ratio	**Catalyst to Oil Molar Ratio**	**Temperature (°C)**	**Time (h)**		
Homogeneous							
Sulphuric Acid	Tributyrin	21:1	0.05:1	130	20	29	(Battistel et al., 2011)
Trifluoro-methanesulphonic acid	Tributyrin	21:1	0.05:1	130	20	93	(Battistel et al., 2011)
Heterogeneous							
Nafion SAC13	Tributyrin	21:1	0.05:1	130	20	83	(Battistel et al., 2011)
Zirconia (SO_3)	Tributyrin	21:1	0.05:1	140	20	42	(Battistel et al., 2011)

2.3 Reaction Parameters in Interesterification

2.3.1 Effect of Reaction Time

In the interesterification to produce biodiesel, there are several factors that affect the yield of FAME such as the reaction time. Different amount of time for the reaction gives different yields. Generally, the yield of FAME will increase as the reaction time increases until a point where the yields remain the same. Hence, sufficient amount of contact time is required for the reaction to produce the highest amount of yields (Trakarnpruk, 2012). The reaction time between the reactant and oil is slow at the beginning due to the mixing and dispersion of the reactant and oil. After that, the reaction will then process rapidly. It is important to find the optimum reaction time as not only shorter time will decrease the yield, but longer time will also affect the yield. This is due to the reversibility of the interesterification reaction that will reduce the product at longer reaction time (Mathiyazhagan and Ganapathi, 2011).

In fact, the reaction time is also varied with different types of catalyst used in interesterification reaction. Generally, interesterification with base catalysts usually require lesser time when compared to acid catalysts (Thanh et al., 2012). This can also be observed from the previous sections that show some of the acid and base catalysts used in biodiesel production with their respective reaction conditions.

2.3.2 Effect of Reaction Temperature

Other than reaction time, the reaction temperature can also affect the biodiesel yield significantly. The FAME yields will increase as the reaction temperature increases. This also reduces the required reaction time as the oil viscosity reduces and increase the rate of reaction (Chozhavendhan et al., 2020). However, higher temperature might cause the decreasing of the yield also as saponification of oils will accelerate. Besides, the reaction temperature should be also based on the boiling points of the reactant used as higher temperature may evaporate the reactants, resulting in reduced biodiesel yield (Chozhavendhan et al., 2020). Hence, it is important to find out the optimum reaction temperature when the yield reaches the peak.

Similar to reaction time, the reaction temperature for biodiesel producing using acid catalyst is often higher than using base catalyst. This is because in the acid-catalysed esterification, the reaction temperature is a significant variable that can strongly affect the rate of reaction (Trakarnpruk, 2012).

2.3.3 Effect of Methyl Acetate to Oil Molar Ratio (MAOMR)

In interesterification, alkyl acetate such as methyl acetate is used as reactant instead of alcohol. Hence, the methyl acetate to oil molar ratio (MAOMR) is one of the influencing parameters in biodiesel production. Since chemical interesterification is reversible, MAOMR becomes significant as it is governed by the total miscibility of the reactants and products (Casas, Ramos and Pérez, 2011b). In one of the studies done by Casas, Ramos and Pérez which used sunflower oil and solid potassium methoxide as catalyst in interesterification, the MAOMR was studied with the FAME yield as well as other intermediates contents at final equilibrium composition of the reaction, as shown in Figure 2.6.

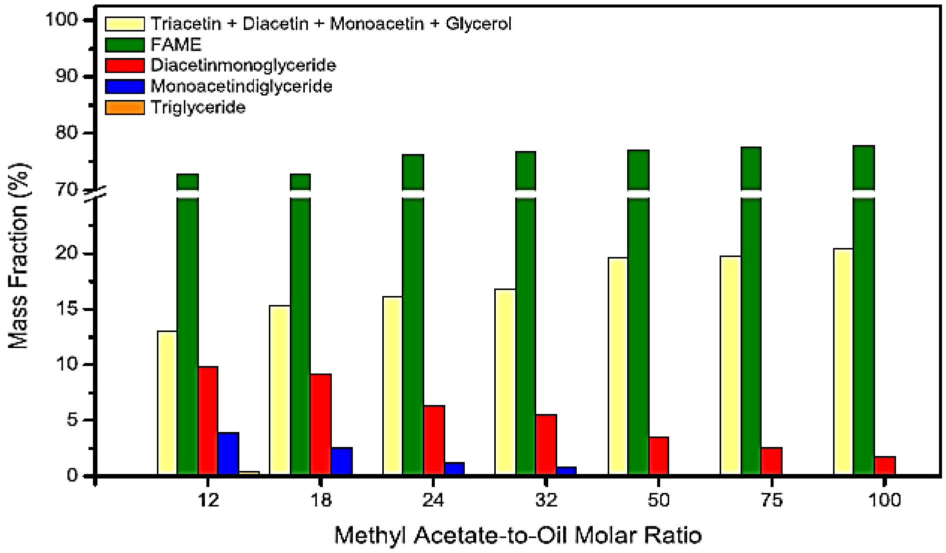


Figure 2.6: Effect of MAOMR in Equilibrium Composition at Catalyst to Oil Molar Ratio of 0.5 and Temperature of 50 °C (Casas, Ramos and Pérez, 2011b)

Theoretically, a minimum MAOMR of 3 is required in the interesterification of triglycerides and methyl acetate. This is because for every mole of triglycerides, 3 moles of methyl acetate are required, based on the stoichiometry of the reaction. Generally, higher value of MAOMR is used to shift the equilibrium towards the formation of FAME. According to the results from the study, FAME and triacetin contents increase as the MAOMR increases.

As for the reaction intermediates, monoacetindiglyceride (MADG) can be removed completely with MAOMR of 50. However, the diacetinmonoglyceride (DAMG) is not able to be eliminated even at an impractical molar ratio of 100. These intermediates can also be separated from FAME and triacetin via distillation due to their high boiling points (Casas, Ramos and Pérez, 2011b). Based on the studies from other researchers, excess of methyl acetate is used to ensure the highest yield of biodiesel is achieved.

2.3.4 Effect of Catalyst to Oil Molar Ratio (COMR)

The amount of catalyst used in the reaction is another important factor that can affect the biodiesel yield. Generally, the triglycerides conversion into FAME increases as the catalyst concentration increases with the oil samples. This is also known as the catalyst to oil molar ratio (COMR). It is important to find the optimum catalyst concentration as incomplete conversion of triglycerides into FAME will occur when there is insufficient amount of catalyst (Mathiyazhagan and Ganapathi, 2011). However, the type of catalyst needs to be considered as excess base catalyst will form more soap and this can affect the biodiesel yield (Leung and Guo, 2006). In the study done by Casas, Ramos and Pérez (2011b) in which potassium methoxide catalyst is used with sunflower oil, COMR was studied and the result is shown in Figure 2.7.

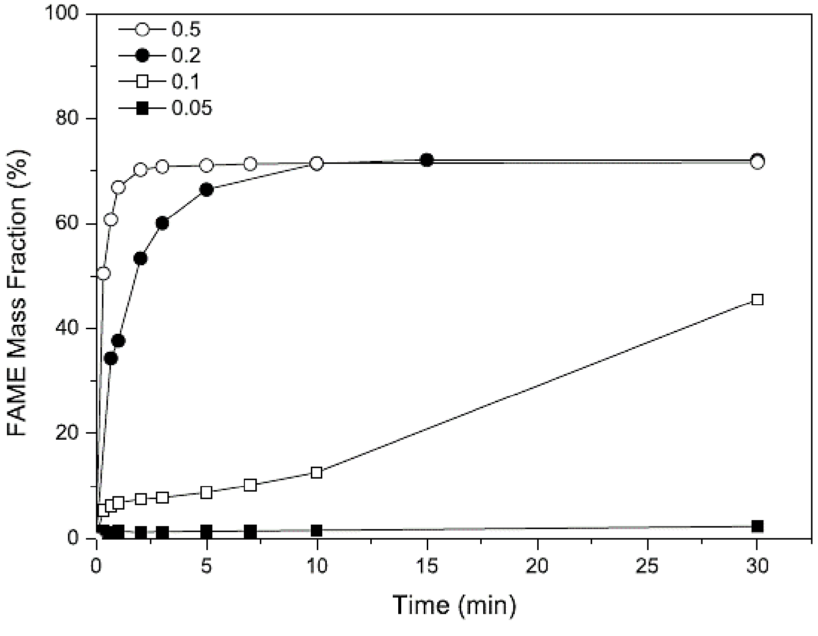


Figure 2.7: Effect of COMR on FAME Content with MAOMR of 12 and Temperature of 50 °C (Casas, Ramos and Pérez, 2011b)

In the study, COMR of 0.05, 0.1, 0.2 and 0.5 were tested and it showed that the equilibrium composition was achieved at the first 10 minutes with COMR of over 0.2. A significant difference was observed when COMR of below 0.1 was used. This showed that the catalyst amount plays a significant role on the reaction and the yield. Based on other studies, it is observed that a relatively low amount of catalyst is required in interesterification for biodiesel production.

2.4 Characterisations of Catalysts and Biodiesel

Catalyst characterisations are very important to study the catalytic properties such as acidity, elemental composition, morphology like physical micro or nano structure, surface properties, porosity and more. It is also important to characterise catalysts to identify both physical and chemical properties of the catalyst since they can affect the reaction and biodiesel yield. There are various types of characterisation and analytical techniques that can be employed for the catalysts used in biodiesel production. This section will briefly introduce every type of characterisation and analytical techniques while some of them will be discussed in detail in the later sections where each catalyst is being reviewed from the journals.

For preliminary study of catalyst, X-ray Diffraction (XRD) can be used to study the crystallinity in the catalyst. Moreover, Fourier Transform Infrared Spectroscopy (FTIR) is typically employed to identify different functional groups present in the catalyst (Changmai et al., 2020). As for the morphology such as surface texture, structure and particle size of the catalyst can be studied by using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) as both are able to produce images of the catalyst surface. Nitrogen Adsorption-Desorption Isotherm can also be applied to determine the texture of the catalyst. Besides, the physical properties of the catalyst such as pore diameter, pore volume and surface area can be determined by using Brunauer-Emmett-Teller (BET) analysis (Changmai et al., 2020).

As for chemical properties of the catalyst, Energy-Dispersive X-ray (EDX) can be employed to investigate the chemical compositions of the catalyst. There are also X-ray Fluorescence (XRF) and X-ray Photoelectron

Spectroscopy (XPS), whereby both techniques are responsible for quantitative detection. XRF is generally employed to detect the amount of metal oxides present in the catalyst, while XPS routinely measures the amount of elements and the chemical state information of the catalyst is also provided in this technique (Changmai et al., 2020). Thermal stability of a catalyst is very important for high temperature interesterification reaction. Hence, the thermal stability of the catalyst can be determined using Thermogravimetric Analysis (TGA). Since there are different types of catalyst such as acid catalyst and base catalyst, the total acid density of the catalyst can be measured by acid-base back titration method. Hammett indicator test can also be applied to test the acidity and basicity of the catalyst.

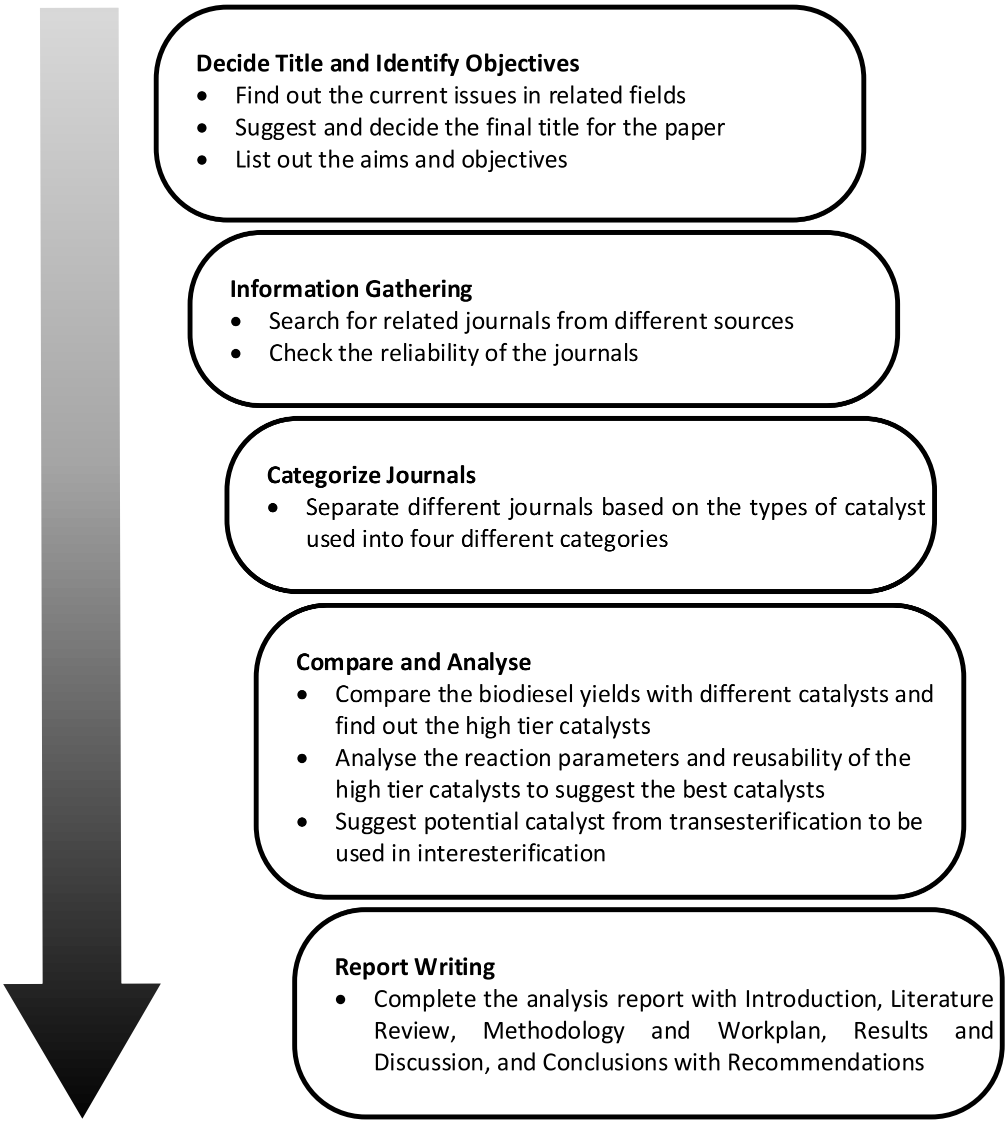
For the characterisation of biodiesel, FTIR analysis can also be employed to confirm the formation of the FAME product. Other than that, Gas Chromatography (GC) can be used to determine the chemical components of the product and the percentage of each component in the biodiesel. This is important as it shows the quality of the biodiesel produced. There are also different approaches and equations to measure the biodiesel yields which are employed by different researchers.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Overall Steps

There are multiple steps in completing this study in order to fulfil the aims and objectives. An overview of every steps and the sequences is shown in Figure 3.1 as a flow diagram.



Decide Title and Identify Objectives
- Find out the current issues in related fields
- Suggest and decide the final title for the paper
- List out the aims and objectives

Information Gathering
- Search for related journals from different sources
- Check the reliability of the journals

Categorize Journals
- Separate different journals based on the types of catalyst used into four different categories

Compare and Analyse
- Compare the biodiesel yields with different catalysts and find out the high tier catalysts
- Analyse the reaction parameters and reusability of the high tier catalysts to suggest the best catalysts
- Suggest potential catalyst from transesterification to be used in interesterification

Report Writing
- Complete the analysis report with Introduction, Literature Review, Methodology and Workplan, Results and Discussion, and Conclusions with Recommendations

Figure 3.1: Flow Diagram

3.2 Decide Title and Identify Objectives

The field that was focused on is the biodiesel production through chemical interesterification due to its benefits over the conventional transesterification. In order to determine the title that would bring contribution to the related field, the current issues and scenarios of that particular field have to be first identified. Hence, studies related to biodiesel production via chemical interesterification had been done. It was found that the catalysts used have a huge impact to the biodiesel yields. It was also seen that the catalysts for interesterification is still developing since there were less journals reporting it, as compared to transesterification. Hence, it is important to figure out the current scenario of catalysts used in this reaction for biodiesel production.

Different titles with different aspects that focus on a particular type of catalyst were suggested such as heterogeneous acid catalyst used in interesterification. However, there were limited journals that used this type of catalyst. Hence, it was better to consider every types of catalysts that can be used in the interesterification. The final decision on the title was to analyse every types of catalysts used in interesterification, including homogeneous and heterogeneous catalysts, as well as acid and base catalysts. After deciding the title, the aims and objectives were listed.

3.3 Information Gathering

After deciding the title and identifying the objectives, information gathering was performed to increase the knowledges regarding to the topic. Numerous journals have been found online from different sources for literature review. It is important to obtain journals from different sources to increase the diversity of the journal types. Besides, it is also vital to ensure that the journals are obtained from reputable, reliable and trustable sources to increase the quality of the analysis. The main sources for the journals and papers are as following:

a) UTAR Library E-Journals
b) ScienceDirect
c) Elsevier
d) ResearchGate
e) SpringerLink
f) Hindawi Publishing
g) Taylor & Francis

The keywords for searching the related journals are ‘biodiesel production’, ‘interesterification’, ‘triacetin’, ‘methyl acetate’ and ‘catalyst in interesterification’. These keywords are important as they simplified and eased the searching process to focus on the related papers. Every research paper regarding chemical interesterification using catalyst for biodiesel production were obtained as there were limited journals as compared to the conventional transesterification route. The searching area included every type of catalyst used as one of the objectives in this study was to analyse and compare different types of catalysts. Besides, journals that reported catalysts used in transesterification were also included as one of the objectives was to suggest potential catalysts that can be used in interesterification for biodiesel production.

3.4 Categorize Journals

Journals categorizing was performed after gathering every journal that reported biodiesel production via chemical interesterification. Journals were categorized into different categories with different types of catalysts used. There were also some researchers who conducted interesterification with different types of catalysts in the same work. Categorizing the catalysts is important as it had provided a clearer picture on different types of catalysts and their effects toward the biodiesel yields. This also helped to ease the comparison processes of catalysts when catalysts were separated into each category. There were four categories for different types of catalysts, namely:

a) Homogeneous Acid Catalyst
b) Homogeneous Base Catalyst
c) Heterogeneous Acid Catalyst
d) Heterogeneous Base Catalyst

3.5 Compare and Analyse

Comparisons of catalysts were conducted based on the biodiesel yields after separating catalysts from journals into each category. Catalysts with high biodiesel yields were listed as high tier catalysts. They were identified for two catalyst types, which were:

a) Homogeneous Catalyst
b) Heterogeneous Catalyst

After obtaining the high tier catalysts, different aspects with the catalyst were investigated and analysed to find out the most suitable homogeneous and heterogeneous catalysts that presented high biodiesel yields under mild or comparatively cost-friendly reaction conditions.

The aspects being investigated in the analysis process were:

a) Biodiesel Yield
b) Reaction Time and Reaction Temperature
c) Catalyst Loading and Acyl Acceptor to Oil Molar ratio
d) Reusability of Catalyst

3.6 Report Writing

The final part was to prepare the analysis that includes every information regarding on the topic. The analysis was presented in five chapters which included:

a) Chapter 1: Introduction
b) Chapter 2: Literature Review
c) Chapter 3: Methodology and Workplan
d) Chapter 4: Results and Discussion
e) Chapter 5: Conclusions

In Chapter 1, brief knowledges, current scenario and issues on the topic of this study were presented in a general approach. For Chapter 2, numerous journals related to the topic were included and studied as the references for the following parts. The methodology was presented in Chapter 3 where each step to conduct the analysis was explained clearly. In Chapter 4, all the comparisons, analyzations and discussions were done in this section. Subsections and summaries were also included for each type of catalysts and each aspect for investigations. Two catalysts that were used in conventional transesterification were also suggested to be the potential catalysts as they were not being reported in chemical interesterification before. Lastly in Chapter 5, conclusions and recommendations for future research were made.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalysts Used in Chemical Interesterification

30 journals were found reporting biodiesel production via chemical interesterification using more than 50 different types of catalysts. There are mainly four types of catalysts being reported from the journals in biodiesel production via chemical interesterification. There are homogeneous acid, homogeneous base, heterogeneous acid and heterogeneous base catalysts. Catalysts from the journals were categorised into their respective types to review and differentiate them. Performances of catalysts and products analysis were also included for different journals. These journals were sorted into different years from 2011 to 2020, as shown in Figure 4.1. It was observed that the research on chemical interesterification with different catalysts began to increase since the year of 2018.

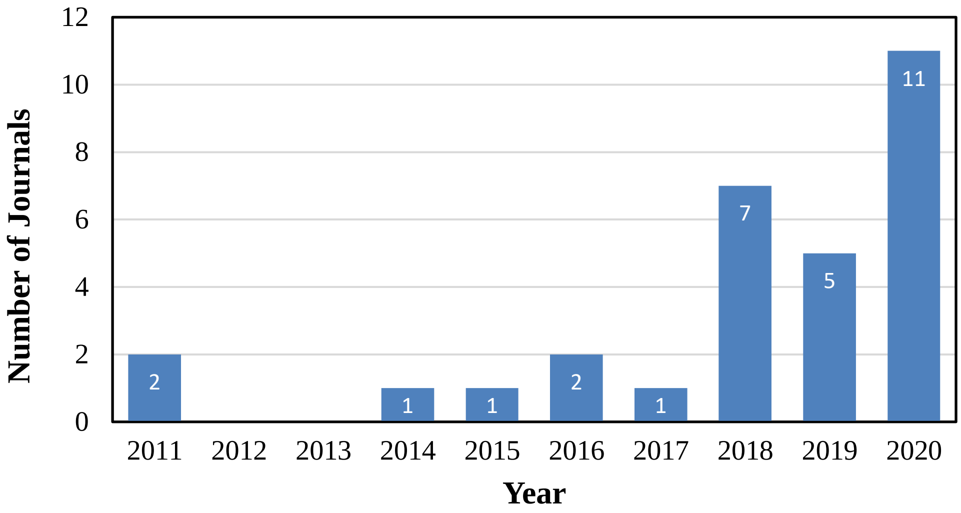


Figure 4.1: Number of Journals Reported in Different Years

4.1.1 Homogeneous Acid Catalyst

Homogeneous acid catalyst is used in transesterification and interesterification to produce biodiesel where an acidic catalyst is added to the reactant in the same phase. This type of catalyst is able to produce high biodiesel yield (above 90%) as reported in the literature via transesterification. However, the reaction usually requires higher temperature above 100 °C and more time up to 20 hours due to the small reaction rate of acid catalyst, thus increasing energy consumption and the cost of process (Silitonga et al., 2020). The reaction is also insensitive to FFA concentration of the feedstocks due to the acidity of catalyst. Despite the advantages, separation issues and purification of biodiesel are still the problem in homogeneous base catalysis. In chemical interesterification, it was found that homogeneous acid catalyst was employed the least currently and they are all listed in Table 4.1.

Battistel et al. (2011) reported chemical interesterification to produce biodiesel using different homogeneous acid catalysts such as methanesulphonic (MS) acid, sulphuric acid, trifluoro-acetic acid and trifluoro-MS acid with addition of acetic acid and acetic anhydride. The homogeneous acid catalysed reactions were conducted in a 20 mL thick-glass vessel with screw capped that contained 2.3 g or 7.6 mmol of tributyrin which was the feedstocks for the reaction. The acyl acceptor for the chemical interesterification was methyl acetate and the amount added into the vessel was 11.2 g or 151 mmol. This showed that the methyl acetate to oil molar ratio (MAOMR) was 20:1. Different catalysts were added with catalyst concentration of 5 mol/mol% of tributyrin which was also catalyst to oil molar ratio (COMR) of 0.05. The biodiesel product was butyrate methyl ester (BuMe) since the feedstock was tributyrin. The biodiesel product BuMe was expressed in molar yields percentages with a scale of 0 to 100%, as shown in Table 4.1.

Chuepeng and Komintarachat (2018) also conducted chemical interesterification using homogeneous catalysts such as sodium hydroxide and acetic acid for biodiesel production with engine validation. Acetic acid catalyst will be discussed in this section as it is a homogeneous acid catalyst. The feedstocks used for this work was waste cooking oil (WCO) with ethyl acetate as the acyl acceptor. The reaction parameters and biodiesel yields are shown in Table 4.1. The biodiesel yield reported was 52.4% which also included the triacetin yield. No further test was done with acetic acid due to its lower yield than sodium hydroxide catalyst. Hence, sodium hydroxide was used for the further experiments for the work. The biodiesel products from the reaction were fatty acid ethyl ester (FAEE) and triacetin (TA).

Table 4.1: Homogeneous Acid Catalysts Used in Chemical Interesterification

Homogeneous Acid Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR^a/ EAOMR^b**	**COMR^c**	**Reaction Temperature (℃)**	**Reaction Time (h)**	**Biodiesel Yield (%)**	**References**
Sulphuric acid	Tributyrin	Methyl acetate	20:1	0.05:1	130	20	29*	(Battistel et al., 2011)
Methanesulphonic (MS) acid	Tributyrin	Methyl acetate	20:1	0.05:1	130	20	4*	
Trifluoro- acetic acid	Tributyrin	Methyl acetate	20:1	0.05:1	130	20	2*	
Trifluoro-MS acid	Tributyrin	Methyl acetate	20:1	0.05:1	130	20	93*	
			20:1	0.05:1	140	20	92*	
			20:1	0.05:1	160	20	88*	
Trifluoro-MS acid + acetic acid	Tributyrin	Methyl acetate	20:1	0.30:1	130	20	91*	

Table 4.1 (Continued)

Homogeneous Acid Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR[a]/ EAOMR[b]**	**COMR[c]**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (%)**	**References**
Trifluoro-MS acid + acetic anhydride	Tributyrin	Methyl acetate	20:1	0.30:1	130	20	92*	(Battistel et al., 2011)
Acetic acid	Waste cooking oil	Ethyl acetate	30:1	0.01:1	80	3	52.4	(Chuepeng and Komintarachat, 2018)
Tin octoate	Rapeseed oil	Ethyl acetate	40:1	0.10:1	210	20	65 FAEE 30 TA	(Galia et al., 2014)
		Methyl acetate	40:1	0.10:1	210	20	90 FAME 60 TA	

[a] MAOMR: methyl acetate to oil molar ratio.
[b] EAOMR: ethyl acetate to oil molar ratio.
[c] COMR: catalyst to oil molar ratio.
* butyrate methyl ester yield (%)
FAEE fatty acid ethyl ester molar yield (%)
FAME fatty acid methyl ester molar yield (%)
TA triacetin molar yield (%)

TA quantification was done by dissolving it in n-heptane and measured by external calibration curves of standard. FAEE identification was performed by comparing the ethyl standard retention times, while the quantification of FAEE was based on the external calibration using FAEE standard solutions which consisted of linoleate, stearate, oleate and ethyl palmitate, at concentration range of 0.01 to 5 mg/mL in n-hexane (Chuepeng and Komintarachat, 2018). The final FAEE yield for each experiment was calculated using Equation (4.1):

$$FAEE = \frac{m_{actual}}{m_{theoretical}} \times 100\% \approx \frac{n \times C_{ester}}{\rho_{oil}} \tag{4.1}$$

where m_{actual} (g) represents the actual ethyl ester mass, $m_{theoretical}$ (g) represents the ethyl ester theoretical mass, n represents the diluted multiple of ethyl ester, C_{ester} (g/mL) represents the mass concentration of FAEE which is obtained from the GC, and ρ_{oil} (g/mL) represents the WCO's density.

Galia et al. (2014) also reported interesterification using rapeseed oil with tin octoate as homogeneous acid catalyst to synthesise biodiesel. Tin octoate was considered homogeneous catalyst as it was completely soluble in the reaction medium at every operating condition adopted in the work. The acyl acceptors used in this work were methyl acetate and ethyl acetate. The aim of this study was to find the optimum operating condition that can achieve highest biodiesel yield using methyl acetate or ethyl acetate as the acyl acceptor. The reaction temperature for the experiments was varied from 120 ℃ to 210 ℃, while the reaction time was varied from 1 hour to 20 hours.

The alkyl ester products from the reactions using methyl acetate and ethyl acetate were FAME and FAEE, respectively. GC was used to obtain the alkyl ester and triacetin concentration from the reaction products. From GC analysis, the cumulative yields for the esters and triacetin were obtained by Galia et al. (2014) based on Equation (4.2):

$$Y_{FAAE} = \frac{N_{FAAE}}{3\frac{W_{oil}^{0}}{PM_{oil}}} \quad , \quad Y_{TA} = \frac{N_{TA}}{\frac{W_{oil}^{0}}{PM_{oil}}} \tag{4.2}$$

where Y_{FAAE} and Y_{TA} are the yields of fatty acid akyl esters and triacetin, respectively, N_{FAAE} and N_{TA} are the moles of fatty acid alkyl esters and triacetin, respectively which were obtained from GC calibration, W_{oil}^{0} and PM_{oil} are the initial mass of the feedstock oil and the average molecular weight of the oil which was obtained from the fatty acid compositions, respectively. The optimum reaction parameters and the results are shown in Table 4.1. Figure 4.2 and Figure 4.3 shows the results of yields over time from 0 to 20 hours with ethyl acetate and methyl acetate, respectively with reaction temperature of 210 °C, COMR of 0.1:1, ethyl acetate to oil molar ratio of 40:1. Galia et al. (2014) concluded that reaction with methyl acetate generated higher FAME yield.

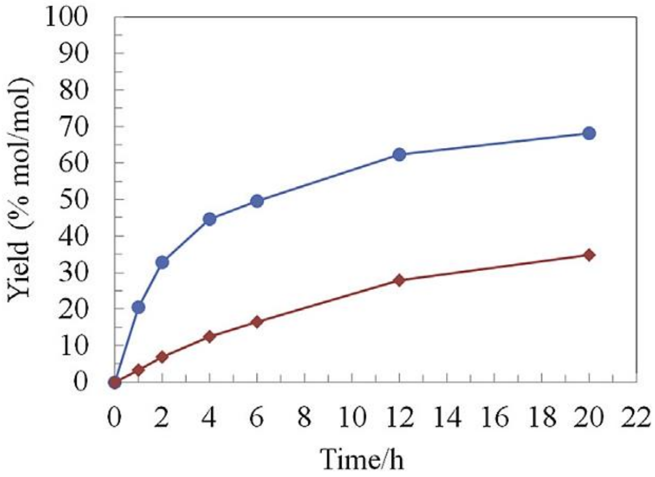


Figure 4.2: FAEE (●) and Triacetin (♦) Molar Yields Over Reaction Time (Galia et al., 2014)

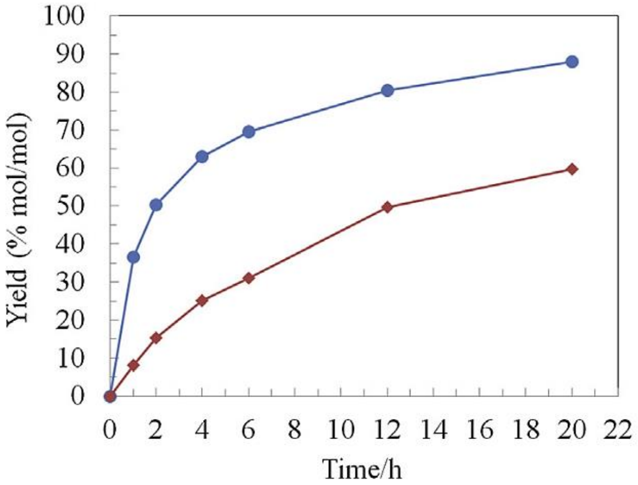


Figure 4.3: FAME (●) and Triacetin (♦) Molar Yields Over Reaction Time (Galia et al., 2014)

4.1.2 Homogeneous Base Catalyst

There are few types of homogeneous base catalysts which include alkali metal based hydroxides such as sodium hydroxide or potassium hydroxide, alkali metal based oxides such as sodium methoxide or potassium methoxide and also carbonates type (Rizwanul Fattah et al., 2020). They are all alkaline liquids that can be dissolved in the reaction mixture due to the homogeneous characteristic. Base catalysts have been used by many researchers in biodiesel production due to their high activity reported in conventional transesterification to synthesis biodiesel (Endalew, Kiros and Zanzi, 2011), as 4000 times faster reaction rate was reported with base-catalysed reaction when compared with acid catalysed reaction (De Lima, Ronconi and Mota, 2016). Typically, alkoxides catalysts have a higher activity than metallic hydroxides catalysts. However metallic hydroxides are often used in the industry due to the lower prices (Rizwanul Fattah et al., 2020). The drawbacks of this type of catalyst are the high sensitivity to FFA content as well as formation of soaps. It was found that homogeneous base catalysts are used the most in interesterification for biodiesel production and they are all tabulated in Table 4.2.

The research work done by Battistel et al. (2011) also included homogeneous base catalysts such as sodium methoxide (CH_3NaO), potassium tert-butoxide (t-BuOK), 1,5,7-Triaza-bicyclo[4.4.0]dec-5-ene (TBD) and 1,8-Diazo-bicyclo-[5.4.0]undec-7-ene (DBU). The interesterification reaction was conducted in the same way as described in homogeneous acid catalyst section where tributyrin was used as the feedstock and methyl acetate as the acyl acceptor to form BuMe. The analysis of the product was also the same done by Battistel et al. (2011) as described previously.

For TBD and DBU catalysts, DBU is a bi-cyclo di-azoamine whereas TBD is a bi-cycloamine which has 45 higher basicity than DBU, indicating that TBD is a very strong base. Despite the high basicity of TBD, it was not able to catalyse the interesterification efficiently, even after raising the reaction temperature. According to Battistel et al. (2011), the behaviour of TBD is not similar in the case of conventional transesterification where it acts as a strong base. In interesterification where esters are exchanged, TBD does not act as strong nucleophile likely due to the hindrance effects. On the other hand, DBU is a weaker base with lower reactivity (Battistel et al., 2011).

Table 4.2: Homogeneous Base Catalysts Used in Chemical Interesterification

Homogeneous Base Catalysts	Feedstocks	Acyl Acceptor	MAOMR/ EAOMR	COMR	Reaction Temperature (°C)	Reaction Time (h)	Biodiesel Yield (wt.%)	References
CH_3NaO	Tributyrin	Methyl acetate	20:1	0.05:1	60	0.2	93 %*	(Battistel et al., 2011)
			20:1	0.05:1	80	0.1	89 %*	
t-BuOK	Tributyrin	Methyl acetate	20:1	0.05:1	60	0.2	92 %*	
			20:1	0.05:1	80	0.2	90 %*	
TBD	Tributyrin	Methyl acetate	20:1	0.05:1	80	5	36 %*	
			20:1	0.05:1	140	5	32 %*	
DBU	Tributyrin	Methyl acetate	20:1	0.05:1	80	5	4 %*	
			20:1	0.05:1	140	5	8 %*	
DBU + Methanol 30%	Tributyrin	Methyl acetate	20:1	0.05:1	140	5	7 %*	

Table 4.2 (Continued)

Homogeneous Base Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**COMR**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
KOH	Jatropha oil	Ethyl acetate	6:1	0.5 % w/w oil[a]	70	6	14 % Yield	(Kusumaningtyas, Pristiyani and Dewajani, 2016)
CH_3OK + Oil	Sunflower oil	Methyl acetate	12:1	0.2:1	50	0.25-0.5	73 FAME	(Casas, Ramos and Pérez, 2011a; b)
CH_3OK + PEG200	Sunflower oil	Methyl acetate	12:1	0.2:1	50	0.25-0.5	60 FAME	
CH_3OK + Methanolic solution	Sunflower oil	Methyl acetate	12:1	0.2:1	50	0.25-0.5	78 FAME	
KPEG	Sunflower oil	Methyl acetate	12:1	0.2:1	50	0.25-0.5	73 FAME	
NaOH	Waste cooking oil	Ethyl acetate	30:1	0.015:1	80	3	92 % Yield	(Chuepeng and Komintarachat, 2018)

Table 4.2 (Continued)

Homogeneous Base Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**COMR**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
t-BuOK/t-BuOH	Rapeseed oil	Methyl acetate	36:1	0.15:1	55	1	73.2 $^{\text{FAME}}$ 16.6 $^{\text{TA}}$	(Sustere and Kampars, 2015)
t-BuOK/THF, 1M	Rapeseed oil	Methyl acetate	27:1	0.12:1	55	1	74 $^{\text{FAME}}$ 13.1 $^{\text{TA}}$	(Kampars, Abelniece and Kampare, 2019)
	Rapeseed oil	Methyl acetate	18:1	0.08:1	25	0.67	70 $^{\text{FAME}}$ 11 $^{\text{TA}}$	(Abelniece and Kampars, 2020)
	Rapeseed oil	Methyl acetate	30:1	0.12:1	55	1	72.5 $^{\text{FAME}}$ 14 $^{\text{TA}}$	(Kampars et al., 2020)
iPrOK/THF, 1M	Rapeseed oil	Methyl acetate	30:1	0.12:1	55	1	76.3 $^{\text{FAAE}}$ 12 $^{\text{TA}}$	(Kampars et al., 2020)
MeOK/iPrOH, 0.5M	Rapeseed oil	Methyl acetate	18:1	0.12:1	55	1	83.5 $^{\text{FAAE}}$ 0.8 $^{\text{TA}}$	

Table 4.2 (Continued)

Homogeneous Base Catalysts	Feedstocks	Acyl Acceptor	MAOMR/ EAOMR	COMR	Reaction Temperature (°C)	Reaction Time (h)	Biodiesel Yield (wt.%)	References
iPrOK/iPrOH/THF	Rapeseed oil	Methyl acetate	30:1	0.12:1	55	1	81.9 $^{\text{FAAE}}$ 5.5 $^{\text{TA}}$	(Kampars et al., 2020)
t-BuOK/THF 1M + iPrOH/oil	Rapeseed oil	Methyl acetate	30:1	0.12:1	55	1	82.4 $^{\text{FAAE}}$ 3.9 $^{\text{TA}}$	
t-BuOLi/THF	Rapeseed oil	Methyl acetate	18:1	0.16:1	55	1	60 $^{\text{FAME}}$	(Kampars, Abelniece and Blaua, 2019)
t-BuONa/THF	Rapeseed oil	Methyl acetate	18:1	0.16:1	55	1	70 $^{\text{FAME}}$	
MeONa	Rapeseed oil	Methyl acetate	36:1	0.12:1	55	1	75.1 $^{\text{FAME}}$ 11.8 $^{\text{TA}}$	(Sustere and Kampars, 2015)
CH_3OK (ultrasonic assisted)	Cotton oil	Methyl acetate	14.87:1	1.17 % w/w oil[a]	50	0.5	98.51 % Conversion	(Medeiros et al., 2018)

Table 4.2 (Continued)

Homogeneous Base Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**COMR**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
CH_3OK (ultrasonic assisted)	Karanja oil	Methyl acetate	9:1	1 % w/w oil[a]	50	0.58	91 % Yield	(Kashyap, Gogate and Joshi, 2019)

* butyrate methyl ester yield (%)

[a] catalyst loading (% w/w oil)

[FAAE] fatty acid alkyl esters

According to the experiments done by Battistel et al. (2011), it was found that sodium methoxide and t-BuOK are homogeneous catalysts due to their solubility in methyl acetate when the water content is strictly minimized in reaction media. It was also found that the yields from the base-catalysed reactions were similar to those achieved by acid catalysed reactions, when t-BuOK and trifluoro-MS acid which were homogeneous base and homogeneous acid, respectively were considered in the comparisons (Battistel et al., 2011). However, t-BuOK was able to achieve the yield in a significantly shorter reaction time. The similar yields achieved with homogeneous base and acid catalysed reactions can be explained by the partially reversible consecutive reaction steps. Although the reaction rate was faster with the base catalysts, the similar yield improvement might be due to the limit of thermodynamic and the independence of the catalyst's nature (Battistel et al., 2011).

Casas, Ramos and Pérez (2011b) conducted interesterification with sunflower oil and methyl acetate to produce biodiesel with different types of base catalysts. The homogeneous base catalysts tested were potassium hydroxide (KOH), potassium methoxide (CH_3OK) and potassium polyethylene glycolate (KPEG). Different types of CH_3OK were used such as addition of oil, methanolic solution and PEG200 which is PEG with 200 g/mol of mean molecular weight. Solid CH_3OK was also used in the experiment and it will be discussed in the heterogeneous catalyst section.

Kusumaningtyas, Pristiyani and Dewajani (2016) reported chemical interesterification to produce biodiesel using potassium hydroxide, KOH as the homogeneous base catalyst. In the research, 14% of biodiesel yield was able to achieve with jatropha oil as the feedstock and ethyl acetate as the acyl acceptor instead of methyl acetate. Upon the interesterification, crude jatropha oil was first neutralised by using soda ash (Na_2CO_3) to avoid the saponification since the feedstocks contained high content of FFA. It was reported that the FFA content of the neutralised oil reduced to 0.17%. The biodiesel yield from the reaction was determined using High Performance Liquid Chromatograph (HPLC) and GC-Mass Spectrometer. Figure 4.4 shows the HPLC chromatograph analysis of the product mixture obtained from the reaction at 60 °C, 1 hour, EAOMR of 6:1 and catalyst concentration of 0.5% w/w oil. It was observed that no triacetin has been detected in the product mixture. At retention times of 2.8, 3.277 and 4.918 min, ethyl acetate, methyl decanoate and methyl oleate were detected, respectively based on the chromatograph (Kusumaningtyas, Pristiyani and Dewajani, 2016).

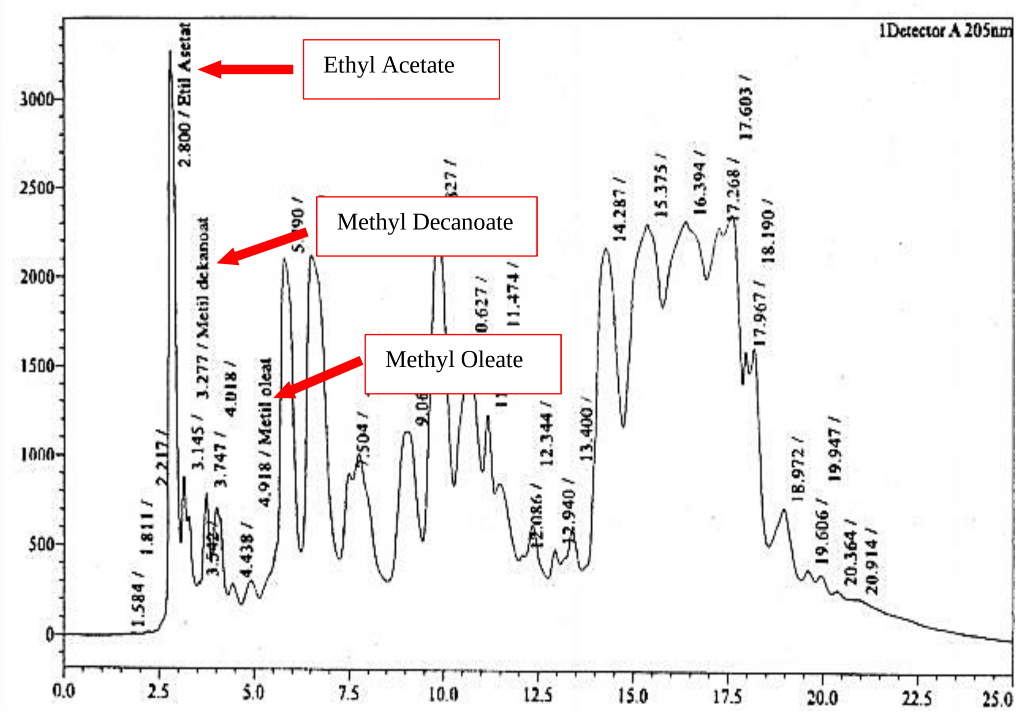


Figure 4.4: HPLC Chromatogram of Biodiesel Product Mixture (Kusumaningtyas, Pristiyani and Dewajani, 2016)

The research done by Chuepeng and Komintarachat (2018) also included a homogeneous base catalyst, NaOH. The first attempt to produce biodiesel using NaOH achieved 77.5% biodiesel yield which was higher than using acetic acid catalyst which was also being tested in the research. Due to the higher yield achieved by the base catalyst, further experiments were done using NaOH as catalyst to determine the optimum operating conditions for the best biodiesel yield. WCO and ethyl acetate were used as the feedstock and acyl acceptor, respectively. The analysis method of the biodiesel product was described previously with acetic acid as the catalyst.

For the analysis of the biodiesel product, FTIR spectroscopy was also used to determine the formation and presence of FAEE and TA in the product mixture. An infrared spectra of FAEE and TA was obtained from the FTIR spectrometer analysis and it is shown in Figure 4.5. It is shown that the spectrum of biodiesel appeared at 1156, 1457, 1743, 2354, 2852, 2920 and 3248 cm^{-1}.

Starting with 1156 cm^{-1}, it represented the presence of -C-O- in ester group which confirmed the formation of FAEE (Reddy et al., 2014) while the small peak at 1457 cm^{-1} represented the presence of -CH_3 group in the product. Based on the spectrum, it is known that triacetin was present due to the strong peak at 1743 cm^{-1} as it indicated carbonyl stretching of the esters (Lacerda et al., 2015). Hydroxyl group (-OH) and C-H stretching were also observed due to the characteristic bands around 2852-3238 cm^{-1}. Presence of CO_2 was observed from strong peak at 2354 cm^{-1} was the consequence of long storage before analysis. There was also no soap formation due to the absence of 1500-1600 cm^{-1} absorption in the spectrum. There was no soap formed in the base catalysed reaction because the water traces were bound to the sodium metal catalyst to prevent free glycerol and partial acetyl esters formation (Miesiac, Rogalinski and Jozwiak, 2013).

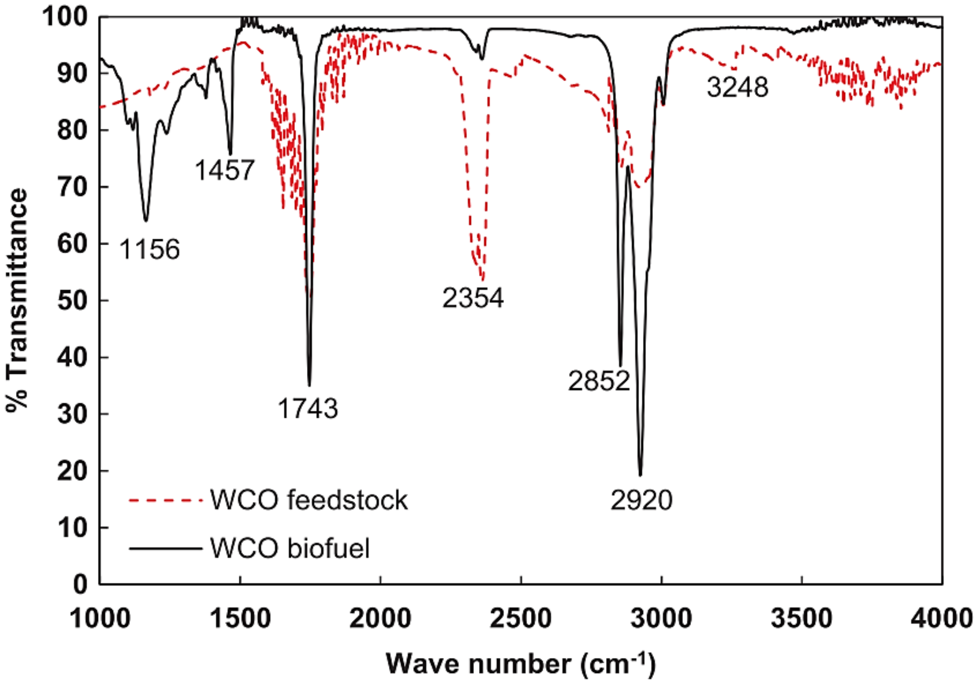


Figure 4.5: FTIR Spectra of Biodiesel Product with NaOH as Catalyst at Optimum Condition (Chuepeng and Komintarachat, 2018)

Sustere and Kampars (2015) were one of the first researchers who used potassium tert-butoxide in tert-butanol (t-BuOK/t-BuOH) as homogeneous base catalyst in chemical interesterification to produce biodiesel. Rapeseed oil was used as the feedstock with methyl acetate as the acyl acceptor. In the research, different catalysts such as sodium methoxide in methanol (MeONa) was also tested and compared with t-BuOK/t-BuOH in terms of their biodiesel yield, specifically FAME and TA yields. The ester content of the biodiesel product was determined based on the modified standard method EN 14103, in which methyl heptadecanoate was used as the internal standard (Sustere and Kampars, 2015). Different compositions of product were obtained from the experiments, MeONa catalysed reaction generated FAME and TA yields of 75.1 wt.% and 11.8 wt.%, respectively. On the other hand, reaction with t-BuOK/t-BuOH as catalyst generated FAME and TA yields of 73.2 wt.% and 16.6 wt.%, respectively. The team concluded that t-BuOK/t-BuOH was the better catalyst to be used due to the much higher triacetin content that can be added up to a higher total biodiesel yield.

In fact, the homogeneous base catalyst, t-BuOK can also be used in tetrahydrofuran (THF) solution (t-BuOK/THF). Abelniece and Kampars (2020) conducted chemical interesterification with t-BuOK/THF as the catalyst for biodiesel production. The research was to investigate the kinetics of rapeseed oil with different reactants, including methanol and methyl formate at room temperature. After obtaining the results, the team concluded that the reaction of rapeseed oil and methyl acetate gave the best FAME yield of 86.5% with highest reaction rate. The FAME and TA contents in mass fraction were 70 wt.% and 11 wt.%, respectively. The FAME yield of 86.5% was determined as the experimentally obtained mass contents percentage from the theoretical values. The result showed that interesterification under such mild reaction conditions was able to obtain biodiesel with fuel properties that were close to the standard requirements (Abelniece and Kampars, 2020).

Kampars et al. (2020) also conducted chemical interesterification using the same homogeneous catalyst, t-BuOK/THF with rapeseed oil as feedstock and methyl acetate as acyl acceptor. The yield of the reaction was obtained from the mass fraction of final composition of FAME and TA in the product. The highest yield achieved from the reaction with t-BuOK/THF was 86.5 wt.% which included 72.5 wt.% FAME and 14 wt.% TA. Beside of t-BuOK/THF, the team also tested different homogeneous base catalysts and mixed with iso-propanol with other catalysts. The objective of the research was to increase the FAME or fatty acid alkyl esters (FAAE) content, while decreasing the TA content in the biodiesel product. The team came up with an innovative way to include iso-propanol (iPrOH) for the competitive interesterification-transesterification conversion of triglycerides (Kampars et al., 2020). Iso-propanol was added to harmonise the reaction product by slowly proceeding after dissolving alkoxide catalyst in the alcohol except t-butanol to promote competitive transesterification. This competitive reaction with iso-propanol was able to reduce the content of TA below 10 wt.%, while increasing the FAAE content which is the ester obtained from the competitive interesterification-transesterification reaction.

In the research, Kampars et al. (2020) tested different catalysts with addition of iso-propanol to produce biodiesel product that is similar to the conventional biodiesel, with partial glycerol conversion, 5-10 wt.% of TA content and 3-5 wt.% of fatty acid iso-propyl esters in the biofuel composition. The glycerol conversion is happened in the interesterification reaction which allows simultaneous conversion of glycerol to TA (Kampars et al., 2020). Other homogeneous catalysts tested in the research were potassium isopropoxide in THF (iPrOK/THF), potassium methoxide in iso-propanol (MeOK/iPrOH), potassium isopropoxide in isopropanol and THF (iPrOK/iPrOH/THF) and t-BuOK/THF mixed with iPrOH/oil. The team concluded that the catalyst iPrOK/iPrOH/THF in competitive interesterification-transesterification was able to produce FAAE up to 81.9 wt.% with 3-5 wt.% of iso-propyl ester content and 5-8 wt.% of TA. The reduced amount of TA and its replacement with iso-propyl ester and higher fatty acid ester content in the biodiesel product make it more similar to the conventional biodiesel (Kampars et al., 2020).

Similar homogeneous alkoxide catalysts with different metal ions like lithium tert-butoxide in THF (t-BuOLi/THF) and sodium tert-butoxide in THF (t-BuONa/THF) were tested in interesterification with rapeseed oil and methyl acetate by Kampars, Abelniece and Blaua (2019). The team found that reaction with t-BuONa/THF and t-BuOK/THF have the similar activity that is higher than t-BuOLi/THF catalysed reaction. The ion pairs with low catalytic activity and the ions association of t-BuOLi/THF catalyst led to the low and diverse activity of the catalyst (Kampars, Abelniece and Blaua, 2019).

Medeiros et al. (2018) had conducted chemical interesterification using cotton oil and methyl acetate assisted with ultrasound. The homogeneous catalyst used in the reaction was potassium methoxide (CH_3OK). The process variables for the ultrasound device were optimised with 67.64% ultrasonic probe amplitude and 67.30% vibration pulse to achieve the highest conversion of triglycerides which was 98.51%. It was found that the ultrasound assisted reaction provides 14% triglycerides conversion higher than the conventional reaction which uses mechanical agitation without ultrasound. Ultrasonic technique also reduces the operating costs as it generates large amount of energy to the reaction mixture so that the temperature can be increased easily without external heating (Mostafaei et al., 2015).

Kashyap, Gogate and Joshi (2019) also conducted similar ultrasound assisted interesterification with Karanja oil instead of cotton oil as feedstock, methyl acetate as acyl acceptor and CH_3OK as the catalyst. The team reported optimised parameters as shown in Table 4.2 with 60% duty cycle to achieve 91% of biodiesel yield. The team also compared the result with interesterification without ultrasound which only gave 60% of biodiesel yield. The biodiesel yield was calculated by dividing the methyl esters weight in the biodiesel by the maximum methyl esters weight expected. Higher yield from the ultrasound assisted reaction was caused by the elimination of mass transfer limitation based on microjets formed by the cavitation (Kashyap, Gogate and Joshi, 2019).

4.1.3 Heterogeneous Acid Catalyst

Heterogeneous acid catalyst generally has fewer toxic and corrosive effects as well as lesser negative impacts to the environment (Aransiola et al., 2014). This type of catalyst has a variety of acidic sites based on the concept of Bronsted acid or Lewis acid with different strengths (Rizwanul Fattah et al., 2020). These acidic catalysts are known to be less active in the reaction when comparing to the base catalysts. Thus, higher reaction temperature and time are often required to complete the transesterification or interesterification process for biodiesel production (Jamil et al., 2018). However, heterogeneous acid catalyst also shares the same benefits of homogeneous acid catalyst such as the insensitivity to FFA content. It can also be separated easily after the reaction to eliminate the washing steps for biodiesel product. It was also reported that reaction using heterogeneous acid catalyst usually requires lesser amount of catalyst. Besides, it can be easily regenerated and recycled for the subsequent runs. The common heterogenous acid catalysts reported in interesterification are listed in Table 4.3.

Table 4.3: Heterogeneous Acid Catalysts Used in Chemical Interesterification

Heterogeneous Acid Catalysts	Feedstocks	Acyl Acceptor	MAOMR/ EAOMR	Catalyst Loading (wt.%)	Reaction Temperature (°C)	Reaction Time (h)	Biodiesel Yield (wt.%)	References
Nafion SAC-13	Tributyrin	Methyl acetate	20:1	5-15[a]	80	20	4%*	(Battistel et al., 2011)
			20:1	5-15[a]	130	20	83%*	
			20:1	5-15[a]	160	8	62%*	
Amberlyst 15	Tributyrin	Methyl acetate	20:1	5-15[a]	120	20	4%*	
Zirconia (SO_3)	Tributyrin	Methyl acetate	20:1	5-15[a]	140	20	42%*	
Zirconia (WO_3)	Tributyrin	Methyl acetate	20:1	5-15[a]	140	20	8%*	
Zeolite β	Tributyrin	Methyl acetate	20:1	5-15[a]	130	20	13%*	
Zeolite HY	Macaw oil	Methyl acetate	30:1	5	250	2	34.81 ^{FAME} 0.34 ^{TA}	(dos Santos Ribeiro et al., 2017)

Table 4.3 (Continued)

Heterogeneous Acid Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**Catalyst Loading (wt.%)**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
Zeolite HY	Soybean oil	Methyl acetate	32:1	5	250	20	56.06 $^{\text{FAME}}$ 2.62 $^{\text{TA}}$	(Simões et al., 2020)
WO_3/USY Zeolite (ultrasonic assisted)	Oleic acid	Methyl acetate	10:1	10	240	1	80.8 $^{\text{FAME}}$	(Ketzer, Celante and de Castilhos, 2020)
Niobium phosphate	Macaw oil	Methyl acetate	30:1	5	250	2.5	52.71 $^{\text{FAME}}$ 0.19 $^{\text{TA}}$	(dos Santos Ribeiro et al., 2017)
	Oleic acid	Methyl acetate	10:1	10	240	2	79.05 $^{\text{FAME}}$	(Alves et al., 2019)
Niobium oxide	Macaw oil	Methyl acetate	30:1	5	250	2	45.77 $^{\text{FAME}}$ 0.21 $^{\text{TA}}$	(dos Santos Ribeiro et al., 2017)
	Soybean oil	Methyl acetate	32:1	5	250	20	50.02 $^{\text{FAME}}$ 2.58 $^{\text{TA}}$	(Simões et al., 2020)

Table 4.3 (Continued)

Heterogeneous Acid Catalysts	Feedstocks	Acyl Acceptor	MAOMR/ EAOMR	Catalyst Loading (wt.%)	Reaction Temperature (°C)	Reaction Time (h)	Biodiesel Yield (wt.%)	References
γ-alumina	Macaw oil	Methyl acetate	30:1	5	250	1	50.61^{FAME} 1.88^{TA}	(dos Santos Ribeiro et al., 2017)
	Macaw oil	Methyl acetate	40:1	2	300	3	55.00^{FAME}	(Brondani, Ribeiro and Castilhos, 2020)
	Macaw oil	Methyl acetate	20:1	2	300	1	48.96^{FAME} 1.84^{TA}	(Ribeiro et al., 2018)
Ferric sulfate	Triolein	Methyl acetate	20:1	7.5	120	12	83% Yield	(Tian et al., 2018)
Tin (II) oxide	Rapeseed oil	Methyl acetate	40:1	0.69:1[b]	210	4	90% Yield	(Interrante et al., 2018)
OEFB derived activated carbon	Oleic acid	Methyl acetate	50:1	10	110	8	52.3% Yield	(Wong et al., 2020b)

* butyrate methyl ester yield (%)

[a] catalyst concentration (% w/v oil)

[b] catalyst to oil molar ratio (COMR)

In the studies done by Battistel et al. (2011), various types of heterogeneous acid catalysts were also included. Sulfonic acid catalysts like Nafion SAC-13 and Amberlyst 15, zirconia sulphate (SO_3), zirconia tungstate (WO_3) and zeolite β were tested in chemical interesterification with tributyrin as feedstock and methyl acetate as acyl acceptor to form BuMe and TA. From the results of the experiments done by the researchers, Amberlyst 15, SO_3 and zeolite β reported very poor BuMe yields. It was reported that reaction using Nafion SAC-13 achieved highest BuMe yield among the catalysts tested with BuMe yield of 83% and TA yield of 60% at 130 °C.

Zirconia sulphate, zirconia tungstate and zeolite β are actually strong acid catalysts. However, their performances in the reaction were limited due to the low degree of tributyrin conversion. Amberlyst 15 consists of the highest concentration of sulphonic groups among all the acid catalysts. Despite its low surface area, the catalyst stays active in conventional transesterification but this is not the case in interesterification as it was not able to stay highly active in the reaction. This was expected due to the low activity of homogeneous methanesulphonic acid in the reaction as tested previously. The silica-based material, Nafion SAC-13 that consists of polymeric perfluorinated chains terminated with sulphonic groups is actually trifluoro-MS acid in heterogeneous phase. It was synthesised by supporting fluorosulphonic acids on porous silica where the isomorphous lattice substitution was exploited to enhance its intrinsic acidity. It was reported that Nafion SAC-13 is both physically and chemically stable up to 280 °C (Battistel et al., 2011). The reusability of the heterogeneous acid catalyst used in the research was not reported in the journal.

dos Santos Ribeiro et al. (2017) had reported chemical interesterification using four different types of heterogeneous acid catalysts which were niobium oxide, niobium phosphate, zeolite HY and γ-alumina. Macaw oil which is also known as *Acrocomia aculeata* was used as the feedstock with methyl acetate as the acyl acceptor. All the catalysts were characterised using XRD and the results are shown in Figure 4.6. The XRD pattern of γ-alumina shows low crystallinity structure with several intense peaks at $2\theta = 37°, 46°$ and $67°$. For niobium oxide and niobium phosphate, amorphous structures were observed with no diffraction peaks. XRD pattern of zeolite HY showed crystalline structure with all of the characteristic peaks.

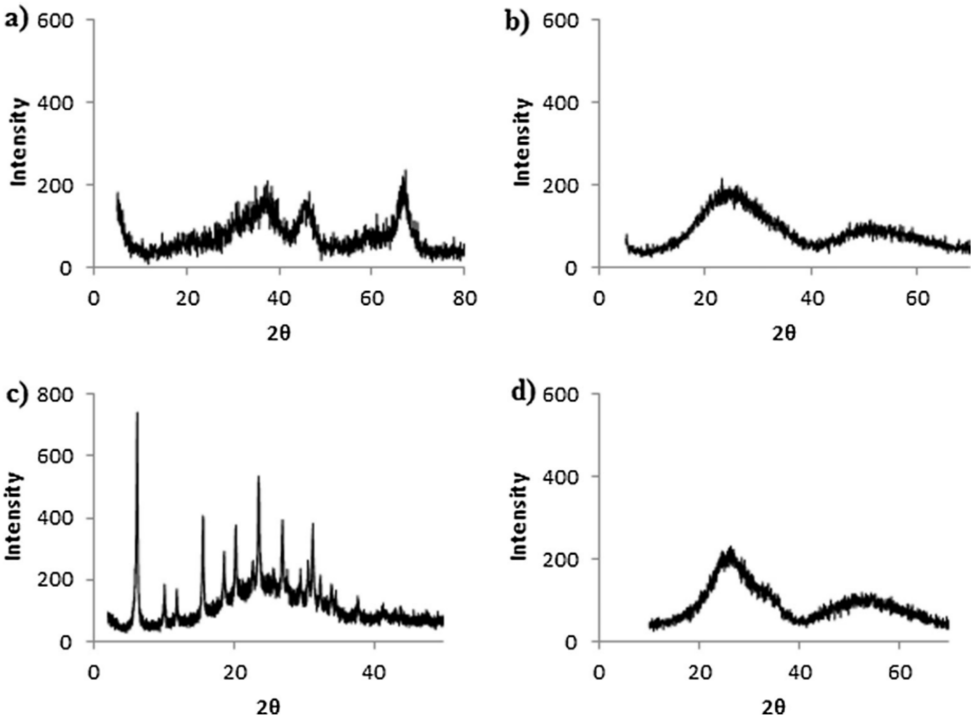


Figure 4.6: XRD Patterns of (a) γ-alumina, (b) Niobium Phosphate, (c) Zeolite HY and (d) Niobium Oxide (dos Santos Ribeiro et al., 2017)

From the results of the experiments, reaction with zeolite HY generated the least yield despite its large surface area. It was reported that the low yield by zeolite HY was caused by the restriction of diffusion affected by the pore size. Water inhibition and the acidity were also the reasons that led to low product yield when zeolite HY was used as the catalyst in biodiesel production (dos Santos Ribeiro et al., 2017). The performance of niobium oxide was lower than niobium phosphate during esterification due to the higher number of surface sites in niobium phosphate (Bassan et al., 2013). It was reported that both γ-alumina and niobium phosphate achieved higher yield from the experiments. However, γ-alumina-catalysed reaction encountered thermal degradation of FAME when approaching 1 hour of reaction time. Niobium phosphate catalysed reaction achieved the highest yield at reaction time of 2.5 hours with significantly less TA content in the product. Hence, it was believe that γ-alumina favours interesterification that yields more TA while niobium phosphate favours esterification (dos Santos Ribeiro et al., 2017).

Reusability of γ-alumina and niobium phosphate in the reaction was tested with 1 hour of reaction time for both catalysts. Both heterogeneous acid catalysts were recycled and reused for 5 consecutive runs and the results are shown in Figure 4.7. For γ-alumina during the fifth cycle, the FAME yield decreased to 48.96 wt.% from its original FAME yield of 54.17 wt.% with the fresh catalyst. The TA yield actually increased during the second run and this might be due to the improved thermal stability of triacetin which caused by the adsorption of acetic acid from esterification to the catalyst surface (dos Santos Ribeiro et al., 2017). The TA yield remained at 2.32 wt.% during the fifth cycle. Small catalyst weight loss during the centrifugation process could explain the FAME yield reduction at the last cycle (dos Santos Ribeiro et al., 2017). For niobium phosphate during the fifth cycle, the FAME yield reduced significantly to 22.72 wt.% from its original FAME yield of 51.56 wt.% with fresh catalyst. The TA yield also decreased from 0.13 wt.% at first run to 0 wt.% at the fifth cycle. The huge reduction of FAME yield could be explained by the leaching in reactive medium, small catalyst weight loss as well as catalyst poison (dos Santos Ribeiro et al., 2017). In this case, γ-alumina was considered as the most efficient heterogeneous acid catalyst among the catalysts used in the studies.

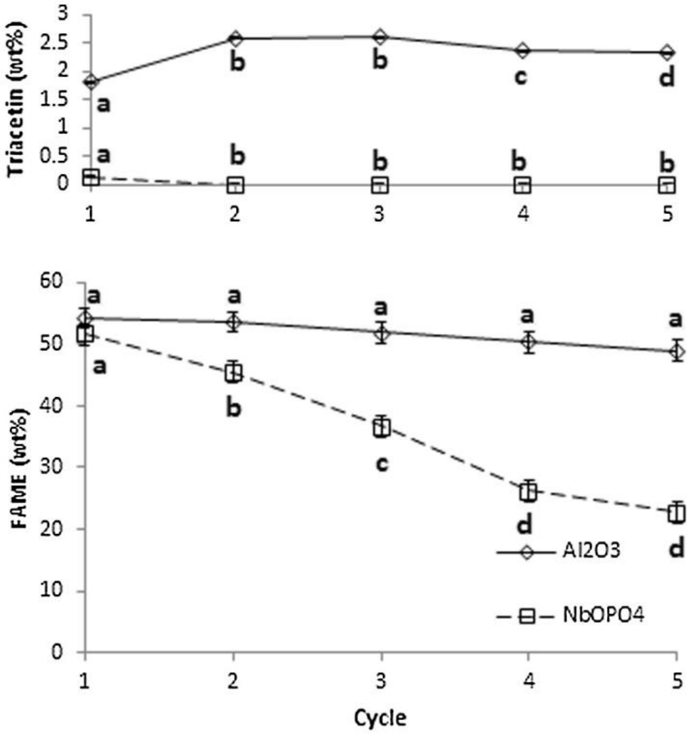


Figure 4.7: Reusability Tests of γ -alumina and Niobium Phosphate in Interesterification with MAOMR 30:1 and 5 wt.% Catalyst at 250 °C for 1 Hour (dos Santos Ribeiro et al., 2017)

According to the previous study that showed the great performance of γ-alumina, Ribeiro et al. (2018) further conducted interesterification and esterification of macaw oil and methyl acetate with γ-alumina as the heterogeneous catalyst. The best reaction conditions were obtained for the highest FAME and TA yields which were 48.96 wt.% and 1.84 wt.%, respectively. 82.46% of conversion efficiency was achieved with the results. The heterogeneous catalyst was also tested for its reusability where the catalyst was recovered and reused for 8 cycles. It was observed that the catalyst could be reused for 6 cycles without significant activity loss, as shown in Figure 4.8. The result was similar to the research done by the same author previously. Later, Brondani, Ribeiro and Castilhos (2020) proposed a new kinetic model with γ-alumina as heterogenous acid catalyst in simultaneous interesterification and esterification reactions to produce FAME and TA. Similar with previous research done by the team, macaw oil was used as the feedstock with methyl acetate as the acyl acceptor. The result showed that with higher excess methyl acetate, slightly higher yield of 0.55 g FAME/g sample was achieved as it slightly favoured the FAME production.

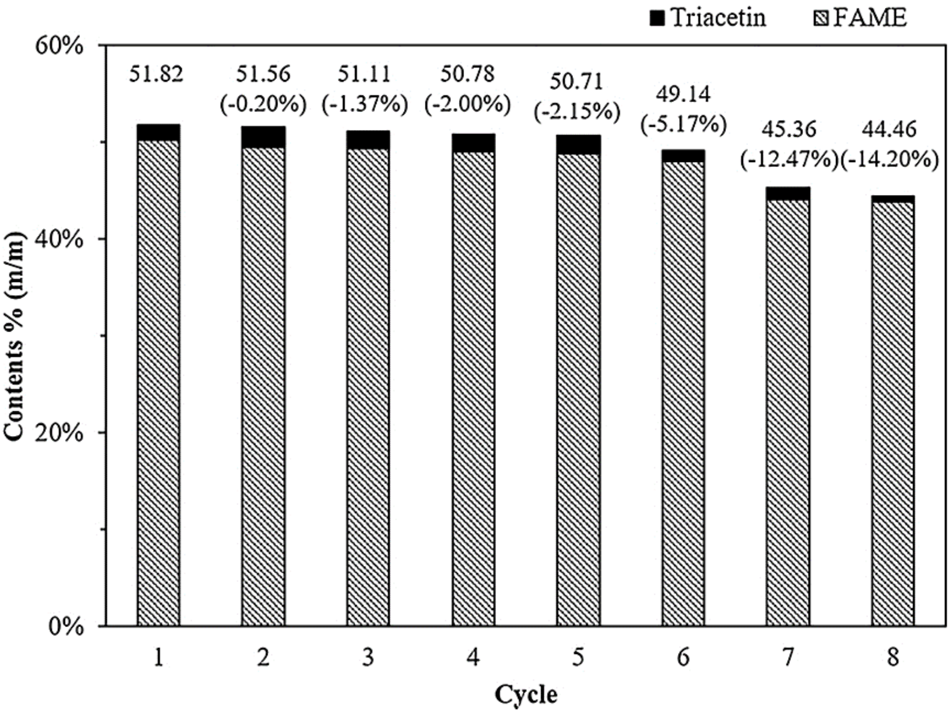


Figure 4.8: Reusability Test of γ -alumina in Interesterification and Esterification with MAOMR 20:1 and 2 wt.% Catalyst at 300 ℃ for 1 Hour (Ribeiro et al., 2018)

Alves et al. (2019) also conducted esterification with methyl acetate using niobium phosphate as the heterogenous acid catalyst to synthesise biodiesel. The feedstock used in the experiments was oleic oil, hence the biodiesel product was methyl oleate, also known as FAME. The optimum reaction conditions were obtained from the reaction kinetic studies through the mathematical and kinetic modelling done by the researchers. The effects of different reaction parameters such as reaction temperature, reaction time, MAOMR and catalyst loading were verified by using central composite experimental design. Besides, ANOVA was also done to investigate the significance of each reaction parameter or variable affecting the FAME contents. From the results, it was reported that all the reaction parameters had significant effects toward the reaction. However, the reaction temperature is most significant since it has the smallest p-value from the variance analysis.

Reusability of the niobium phosphate catalyst was also evaluated since it is a heterogenous catalyst that can be recovered and reused. The solid acid catalyst was separated from the FAME quantification and reused for 5 cycles without any catalyst treatment and washing treatment between the cycles. The successive reactions were conducted using the same optimum reaction conditions. Figure 4.9 shows the results of methyl oleate contents achieved in each cycle with the recycled catalyst. In the first cycle with fresh niobium phosphate catalyst, the methyl oleate content achieved was 79.05 wt.% and it reduced to 76.13 wt.% in the second cycle. The methyl oleate further reduced to 62.12 wt.% in the fifth cycle with 21.42 wt.% of reduction from the first run. During each new cycle, the mass of catalyst would decrease and this might cause the loss of catalytic activity after each cycle (Alves et al., 2019). The decline of catalyst active sites might also cause the catalytic activity loss as the reactant and reaction products accumulated at the catalyst surface (Bala et al., 2015).

Heterogeneous catalyst screening for production of FAME via interesterification was carried out by Simões et al. (2020), where heterogeneous acid catalysts such as zeolite HY and niobium oxide were involved in the screening. These catalysts were tested with other heterogeneous base catalysts and the results showed that both zeolite HY and niobium oxide presented the lowest yields of 50 wt.% to 60 wt.% FAME in the product. This indicated that base catalyst possess better performance in catalytic activity, which is the benefit of alkaline catalyst when compared to acidic catalyst (Simões et al., 2020). The reusability of these catalysts were not tested due to the low performance of the catalysts. Researchers tested the reusability for one of the heterogeneous base catalysts with higher FAME yield. Experiments were also done to obtain the optimum reaction conditions for the selected heterogeneous base catalyst to achieve its highest yield possible for consecutive reactions.

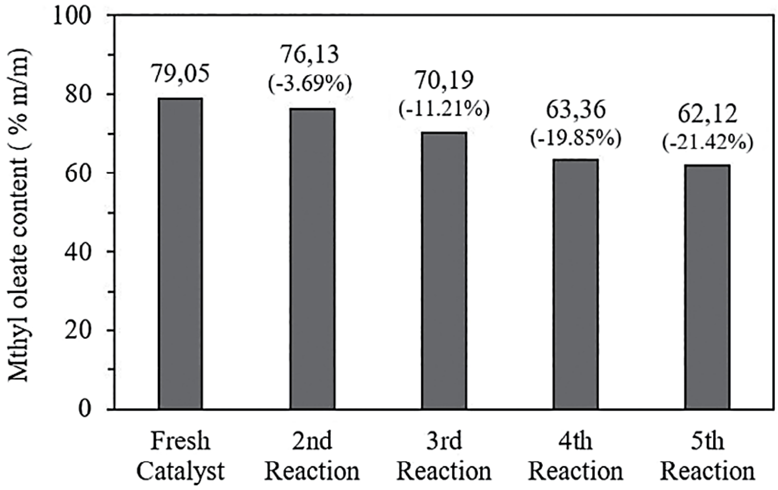


Figure 4.9: Reusability Test of Niobium Phosphate in Esterification with MAOMR 10:1 and 10 wt.% Catalyst at 240 ℃ for 2 Hours (Alves et al., 2019)

Apart from zeolite HY, zeolite USY which represents ultrastable Y zeolite was employed with oxide tungsten activation in esterification of oleic acid and methyl acetate. Ketzer, Celante and de Castilhos (2020) tested WO_3/USY zeolites as heterogenous catalyst assisted by ultrasonic on its catalytic performance in methyl oleate synthesis. The research concluded that 20% WO_3/USY zeolite with ultrasonic-assisted generated the highest methyl oleate conversion of 80.8%. The conversion was calculated as methyl oleate content in the product divided by the maximum methyl oleate content in final product which corresponds to 100 wt.% conversion of oleic acid in methyl oleate based on Hartman and Lago method. This indicated that the conversion was same as the FAME weight percent in the product. It was also reported that the results were similar to the results with alcohol as acyl acceptor in the literature. From the results, significantly lesser methyl acetate and shorter reaction time were observed when compared to reaction with zeolite HY without ultrasound assisted. With ultrasonic activation, the catalyst presented higher decrease in texture properties and greater crystalline lattice changes. The irradiation from ultrasonic waves also endowed stronger interaction of tungsten oxide support during the impregnation process. This caused blockade of superior strong site by the moderate and weak sites, thus favouring the conversion of oleic acid into methyl oleate (Ketzer, Celante and de Castilhos, 2020).

Tian et al. (2018) conducted interesterification with triolein and methyl acetate by using ferric sulfate as heterogenous acid catalyst to synthesis FAME which was methyl oleate in this case. The researchers also investigated the addition of different FAME concentration (C14:0 ME) like methyl myristate as co-solvent in the reaction as well as the effect of water to improve the catalytic action with the materials already present in the reaction system to prevent additional product separations at downstream (Tian et al., 2018). The results were reported in overall conversion yield which was determined with the methyl oleate yield from triolein and the highest yield with optimum reaction conditions was 83%, with addition of 7.7 g/L C14:0 ME as FAME co-solvent. The effect of different concentrations of FAME added as co-solvent as well as reaction with no addition of FAME are shown in Figure 4.10. The reusability of ferric sulfate was not investigated in the journal. The journal concluded that ferric sulfate provided improvement in reaction yields when compared to other published reactions with heterogenous catalysts. Further exploration are needed for this potential reaction system in biodiesel production.

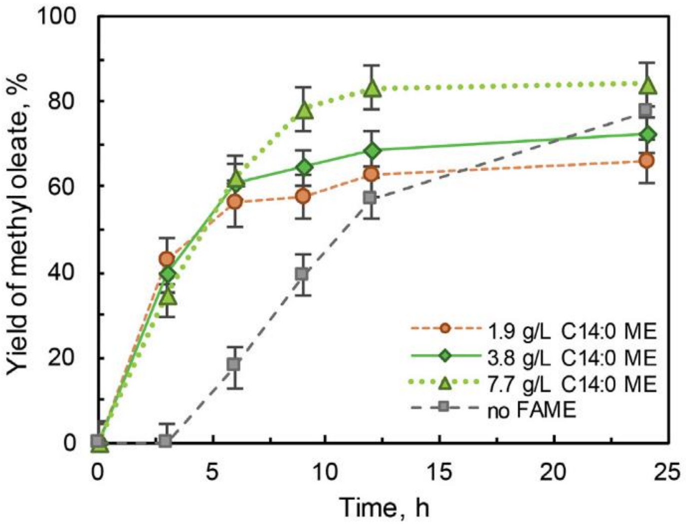


Figure 4.10: Methyl Oleate Yield at Varying FAME Co-Solvent Concentration with MAOMR 20:1, 7.5 wt.% Ferric Sulfate at 120 °C (Tian et al., 2018)

Other than that, tin(II) oxide was reported for the first time in chemical interesterification to yield FAME and TA. Interrante et al. (2018) employed low surface area tin(II) oxide (SnO) as heterogeneous acid catalyst with rapeseed oil and methyl acetate as acyl acceptor. In the research, reaction parameters such as MAOMR, catalyst loading, reaction time and reaction temperature were investigated to obtain the highest possible yield. The results were obtained as cumulative yields of FAME and TA, calculated by dividing the FAME and TA mole numbers by the initial mole number of the rapeseed oil. Highest FAME and TA yields of 90% and 70%, respectively were achieved at the optimum reaction conditions. Addition of water as impurities to the reaction system was also investigated and the results were interesting. With 2 wt.% of water with respect to the oil added to the reaction, the FAME yield was unexpectedly higher than the reaction without water addition. It was believed that SnO is able to catalyse the reaction to form acetic acid and methanol during the hydrolysis of methyl acetate when water is present, as shown in the Equation (4.3):

$$CH_3COOCH_3 + H_2O \overset{H^+}{\leftrightarrow} CH_3OH + CH_3COOH \tag{4.3}$$

In the hydrolysis reaction shown in Equation (4.3), it continuously shifted to the right due to the reaction equilibrium. This causes transesterification of methanol with triglyceride molecules in the reaction, which has higher reaction rate than interesterification with methyl acetate, thus yielding more FAMEs under fixed operative conditions (Interrante et al., 2018). This also indicated that SnO can be used in reaction with vegetable oil that consists of high water content.

The reusability of heterogeneous acid catalyst, SnO was investigated as well. The catalyst was recovered and reused for 3 consecutive cycles, with catalyst washing by using methyl acetate before recycling to be reused in the next cycle. The reusability test was conducted in 1 hour of reaction time for every cycle, while other reaction parameters remained the same as the optimum conditions. The result was surprising as the product yields were higher in the subsequent cycles after the reaction compared to fresh milled catalyst, with 72% FAME and 25% TA yields in the third cycle, compared with the first cycle with

60% FAME and 16% TA yields. The unexpected result could be caused by the increase of the catalyst’s total surface area, which could be contributed by the fragmentation of the native crystals. This was confirmed by the SEM micrographs of the milled catalyst at every cycle of interesterification, as shown in Figure 4.11 where populations of smaller size of SnO particles were observed in the images of the recycled catalyst in two and three consecutives interesterification reactions (Interrante et al., 2018).

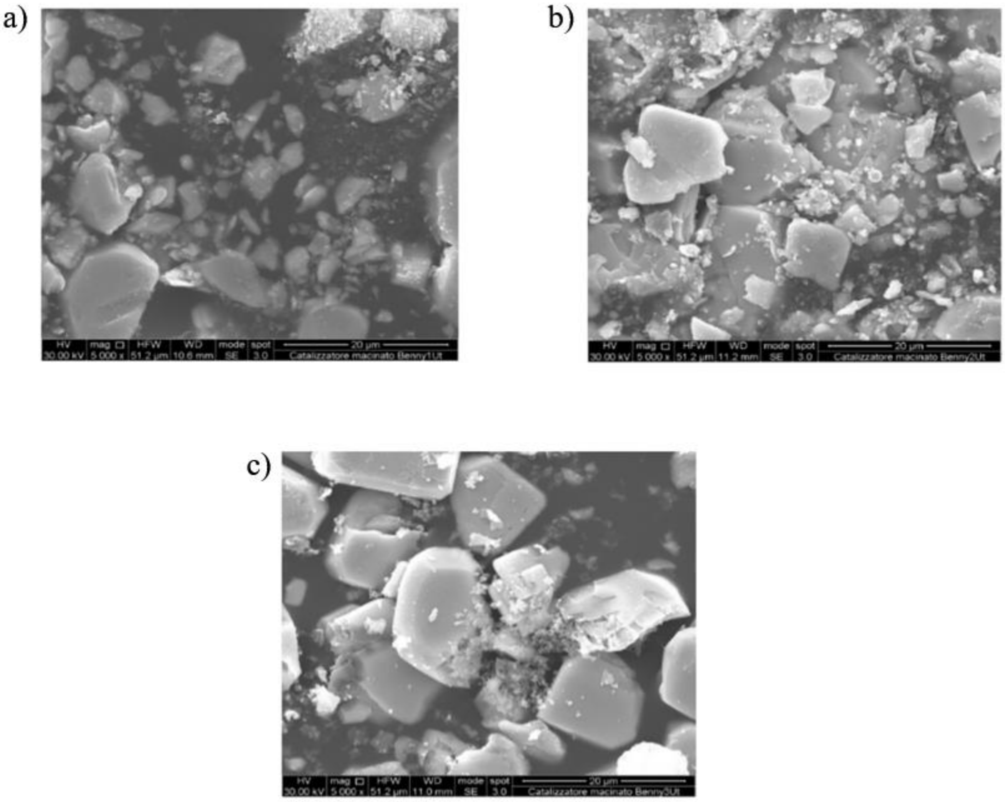


Figure 4.11: SEM Micrographs of Milled SnO Catalyst: a) First Run, b) Second Run, c) Third Run (Interrante et al., 2018)

Wong et al. (2020a) successfully synthesised a sustainable, low cost and environmentally benign catalyst from the biomass wastes to be used in interesterification of oleic acid and methyl acetate to produce methyl oleate. The biomass-derived carbon-based solid acid catalyst was produced by using oil palm empty fruit bunch (OPEFB) derived activated carbon. The catalyst was prepared by using concentrated sulfuric acid through direct sulfonation. The reaction parameters were investigated and the highest FAME yield of 52.3% was achieved under the optimum reaction conditions with sulfonation temperature of 100 °C. The FAME yield was calculated based on Equation (4.4):

$$FAME\ Yield = \frac{C\left(\frac{g}{L}\right) \times V_f(L)}{m_i(g)} \times 100\% \tag{4.4}$$

where C represents the methyl oleate concentration in the product, V_f represents the total volume of the product and m_i represents the total mass of oleic acid as the feedstock. The reusability of the synthesised solid acid catalyst was also studied and the results are shown in Figure 4.12. The catalytic activity at the fifth cycle was 82% of the catalyst used in the first cycle, with catalyst regeneration treatment using concentrated sulphuric acid after each run of experiment (Wong et al., 2020a).

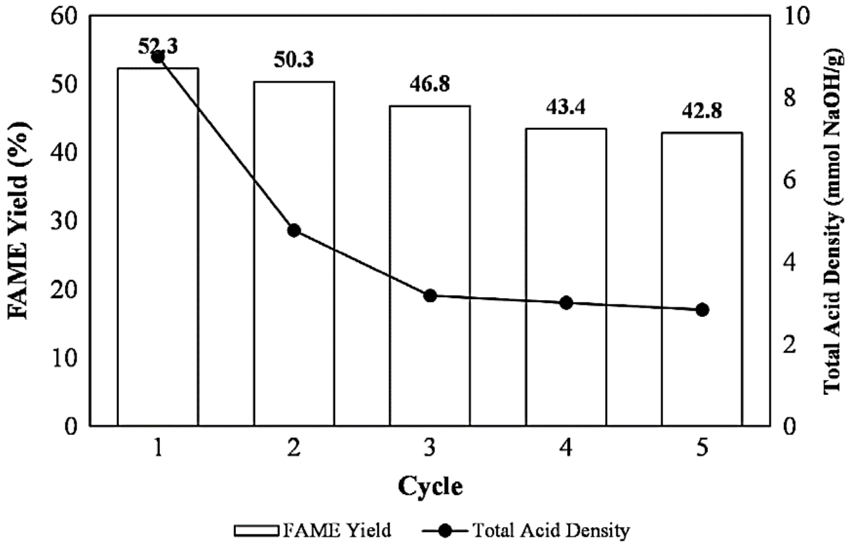


Figure 4.12: Reusability Test of OPEFB Derived Activated Carbon Catalyst in Interesterification with MAOMR 50:1 and 10 wt.% Catalyst at 110 °C for 8 Hours (Wong et al., 2020a)

Wong et al. (2020b) further investigated the conditions for carbonization and sulfonation in the synthesis of the activated carbon and the sulfonated carbon catalyst. It was reported that the optimum carbonization temperature and duration were 600 °C and 3 hours, while the optimum sulfonation temperature and duration were 100 °C and 6 hours (Wong et al., 2020b). From the results of the experiments, the highest methyl oleate yield achieved was 50.5% with the optimum catalyst preparation conditions and reaction conditions of 50:1 MAOMR with 10 wt.% catalyst loading for 8 hours at 100 °C.

4.1.4 Heterogeneous Base Catalyst

Similar to heterogeneous acid catalyst, heterogeneous base catalyst has the advantage of reduced downstream separation processes and the ability to be recycled and reused for consecutive runs. Base catalyst also show great catalytic activity under mild reaction conditions (Calero et al., 2014), unlike acid catalyst that generally requires higher reaction conditions. Besides, base catalysts are mostly non-corrosive, environmental friendly and easy to dispose. There are different types of heterogenous base catalysts such as metal-based oxides, mixed metal-based oxides, transition metal-based oxides, boron group-based types, hydrotalcites as well as waste-based catalyst like CaO from waste products with high calcium contents (Rizwanul Fattah et al., 2020). Table 4.4 shows every heterogeneous base catalyst and their biodiesel yield with respective reaction parameters via chemical interesterification.

In the research of Battistel et al. (2011), various types of heterogeneous base catalysts are included to be compared with other types of catalysts used in glycerol-free biodiesel production to produce butyrate methyl ester (BuMe) as well as TA in the biodiesel products. The solid base catalysts used in the research were ETS-10, Katalco 59-3, Pural Mg 70, mixed oxide Mg-Al 3:1 and mixed oxide Mg-Al 3:1 with addition of 10% Fe. Titanium-silicalite ETS-10 in alkaline form is a crystal structure with microporous structure that is topologically similar to zeolite β which is a heterogenous acid catalyst. Katalco 59-3, also known as sodium aluminate Katalco is a spherical absorbent with high porosity. Pural Mg 70 is actually a commercial hydrotalcite from Sasol Germany GmBH (DE). ETS-10, Katalco 59-3 and Pural Mg 70 all showed extremely low activities that gave BuME yields of below 10%.

Both mixed oxides Mg-Al 3:1 and Mg-Al 3:1 + 10% Fe used in the research were synthesised from layered double hydroxides hydrotalcites. These catalysts are porous amorphous mixed oxides and it was reported that the Mg/Al ratio will affect the intrinsic basicity of the oxide surface (Battistel et al., 2011). Two Mg-Al ratios, 3:1 and 6:1 were tested in the research and Mg-Al ratio of 3:1 was able to generate higher yield based on the results. Addition of Fe to the mixed oxides was also tested due to the improvement of catalytic activity in transesterification after frame insertion of Fe^{3+} ions to increase the active sites, as suggested by other researchers (MacAla et al., 2008).

Table 4.4: Heterogeneous Base Catalysts Used in Chemical Interesterification

Heterogeneous Base Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**Catalyst Loading (wt.%)**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
ETS-10	Tributyrin	Methyl acetate	20:1	10^a	80	8	2%*	(Battistel et al., 2011)
Katalco 59-3	Tributyrin	Methyl acetate	20:1	10^a	80	8	2%*	
Pural Mg 70	Tributyrin	Methyl acetate	20:1	10^a	80	8	9%*	
Mg-Al 3:1 oxide	Tributyrin	Methyl acetate	20:1	15^a	140	8	24%*	(Battistel et al., 2011)
	Soybean oil	Methyl acetate	50:1	18.6	200	4	95.9% Conversion	(Dhawan, Barton and Yadav, 2020)
Mg-Al 4:1 oxide	Soybean oil	Methyl acetate	32:1	5	250	20	89.74^{FAME} 0.00^{TA}	(Simões et al., 2020)
Mg-Al 3:1/HMS	Soybean oil	Methyl acetate	50:1	18.6	200	4	92.7% Conversion	(Dhawan, Barton and Yadav, 2020)

Table 4.4 (Continued)

Heterogeneous Base Catalysts	**Feedstocks**	**Acyl Acceptor**	**MAOMR/ EAOMR**	**Catalyst Loading (wt.%)**	**Reaction Temperature (°C)**	**Reaction Time (h)**	**Biodiesel Yield (wt.%)**	**References**
Ca-Al 3:1 oxide	Soybean oil	Methyl acetate	50:1	18.6	200	4	92.5% Conversion	(Dhawan, Barton and Yadav, 2020)
Fe 10% Mg-Al 3:1 oxide	Tributyrin	Methyl acetate	20:1	15[a]	140	8	22%*	(Battistel et al., 2011)
Ca 40% Mg-Al 3:1 oxide	Soybean oil	Methyl acetate	32:1	5	250	20	87.16 ^{FAME} 4.66 ^{TA}	(Simões et al., 2020)
MgO	Soybean oil	Methyl acetate	32.1	5	250	20	96.16 ^{FAME} 0.00 ^{TA}	(Simões et al., 2020)
	Soybean oil	Methyl acetate	50:1	18.6	200	4	85.4% Conversion	(Dhawan, Barton and Yadav, 2020)
Al_2O_3	Soybean oil	Methyl acetate	50:1	18.6	200	4	70.5% Conversion	(Dhawan, Barton and Yadav, 2020)
CH_3OK (solid)	Sunflower oil	Methyl acetate	12:1	0.2:1[b]	50	0.25	55.0 ^{FAME}	(Casas, Ramos and Pérez, 2011b)

Table 4.4: (Continued)

Heterogeneous Base Catalysts	Feedstocks	Acyl Acceptor	MAOMR/ EAOMR	Catalyst Loading (wt.%)	Reaction Temperature (°C)	Reaction Time (h)	Biodiesel Yield (wt.%)	References
CaO	Waste cooking oil	Ethyl acetate	30:1	4.0	80	5	90.5	(Komintarachat, Tongroon and Chuepeng, 2019)
	Soybean oil	Methyl acetate	40:1	10	325	4	62.3 $^{\mathrm{FAME}}$ 1.00 $^{\mathrm{TA}}$	(Nunes and Castilhos, 2020)

* butyrate methyl ester yield (%)
[a] catalyst concentration (% w/v oil)
[b] catalyst to oil molar ratio (COMR)

However, Fe^{3+} ions insertion did not improve the BuMe yield in interesterification, it further decreased the yield slightly. All these heterogeneous base catalysts reported in the research showed very weak catalytic activities and low BuMe and TA yields, as compared to that observed in homogeneous condition. It was explained due to the weak intrinsic basicity of these catalyst surfaces that were able to catalyse well in transesterifications, but weak at ester exchange reactions in interesterifications (Battistel et al., 2011).

Simões et al. (2020) had tested different types of heterogeneous acid and base catalysts in soybean biodiesel production. The reported acid catalysts were introduced in the previous section, namely niobium oxide and zeolite HY. The solid base catalysts tested in the research were MgO, hydrotalcites with different Mg-Al ratios such as Mg-Al 2:1 oxide, Mg-Al 3:1 oxide, Mg-Al 4:1 oxide, Ca 20% Mg-Al 3:1 oxide and Ca 40% Mg-Al 3:1 oxide. Catalyst screening was carried out to find out the most suitable catalyst to be employed in soybean biodiesel production. All the base catalysts tested by Simões et al. (2020) presented great activities with high FAME yields but low TA yields. The extremely low TA yields could be the consequence of the parallel undesired decomposition reactions catalysed by the catalysts (Simões et al., 2020). Triacetin decomposition could also happen via several pathways at high temperature (Laino et al., 2012).

Among the heterogeneous base catalysts tested by Simões et al. (2020), MgO, Mg-Al 4:1 oxide and Ca 40% Mg-Al 3:1 oxide were reported as the most active catalysts. For Mg-Al oxides, the results showed increase of FAME yields and decrease of TA yields, when the Mg content was increased. For Ca-Mg-Al mixed oxides, the yields of both FAME and TA increased with the Ca content at 40 wt.%. Impregnation of CaO would be the reason of increased yields as it improved the alkalinity of the catalysts (Simões et al., 2020). Researchers concluded that Ca 40% Mg-Al 3:1 oxide as the most suitable catalyst to produce soybean biodiesel due to the fact that it presented the highest TA yield. Besides, the global yield which is representing the sum of 87.16 wt.% FAME and 4.66 wt.% TA yields was statistically similar to the results achieved with MgO and Mg-Al 4:1 oxide, as shown in Table 4.4.

Hence, further experiments were conducted using Ca 40% Mg-Al 3:1 oxide as the heterogeneous base catalyst that was chosen during the catalyst screening done by Simões et al. (2020). Reaction parameters such as temperature, catalyst concentration and MAOMR were investigated to find out the optimum reaction conditions for the soybean biodiesel production using the selected base catalyst. The experiments were conducted for only 3 hours instead of 20 hours which was conducted for the catalyst screening. Hence, the yield would be lower as compared to the yield from the results of catalyst screening. The optimum reaction conditions were reported as reaction temperature of 325 ℃, MAOMR of 40:1, 5 wt.% of catalyst for 80 minutes or 1.3 hours at pressure between 5 MPa to 10 MPa to give the expected FAME and TA yields of 61.74% and 6.81%, respectively resulting a global yield (FAME + TA) of 68.55%.

The reusability of Ca 40% Mg-Al 3:1 catalyst was also studied, where the solid base catalyst was recycled and reused for 5 consecutive runs without treatment between cycles under the optimum reaction conditions. The results are shown in Figure 4.13, where the bracketed values represent the decay percentage. It was observed that the catalyst activity decayed slightly over each reaction. Similar to the global yield expected, the yield from reaction with fresh catalyst was about 70% and it may further reduce to yield similar to reaction without catalyst. The results showed that the catalyst can be recycled and reused for at least 3 cycles, with only about 15% of activity decay (Simões et al., 2020).

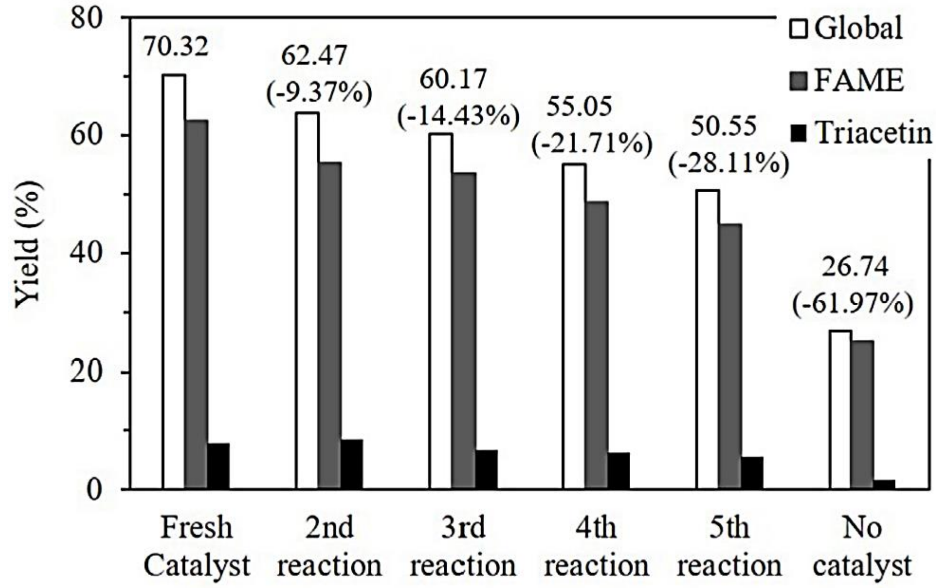


Figure 4.13: Reusability Test of Ca 40% Mg-Al 3:1 Oxide Catalyst at Optimum Reaction Conditions for 80 Minutes (Simões et al., 2020)

Similar hydrotalcites were also employed as heterogeneous base catalysts in interesterification of triglycerides with methyl acetate conducted by Dhawan, Barton and Yadav (2020) to produce biodiesel and triacetin. The hydrotalcites tested in the research were calcined Mg-Al hydrotalcite with mole ratio of 3:1 (Mg-Al 3:1 oxide), calcined Ca-Al hydrotalcite with mole ratio of 3:1 (Ca-Al 3:1 oxide) and 10% w/w Mg-Al 3:1 supported on hexagonal mesoporous silica (Mg-Al 3:1/HMS), all prepared by co-precipitation method. Different ratios of Mg-Al oxides such as 2:1 and 1:1 were also included. Other than hydrotalcites, MgO and Al_2O_3 were also tested as heterogeneous base catalysts in the same research. All the experiments with different catalysts were conducted at 200 °C for 4 h with MAOMR of 50:1 and catalyst loading of 0.04 g/cm^3 or 1.6 g (total volume 40 cm^3) as well as agitation speed of 1000 rpm. It was reported that the soybean oil was 7.0 g, hence the catalyst loading would be 18.6 wt.%. Researchers calculated the conversions of triglycerides and TA selectivity based on Equation (4.5) and Equation (4.6), respectively,

$$Conversion = \frac{C_T^0 - C_T^t}{C_T^0} \tag{4.5}$$

$$TA\ Selectvity = \frac{C_{TA}^t}{C_{MADG}^t + C_{DAMG}^t + C_{TA}^t} \tag{4.6}$$

where C_T^0 (M) represents the initial triglyceride concentration and C_T^t (M), C_{MADG}^t (M), C_{DAMG}^t (M), C_{TA}^t (M) are triglyceride, MADG, DAMG and TA concentrations at time 't' (min). The concentrations of triglycerides, intermediates and TA were analysed and obtained from HPLC.

From the results reported by Dhawan, Barton and Yadav (2020), all the hydrotalcites presented high conversion of above 90% while MgO and Al_2O_3 gave comparative low conversions with very low TA selectivity. For the hydrotalcites, Mg-Al 3:1/HMS showed great conversion of 92.7%. However, the TA selectivity was as low as 2.8% and it could be explained by hexagonal mesoporous silica (HMS) that hindered the basic sites of the catalyst (Dhawan, Barton and Yadav, 2020). Besides, Ca-Al 3:1 hydrotalcite also showed high conversion and TA selectivity of 92.5% and 4.3%, respectively. The reported results showed that Mg-Al 3:1 hydrotalcite presented the highest conversion of triglycerides of 95.9% with TA selectivity of 5.3%. The high activity of Mg-Al 3:1 was expected due to its high basicity based on characterisation of heterogeneous catalysts by temperature-programmed desorption (TPD). TPD analysis was employed to test the basicity and acidity of the catalysts.

With the highest performance achieved by Mg-Al 3:1 hydrotalcite, it was used to conduct further experiments for reaction optimisation. It was found that the reaction conditions used for every catalyst previously were optimum as it gave the highest conversion of 95.9% and TA selectivity of 5.3%. The catalyst was then used in multiple reactions consecutively to evaluate its reusability as a heterogeneous catalyst. The catalyst was recycled and reused after the first reaction with fresh catalyst. After each completion of interesterification, methanol was used to wash the catalyst for removal of adsorbed compounds. The recovered catalyst was then dried at 100 ℃ for 12 h and calcined at 500 ℃ for 6 h (Dhawan, Barton and Yadav, 2020). Fresh catalyst was also used to replace the lost catalyst during filtration to maintain the same amount of catalyst in every reaction. It was reported only 1.6% decrease in the triglyceride conversion and 0.5% in the TA selectivity during the third cycles of catalyst. The results of its reusability test were shown in Figure 4.14. Hence, the catalyst was found to be reusable for at least 3 cycles after its first reaction without significant loss of activity.

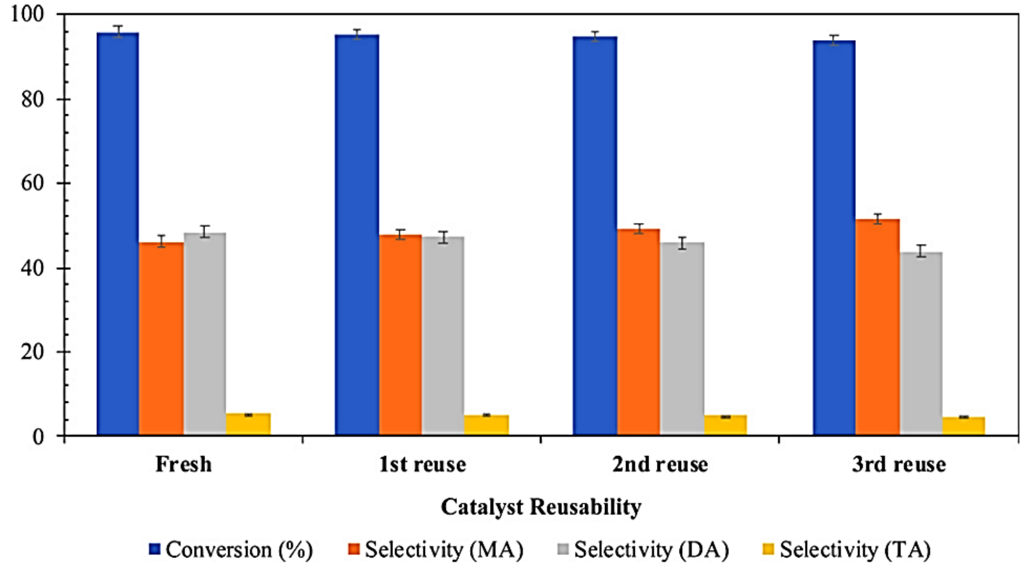


Figure 4.14: Reusability Test for Mg-Al 3:1 Hydrotalcite in Interesterification with MAOMR 50:1, Catalyst Loading 0.04 g/cm^3 (18.6 wt.%) at 200 ℃ and 100 rpm for 4 Hours (Dhawan, Barton and Yadav, 2020)

In the research done by Casas, Ramos and Pérez (2011b) that mainly focused on homogeneous base catalysts, several heterogeneous base catalysts were also reported such as potassium hydroxide (KOH) and potassium methoxide (CH_3OK) in powder forms. Sunflower oil was used as the feedstock with methyl acetate as acyl acceptor in the interesterification reaction. Reaction with KOH presented zero formation of FAME as the catalyst reacted irreversibly with the esters and it caused the formation of potassium acetate and potassium soaps (Casas, Ramos and Pérez, 2011b). On the other hand, solid CH_3OK presented average performance with FAME yield of 55 wt.% in the product, which was lower than other CH_3OK in homogeneous conditions tested in the same study. CH_3OK was initially immiscible in the reaction mixture of oil and methyl acetate. Hence, it was believed that the overall reaction kinetics were limited by the mass transfer step of the dissolution of solid CH_3OK into the reaction mixture (Casas, Ramos and Pérez, 2011b). Therefore, CH_3OK was added with PEG, methanolic solution or mixed with oil ahead of the reaction to improve the FAME yield in homogeneous condition.

Apart from metal-based oxides and hydrotalcites, waste-based catalyst such as calcium oxide (CaO) was employed in interesterification as heterogeneous base catalyst. Komintarachat, Tongroon and Chuepeng (2019) had synthesised biodiesel via interesterification of waste cooking oil and ethyl acetate as the acyl acceptor with CaO as the catalyst. CaO catalyst was obtained from waste egg shells via 4 hours of calcination between 700 and 900 °C to convert calcium carbonate ($CaCO_3$), which was the main component in eggshells into CaO in powder form (Komintarachat, Tongroon and Chuepeng, 2019). The reaction parameters such as EAOMR, temperature and time were investigated, while the catalyst amount was fixed at 4 wt.%. From the results, EAOMR of 30:1 was optimum as it was found that excess ethyl acetate caused the reaction equilibrium to shift backwards, thus reduced the biodiesel yield. Reaction temperature of 80 °C was found to obtain highest yield as it was close to the boiling point of ethyl acetate. Higher temperature would cause evaporation of ethyl acetate (Komintarachat, Tongroon and Chuepeng, 2019). With reaction time of 5 hours, a maximum biodiesel yield of 90.5 wt.% was achieved, which consisted of mixture of FAME and TA. The reusability of the heterogeneous catalyst was not studied in the research.

The fuel properties were also studied for the biodiesel product formed with CaO as catalyst. The biofuel synthesised was compared with the waste cooking oil, where the oil turned from dark brown in colour to clear brown. Other major fuel properties were investigated according to the limits of EN 14214. It was reported that the density of the biofuel was slightly higher than the limit of EN 14212 due to the presence of TA in the biofuel. Besides, the kinematic viscosity was also investigated and it lies between the limits. However, the carbon residue which is the amount of carbon deposit formed at the combustion chamber exceeded the limit, probably due to the reaction intermediates like diacetin in the biofuel. From the results, it was emphasised that the cloud point, pour point and cold filter plugging point of the synthesised biofuel were reduced (Komintarachat, Tongroon and Chuepeng, 2019).

The same catalyst, CaO was also tested by Nunes and Castilhos (2020) for biodiesel production via chemical interesterification. Soybean oil was used as the feedstock with methyl acetate as the acyl acceptor instead of ethyl acetate which was used by Komintarachat, Tongroon and Chuepeng (2019). In this study, Nunes and Castilhos (2020) had investigated the effect of calcination temperature of $CaCO_3$ to CaO. It was reported that calcination temperature of 800 °C was able to generate the highest yield. The catalyst was then calcined at the optimum calcination temperature to be used in further experiments to investigate the optimum reaction conditions. From the results, highest FAME yield of 62.3 wt.% and TA yield of 1.0 wt.% were achieved in 4 hours with MAOMR 40:1 and 10 wt.% catalyst at 325 °C.

The synthesised heterogeneous CaO catalyst was also tested for its reusability under the optimum calcination temperature and reaction conditions for four cycles. The results are shown in Figure 4.15, where it showed that the FAME content declined from 62.3 wt.% to 40.85 wt.% in the fourth cycle, indicating a catalytic efficiency decay of 21.15%. The lack of washing step between cycles could explain the reduced yields as the active sites of the catalyst might be blocked by the reactants during the reaction. Besides, the mass loss of catalyst during the separation by centrifugation could also decrease yields. Moreover, with the aid of atomic emission spectroscopy and FTIR analyses, leaching phenomena of CaO was observed between the cycles of reaction, causing the deactivation of CaO catalyst (Nunes and Castilhos, 2020).

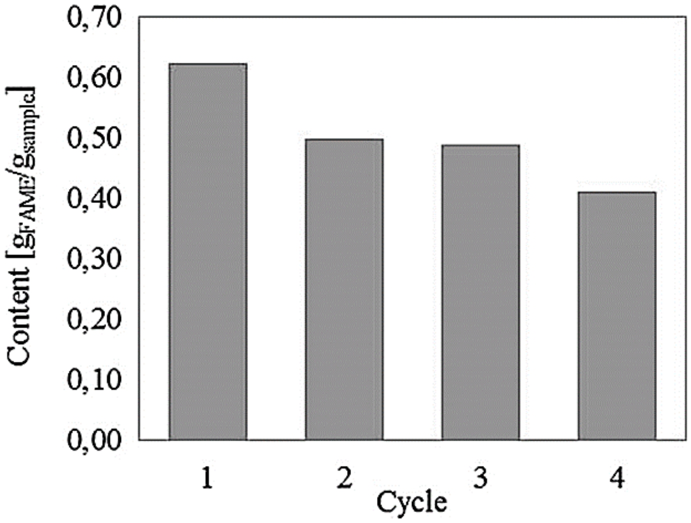


Figure 4.15: Reusability Test of CaO in Interesterification with MAOMR 40:1 and 10 wt.% Catalyst at 325 °C for 4 Hours (Nunes and Castilhos, 2020)

4.1.5 Summary of Catalyst Types

There are four types of catalysts used in chemical interesterification for biodiesel production, namely homogeneous acid catalyst, homogeneous base catalyst, heterogeneous acid catalyst and heterogeneous base catalyst. These catalysts have been introduced in previous sections, where their respective reaction conditions and yields are included, as reported by different researchers. This section summarises the reaction conditions and yields achieved by different types of catalysts, as shown in Table 4.5 and Table 4.6 for homogeneous catalyst and heterogeneous catalyst, respectively.

Table 4.5 and Table 4.6 show the ranges of reaction parameters and product yields used and obtained by different researchers in biodiesel production via interesterification for various types of catalysts. From the summary tables, there are some different terms for the same reaction parameters such as the catalyst amount and also for the product yields. This is because some of the researchers used different terms and units for the catalyst amount such as COMR, catalyst loading and catalyst concentration for both homogeneous and heterogeneous catalysts. Besides, different product analysis methods were also adopted by different researchers, where some researchers calculated the biodiesel yields by accounting the initial oil amounts, while some researchers calculated the conversions of triglycerides or the weight percentages of FAME and TA contents in the biodiesel products.

Table 4.5: Summary of Homogeneous Catalysts

Homogeneous Catalysts	**Ranges of Reaction Conditions**					**Biodiesel Products Range**		
	MAOMR/ EAOMR	Catalyst Amount		Temperature (℃)	Time (h)	Yield (%)	Conversion (%)	FAME Content (wt.%)
		COMR	Loading (wt.%)					
Acid	20:1 – 40:1	0.01:1 – 0.3:1	-	80 – 210	3 – 20	2 – 93	-	-
Base	6:1 – 36:1	0.015:1 – 0.2:1	0.5 – 1.17	25 – 140	0.2 – 6	8 – 93	98.51	60 – 83.5

Table 4.6: Summary of Heterogeneous Catalysts

Heterogeneous Catalysts	**Ranges of Reaction Conditions**						**Biodiesel Products Range**		
	MAOMR/ EAOMR	Catalyst Amount			Temperature (℃)	Time (h)	Yield (%)	Conversion (%)	FAME Content (wt.%)
		Loading (wt.%)	Concentration (% w/v oil)	COMR					
Acid	10:1 – 50:1	2 – 10	5 – 15	0.69:1	110 – 300	1 – 20	4 – 90	-	34.81 – 80.8
Base	12:1 – 50:1	4 – 18.6	10 – 15	0.20:1	50 – 325	0.25 – 20	2 – 24	70.5 – 95.9	55 – 96.16

4.2 Analysis and Comparison of Catalysts

After gathering the results of different types of catalysts reported by researchers, it was found that there are a total of 55 different types of catalysts tested in chemical interesterification for biodiesel production. A total of 67 results were reported as similar catalysts were tested by different researchers in different journals. All the results were obtained from 30 journals that reported chemical interesterification by using various types of catalysts in glycerol-free biodiesel production. Table 4.7 shows the numbers of catalysts, results and journals for each type of catalyst for analysis purpose in following sections. The data from Table 4.7 was used to evaluate the statistics such as the percentages of experiments that achieved high biodiesel yields with different types of catalysts in chemical interesterification. The percentages of each catalyst types were also calculated based on the total number of catalysts obtained from the journals.

Table 4.7: Statistics of Catalysts, Results and Journals

Catalyst Types	No. of Catalysts	No. of Results	No. of Journals	Catalyst Types (%)
Homogeneous Acid	8	9	3	14
Homogeneous Base	21	24	11	38
Total	**29**	**33**	**14**	**52**
Heterogeneous Acid	13	18	10	24
Heterogeneous Base	13	16	6	24
Total	**26**	**34**	**16**	**48**
Sum of Totals	**55**	**67**	**30**	**100**

The biodiesel yield was the first aspect to be analysed as this is the most significant aspect in biodiesel production. After obtaining the results of catalysts with high yields for homogeneous and heterogeneous types, the reaction parameters such as reaction temperature, reaction time, catalyst amount and acyl acceptor to oil molar ratio for every catalyst with high yield were analysed to find the best homogeneous and heterogeneous catalysts with high yields under mild reaction conditions. Reusability of catalysts were also taken into account for heterogeneous catalysts. The objective was to find the most suitable homogeneous and heterogeneous catalysts in terms of the overall aspects.

4.2.1 Biodiesel Yield

Researchers used different ways to obtain and present the biodiesel product results such as biodiesel yields, FAME and TA contents as well as conversions of triglycerides. Hence, every result with biodiesel yields (%), FAME and TA contents (wt.%) and conversions (%) of above 90 were chosen as the high tier catalysts. The high tier catalysts were tabulated in Table 4.8 and Table 4.9 for homogeneous catalyst and heterogeneous catalyst, respectively. Since every result reported did not fulfil the requirements of biodiesel standard EN 14214 that requires at least 96.5% of methyl ester content in the product, results that reported FAME and TA content separately were added together in Table 4.8 and Table 4.9. This also indicated that further research and optimisations with the catalysts were needed for improvement to reach the standard of EN 14214.

From Table 4.8, it was shown that 9 results with homogeneous catalysts out of 33 total number of results with homogeneous catalysts collected were ranked as the high tier catalysts. This indicated that about 27% of the results reported in homogeneous catalysis achieve remarkable results with high biodiesel yields via chemical interesterification.

In heterogeneous catalysis as shown in Table 4.9, only 7 results reported were ranked as the high tier catalysts out of the total results reported of 34, indicating only about 20% of the heterogeneous catalysis results. This analysis showed that homogeneous catalyst is more capable to produce high biodiesel yield through chemical interesterification. This could also because of the higher number of results collected in homogeneous catalysis were base catalysts, as shown in Table 4.7, where 24 results of acid catalyst and 9 results of base catalyst were collected in homogeneous catalysis. This will lead to higher proportion of base catalyst in the results, thus increasing the percentage of high tier base catalyst in homogeneous condition as base catalyst tends to have higher catalytic activity as compared to acid catalyst (Calero et al., 2014).

Table 4.8: High Tier Homogeneous Catalysts in Chemical Interesterification

Catalysts	Nature	Reaction Conditions				Yields	References
		MAOMR	COMR	Temperature (°C)	Time (h)		
CH_3NaO	Base	20:1	0.05:1	60	0.2	93.00%	(Battistel et al., 2011)
Trifluoro-MS acid	Acid	20:1	0.05:1	130	20	93.00%	
Trifluoro-MS acid + acetic anhydride	Acid	20:1	0.30:1	130	20	92.00%	
t-BuOK	Base	20:1	0.05:1	60	0.2	92.00%	
NaOH	Base	30:1[a]	0.015:1	80	3.0	92.00%	(Chuepeng and Komintarachat, 2018)
CH_3OK (ultrasonic assisted)	Base	9:1	1 %[b]	50	0.58	91.00%	(Kashyap, Gogate and Joshi, 2019)
	Base	15:1	1.17 %[b]	50	0.50	98.51% Conversion	(Medeiros et al., 2018)
Trifluoro-MS acid + acetic acid	Acid	20:1	0.30:1	130	20	91.00%	(Battistel et al., 2011)
Tin octoate	Acid	40:1	0.10:1	210	20	90.00%	(Galia et al., 2014)

[a] EAOMR

[b] catalyst loading (% w/w oil)

Table 4.9: High Tier Heterogeneous Catalysts in Chemical Interesterification

Catalysts	**Nature**	**Reaction Conditions**				**Yields**	**References**
		MAOMR	**Catalyst Loading (wt.%)**	**Temperature (℃)**	**Time (h)**		
MgO	Base	32:1	5.0	250	20	96.16 wt.%	(Simões et al., 2020)
Ca 40% Mg-Al 3:1 oxide	Base	32:1	5.0	250	20	91.82 wt.%	
CaO	Base	30:1[a]	4.0	80	5	90.50 wt.%	(Komintarachat, Tongroon and Chuepeng, 2019)
Tin (II) oxide	Acid	40:1	0.69:1[b]	210	4	90.00%	(Interrante et al., 2018)
Mg-Al 3:1 oxide	Base	50:1	18.6	200	4	95.90% Conversion	(Dhawan, Barton and Yadav, 2020)
Mg-Al 3:1/HMS	Base	50:1	18.6	200	4	92.70% Conversion	
Ca-Al 3:1 oxide	Base	50:1	18.6	200	4	92.50% Conversion	

[a] EAOMR; [b] COMR

For the heterogeneous catalysis results, there were 18 results with acid catalysts and 16 results with base catalysts, as shown in Table 4.7. Although the number of collected results with acid and base catalysts were similar, Table 4.9 shows majority of base catalysts that achieved high biodiesel yields. This could be due to the higher catalytic activity of solid base catalyst than that of the solid acid catalyst (Ranganathan, Narasimhan and Muthukumar, 2008). From this biodiesel yield analysis, a total of 15 catalysts were reported with yields, FAME and TA contents and conversions of above 90%.

Highest biodiesel yield of 96.16 wt.% was achieved with MgO as heterogeneous base catalyst by Simões et al. (2020), in which the reaction yielded 96.16 wt.% FAME without formation of TA. In homogeneous catalysis, the highest biodiesel yield was 93%, achieved with sodium methoxide (CH_3NaO) and trifluoro-MS acid as homogeneous base and homogeneous acid catalysts, respectively by Battistel et al. (2011). The products from the reactions were butyrate methyl esters (BuMe) since tributyrins were used as the feedstocks in the experiments. Besides, a conversion as high as 98.51% was achieved with potassium methoxide (CH_3OK) as homogeneous base catalyst with ultrasonic assisted, conducted by Medeiros et al. (2018).

4.2.2 Reaction Time and Reaction Temperature

After obtaining the high tier catalysts for both homogeneous and heterogeneous types, it is important to also look into their required reaction conditions such as reaction time and temperature. This is because in the biodiesel industry, a reaction with high yield under mild reaction conditions is most favourable as it greatly reduces the cost of production due to the lesser energy required.

Table 4.10 shows the high tier homogeneous catalysts selected in previous section with their reaction temperatures of below 100 °C as well as their reaction times. Reaction temperature is known to be one of the most important factors in biodiesel production to affect the biodiesel yield and production cost (Chozhavendhan et al., 2020).

Table 4.10: High Tier Homogeneous Catalysts with Low Reaction Temperature and Reaction Time

Catalysts	**Reaction Conditions**		**Yields (%)**	**References**
	Temperature (°C)	**Time (h)**		
CH_3OK (ultrasonic assisted)	50	0.58	91	(Kashyap, Gogate and Joshi, 2019)
CH_3NaO	60	0.2	93	(Battistel et al., 2011)
t-BuOK	60	0.2	92	(Battistel et al., 2011)
NaOH	80	3.0	92	(Chuepeng and Komintarachat, 2018)

Based on Table 4.10, CH_3NaO which is a homogeneous base catalyst was selected as the best homogeneous catalyst in the aspect of reaction temperature and time. This can be justified by its biodiesel yield of 93% which was the highest among the high tier homogeneous catalysts, under low reaction temperature of 60 °C and reaction time of 0.2 h. In fact, CH_3OK assisted with ultrasound required the lowest reaction temperature of 50 °C. However, it required a higher reaction time of 0.58 h with biodiesel yield of 91%. Hence, CH_3NaO is a better catalyst to be used due to its higher biodiesel yield at shorter amount of time, with only an additional reaction temperature of 10 °C as compared to the reaction with ultrasonic-assisted CH_3OK.

For the high tier heterogeneous catalysts, base catalyst CaO was selected as the best heterogeneous catalyst in terms of reaction temperature and reaction time. The catalyst was able to yield 90.5 wt.% of biodiesel under mild conditions of 80 °C for 5 h, as compared to other high tier heterogeneous catalyst in which all required reaction temperature of 200 °C or above. The huge difference in the reaction temperature clearly shows that CaO is more feasible and practical to be used in biodiesel production with great biodiesel yield.

4.2.3 Catalyst Loading and Acyl Acceptor to Oil Molar Ratio

With the high tier catalysts selected with low reaction temperature and time, other reaction parameters such as catalyst loading and acyl acceptor to oil molar ratio were also investigated. Table 4.11 shows the high tier homogeneous catalysts selected in previous section with their respective MAOMR/EAOMR and COMR. For homogeneous catalysts, it will be focusing more on the acyl acceptor to oil molar ratio due to the high cost of acyl acceptor in biodiesel production (Musa, 2016). On the other hand, the catalyst amounts for every catalyst were similarly low.

Table 4.11: Selected High Tier Homogeneous Catalysts with Acyl Acceptor to Oil Molar Ratio and Catalyst Loading

Catalysts	**Reaction Parameters**		**Yields (%)**	**References**
	MAOMR	**COMR**		
CH_3OK (ultrasonic assisted)	9:1	1 %[b]	91	(Kashyap, Gogate and Joshi, 2019)
CH_3NaO	20:1	0.05:1	93	(Battistel et al., 2011)
t-BuOK	20:1	0.05:1	92	(Battistel et al., 2011)
NaOH	30:1[a]	0.015:1	92	(Chuepeng and Komintarachat, 2018)

[a] EAOMR
[b] catalyst loading (% w/w oil)

As shown in Table 4.11, CH_3OK assisted with ultrasound required the lowest MAOMR of 9:1. However, the reaction required ultrasound device to be installed. Ultrasonic-assisted reaction is normally used to reduce the required reaction temperature to be heated easily without external heating (Mostafaei et al., 2015). In this case, the reaction with CH_3NaO required temperature of only 60 ℃ to give 93% biodiesel yield. Hence, CH_3NaO is still considered as the best homogeneous catalyst due to its highest yield with a relatively low MAOMR and COMR, as compared to other homogeneous catalysts that were reported in the literature in previous section.

For the high tier heterogeneous catalysts, base catalyst CaO remains as the best heterogeneous catalyst. The reaction with CaO used ethyl acetate as the acyl acceptor instead of methyl acetate. It has the lowest EAOMR of 30:1 as compared to other catalysts in the tier list with MAOMR of 32:1 or above. Besides, it also required the lowest catalyst loading of 4 wt.%, as compared to that of the other catalysts with 5 wt.% and 18.6 wt.%. Low EAOMR and catalyst loading further reduce the cost of production in biodiesel industry.

4.2.4 Reusability of Catalyst

The reusability of catalyst was also studied only for heterogeneous catalyst as homogeneous catalyst could not be recycled and reused. For the high tier heterogeneous catalysts, most of them were able to be recycled and reused for at least three consecutive runs without significant loss of catalytic activities. Based on the results of the reusability test done by different researchers on different heterogeneous catalysts as stated in previous sections of heterogeneous acid and base catalysts, the catalytic efficiency decay of these catalysts were only up to 15% at their third cycles.

For CaO which was selected as the best heterogeneous catalyst previously, Komintarachat, Tongroon and Chuepeng (2019) did not conducted the reusability test for the CaO. However, another reaction with CaO as heterogeneous base catalyst was done by Nunes and Castilhos (2020) and the reusability test of CaO was conducted in the study, as shown in Figure 4.15. It was reported that the catalyst was able to be used for three consecutive cycles with little catalytic activity decay of 13.22% at the third cycle, without washing between the cycles. The CaO reusability was commonly reported in transesterification, Zhao, Qiu and Stagg-Williams (2013) reported commercial nano CaO with only slight biodiesel yield decay after ten cycles. However, the reaction with CaO done by Komintarachat, Tongroon and Chuepeng (2019) still requires further reusability test under its reaction conditions.

4.2.5 Summary of Catalysts in Overall Aspects

The overall aspects of the best homogeneous and heterogeneous catalysts selected previously namely CH_3NaO and CaO, respectively were investigated. For homogeneous CH_3NaO base catalyst, it has the highest biodiesel yield of

93% under mild reaction temperature of 60 °C for only 0.2 h (12 minutes) with 20:1 MAOMR and 0.05:1 COMR, conducted by Battistel et al. (2011). CH_3NaO is undeniably the best homogeneous base catalyst due to its ability to generate the highest biodiesel yield among its catalyst type. Besides, interesterification with CH_3NaO catalyst is also less energy intensive due to its mild reaction conditions. Hence in this study, CH_3NaO is said to be the best homogeneous base catalyst to be used in chemical interesterification to produce biodiesel.

For the heterogeneous catalyst, the reaction with CaO did not give the highest biodiesel yield among its catalyst type. However, the reaction conditions with the catalyst were significantly less energy intensive, making the reaction more cost-effective. The heterogeneous base catalyst, CaO was able to achieve 90.5 wt.% biodiesel yield with low EAOMR and catalyst loading of 30:1 and 4 wt.%, respectively at only 80 °C for 5 hours, conducted by Komintarachat, Tongroon and Chuepeng (2019). Besides, CaO is a waste-based catalyst that is sustainable and environmental-friendly to be employed in biodiesel production (Pandit and Fulekar, 2017). Moreover, the waste-based catalyst is easily available at low cost (Marwaha et al., 2018), it is also known as the most versatile heterogeneous base catalyst (Rizwanul Fattah et al., 2020).

4.3 Potential Catalyst from Transesterification

The numbers of catalysts reported used in chemical interesterification are still limited since it is a new alternative route in biodiesel production and it has not been widely investigated yet. Most of the catalysts used in this alternative route were employed due to their good performances reported in the conventional transesterification. This section provides two potential catalysts to be used in chemical interesterification, specifically heterogeneous catalysts. This is because of their superiority over homogeneous catalysts as described previously. Two heterogeneous catalysts were suggested, namely tungsten phosphoric acid and sodium silicate.

4.3.1 Tungsten Phosphoric Acid

Tungsten phosphoric acid is a type of heteropoly acids (HPAs) which is an acidic catalyst with good thermal stability, high oxidizing ability and also high acidity (Hanif, Nisar and Rashid, 2017). These characteristics make HPA catalyst a versatile green catalyst, they can also be recycled and reused to save the cost of process. Tungsten phosphoric acid is also known as 12-tungstophosphoric acid (TPA) with the chemical formula of $H_3PW_{12}O_{40}$. It is one of the super-acids as it has a very high acidic strength, even higher than pure sulphuric acid. High acidity of HPA is suitable to be used in transesterification and other organic processes efficiently. It can also reduce the activation energy of the reaction as heteropoly anion stabilises the cationic reaction intermediates, thus increasing its catalytic activity (Hanif, Nisar and Rashid, 2017).

Generally, supported HPAs are used in transesterification of biodiesel production to increase the surface area and improve the catalytic activities due to the dispersion of acid on the supportive materials. Normally, the active component of the acid catalyst is introduced on the supportive materials to form a supported solid acid catalyst. This is important as it obtains large amounts of the highly active form by applying the catalyst’s active components to supportive material (Emeji, 2015). Table 4.12 shows different types of TPA used in transesterification to produce biodiesel with their reaction parameters and yields as reported by the researchers. Different supports were used such as silica (SiO_2), hydrous zirconia, Montmorillonite (K-10) clay, magnetic nanoparticles (MNPs) with poly-glycidylmethacrylate (PGMA) shell and cesium-doped TPA. Researchers had also modified TPA with 1,2,3-Trizaole-4,5-dicarboxylic acid (TDA) to achieve high biodiesel yield.

4.3.2 Sodium Silicate

Sodium silicate (Na_2SiO_3) is a heterogeneous base catalyst commonly used in transesterification to produce biodiesel. The solid catalyst can be manufactured from reaction with soda ash (Na_2CO_3) and sand (SiO_2) at high temperature of 1400 to 1500 °C. Figure 4.16 illustrates the suggested industrial process of manufacturing sodium silicate in a plant. The catalyst performances were reported by different researchers with high biodiesel yields and the ability to be reused for multiple runs without significant loss of catalytic activity.

Table 4.12: Different Types of TPA used in Transesterification for Biodiesel Production

Types of TPA	**Feedstocks**	**Reaction Conditions**				**Biodiesel Yield (%)**	**Reference**
		Catalyst Loading (wt. %)	**Alcohol to Oil Molar Ratio**	**Temperature (°C)**	**Time (h)**		
TPA/SiO_2	Palm fatty acids	15	12:1	85	15	96.7	(Trakarnpruk, 2012)
TPA/Hydrous Zirconia	Canola oil	3	9:1	200	10	90.0	(Kulkarni et al., 2006)
10%TPA/K-10	Refined sunflower oil	5	15:1	170	8	66.0	(Bokade and Yadav, 2007)
TPA-PGMA-MNPs	Waste grease	4	33:1	122	24	98.0	(Zillillah, Ngu and Li, 2014)
TDA-TPA	Oleic acid	5	8:1	80	6	99.5	(Wang, Liu and Gong, 2017)
Cesium Doped TPA	Sesame oil	3	40:1	260	1	92.0	(Shin et al., 2012)

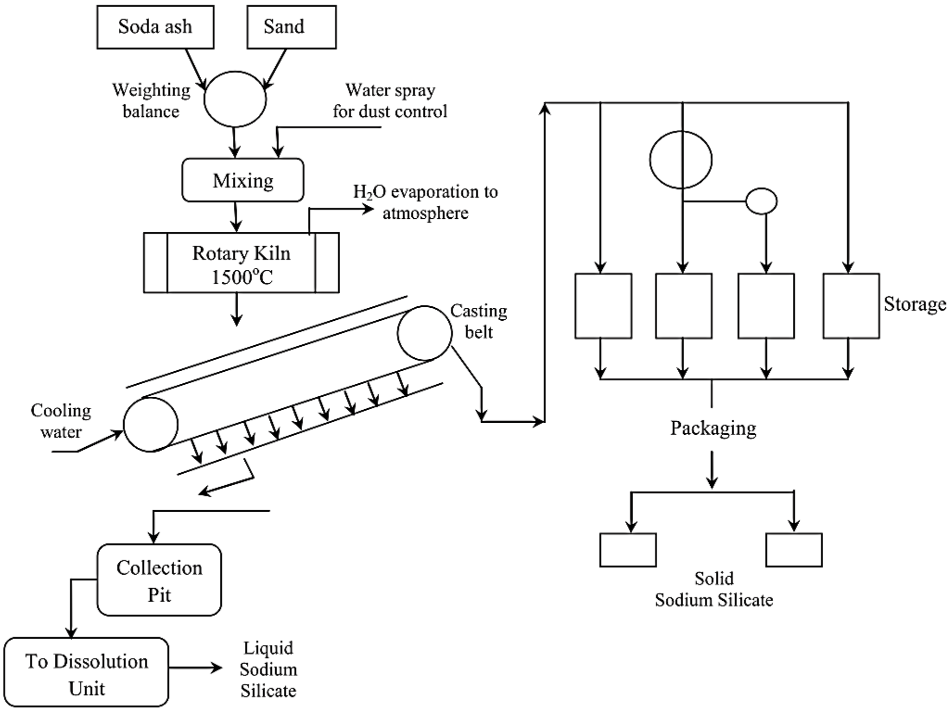


Figure 4.16: Suggested Industrial Process to Manufacture Sodium Silicate (El Shimi et al., 2016)

Table 4.13 shows some of the results reported by researchers using sodium silicate in transesterification. The catalysts were calcined at different temperature for different amount of time to find the optimum conditions for highest biodiesel yields. Guo et al. (2010) also showed that the calcined sodium silicate at 400 °C for 2 hours was able to tolerate up to 4 wt.% water or 2.5 wt.% of FFA contents in soybean oil. It was stated that the low cost solid base catalyst can adsorb FFA and purify the biodiesel (Guo et al., 2010). Roschat et al. (2016) also conducted transesterification with sodium silicate synthesised from rice husk and NaOH solution. From the result, 97% biodiesel yield was achieved after 30 minutes of reaction at 65 °C. The team also tested the catalyst at room temperature and biodiesel yield of 94% was achieved after 2.5 hours of reaction. Moreover, the solid base catalyst can also be synthesised from silica rich geothermal sludge, as reported by Perdana et al. (2016).

Table 4.13: Sodium Silicate as Catalyst in Transesterification for Biodiesel Production

Catalyst	**Feedstocks**	**Reaction Conditions**				**Biodiesel Yield (%)**	**Reference**
		Catalyst Loading (wt. %)	**Methanol to Oil Molar Ratio**	**Temperature (℃)**	**Time (h)**		
Sodium Silicate	Rapeseed oil	3	9:1	60	1	99.6	(Long et al., 2011)
	Sunflower oil	2.5	12:1	65	0.5	97.0	(Roschat et al., 2016)
	Soybean oil	3	7.5:1	60	1	97.0	(Guo et al., 2010)
	Palm oil	1	8.8:1	60	1	93% Conversion	(Perdana et al., 2016)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Two pathways to produce biodiesel were compared, namely transesterification which is the conventional method and chemical interesterification which is an alternative route. This study focused on the latter which is the new alternative pathway to produce biodiesel. Chemical interesterification has huge advantage over the conventional method in terms of its process of biodiesel production. In chemical interesterification, triacetin is produced as the by-product instead of glycerol which is produced from transesterification and normally acts as a waste product. The ability of triacetin being able to be mixed with the biodiesel also eliminates the separation process required in conventional transesterification. Reaction parameters affecting the reaction were also discussed such as reaction time, reaction temperature, catalyst amount and acyl acceptor to oil molar ratio.

The differences of homogeneous catalysis and heterogeneous catalysis were also discussed with the higher benefits of using heterogeneous catalysts. Due to the immature of chemical interesterification in biodiesel production, the results with different catalysts in interesterification reported by researchers are limited. 30 journals reporting biodiesel production via interesterification with different catalysts were collected in this study for analysis purposes.

It was found that both homogeneous and heterogeneous catalysts were able to achieve high biodiesel yields (above 90%) via interesterification. These catalysts were classified as the high tier catalysts, with mostly base catalysts probably due to their higher reaction rates as discussed in the literatures. Among the high tier catalysts, CH_3NaO (homogeneous base) and CaO (heterogeneous base) were found to be the most suitable catalysts to be used in biodiesel production due to their abilities to produce high yields under mild reaction conditions. Hence in this study, the best homogeneous catalyst was found to be CH_3NaO (60 °C; 0.2 h; 20:1 MAOMR; 0.05:1 COMR) with biodiesel yield of 93%. On the other hand, the best heterogeneous catalyst was found to be CaO (80 °C; 5 h; 30:1 EAOMR; 4 wt.% catalyst) with biodiesel yield of 90.5 wt.%.

In this analysis study, the performances of homogeneous and heterogeneous catalysts were compared in terms of their biodiesel yields, reaction parameters such as reaction time, reaction temperature, catalyst amount and acyl acceptor to oil molar ratio as well as the catalyst reusability in chemical interesterification. This was one of the objectives of this analysis study. It was found that homogeneous base catalysts (38%) were being tested the most by researchers due to the higher reaction rates of these catalysts under mild conditions. Analysis also showed that acid catalysts require higher reaction temperature of above 100 ℃ and reaction time up to 20 hours.

The second objective of this analysis was also achieved where the most suitable catalysts were chosen based on the overall aspects. A homogeneous base catalyst and a heterogeneous base catalyst were selected as the best catalysts and they are CH_3NaO and CaO, respectively. These catalysts were able to achieve high biodiesel yield of above 90% at reaction temperature of below 100 ℃, as reported by the researchers and discussed previously.

Lastly, the third objective in this study was to suggest potential catalysts to be used in chemical interesterification. Heterogeneous catalysts namely tungsten phosphoric acid (TPA) and sodium silicate were suggested due to their high performances reported in conventional transesterification. These catalysts may be tested in future research to investigate their performances in chemical interesterification to produce biodiesel.

5.2 Recommendations for Future Research

Catalysts in chemical interesterification are very important as they directly affect the biodiesel yields. This alternative pathway to produce biodiesel is also not widely investigated yet. Hence, there are some recommendations for the future research in chemical interesterification specifically catalyst development and they are listed in the following.

i. Various types of catalysts can be tested to further expand the development of catalysts in chemical interesterification for biodiesel production since it is still immature.

ii. Base catalysts can be focused in future research for chemical interesterification due to their high biodiesel yields with mild reaction conditions as well as the ability to be recycled and reused when heterogeneous catalyst is used.

iii. Optimisations of the reaction with those high tier catalysts reported in this study can be studied and investigated especially CH_3NaO and CaO in order to fulfil the requirement of ester contents (96.5 wt.%) based on the standard of EN 14214.

iv. In addition to tungsten phosphoric acid and sodium silicate, other catalysts with high performances in transesterification can also be tested in chemical interesterification, specifically heterogeneous catalysts due to their advantages over homogeneous catalysts.

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