BIODIESEL PRODUCTION USING ACID-BASE BI-FUNCTIONALIZED HYDROTALCITE CATALYST

NG KAI JUN

UNIVERSITI SAINS MALAYSIA
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BIODIESEL PRODUCTION USING ACID-BASE BI-FUNCTIONALIZED HYDROTALCITE CATALYST

by

NG KAI JUN

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LIST OF ABBREVIATIONS

Al	Aluminum
Al^{3+}	Aluminum ion
$Al(OH)_3$	Aluminum hydroxide
A^{n-}	Anion
BET	Brunauer Emmett Teller
BJH	Barrett-Joyner-Halenda
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
CsHPW	Cesium-doped heteropoly tungstate
DG	Diglyceride
DME	Dimethyl ether
DF	Dilution factor
EDX	Energy dispersive X-ray
FAME	Fatty acid methyl ester
FFA	Free Fatty Acid
FID	Flame ionization detector
GC	Gas chromatography

HT	Hydrotalcite
LDH	Layered double hydroxide
M^{2+}	Divalent metal cation
M^{3+}	Trivalent metal cation
MG	Monoglyceride
Mg	Magnesium
Mg^{2+}	Magnesium ion
MgO	Magnesium oxide
$Mg(OH)_2$	Magnesium hydroxide
MgAlO	Metal oxides
NH_3-TPD	Ammonia temperature programmed desorption
OH^-	Hydroxyl ion
PFAD	Palm fatty acid distillate
rpm	Rotation per minutes
SEM	Scanning electron microscope
TG	Triglyceride
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	**Description**	**Unit**
A/O	Alcohol to oil ratio	
Mg/Al	Magnesium to aluminum ratio	
R_{sample}	Relative area ratio of FAME sample	
$R_{standard}$	Relative area ration of FAME standard	
V_{sample}	Volume of FAME product sample	L
W_{FAME}	Weight of FAME product sample	g
W_{oil}	Weight of oil used	g
$\rho_{FAME,st}$	Mass concentration of FAME standard	g/L

PENGHASILAN BIODIESEL MENGGUNAKAN MANGKIN HIDROTALSIT DIDWIFUNGSIKAN DENGAN ASID-BES

ABSTRAK

Pengurangan bahan api fosil dan kesan negative bahan api fosil kepada persekitaran menyebabkan penyelidikan terhadap penghasilan biodiesel sebagai pennggganti mendapat lebih banyak perhatian. Kini, penyelidikan tentang penghasilan biodiesel daripada minyak yang tidak boleh dimakan untuk menggantikan minyak yang boleh dimakan sebagai bahan mentah menjadi semakain popular. Tetapi, minyak yang tidak boelh dimakan biasanya mengandungi jumlah asid bebas dan kelembapan yang tinggi. Dengan itu, mangkin hidrotalsit (HT) didwifungsikan dengan asid-bes dipilih untuk mengaji disebabkan kebolehan untuk menjalankan tindak balak transesterifikasi dan pengesteran secara serentak tanpa menjalankan tindak balas saponifikasi. Mangkin HT telah disintesiskan melalui kaedah pembakaran yang memerlukan masa yang lebih pendek. Dua parameter penting untuk mensintesiskan mangkin HT berasaskan MgAl iaitu auhu pengkalsinan (550^{o}C-750^{o}C) dan nisbah Mg/Al (2:1, 3:1) telah dikaji. Morfologi permukaan, penghabluran, pencirian struktur dan kekuatan asid bagi HT telah dikaji menggunakan beberapa teknik pencirian. Kesan parameter semasa HT sintesis terhadap pencirian HT dan prestasi pemangkinan untuk penghasilan biodiesel telah Berjaya dikaji. HT berasaskan MgAl yang dikalsin pada 650^{o}C dan disediakan dengan nisbah Mg/Al 3:1 menunjukkan hasil biodiesel yang tertinggi (kira-kira 68.75 %) selepas menjalankan tindak balas transesterifikasi dari minyak masak campuran canola dengan bunga matahari yang segar dengan menggunakan cara konvensional, iaitu pengacauan mekanikal.

BIODIESEL PRODUCTION USING ACID-BASE BIFUNCTIONALIZED HYDROTALCITE CATALYST

ABSTRACT

Due to fossil fuels depletion and its negative impacts towards environment, research on biodiesel production as substitute is gaining more attention. Currently, biodiesel production from non-edible oil is gaining popularity to replace edible oil as feedstocks. However, non-edible oil normally contains high amount of free fatty acid (FFA) and moisture. Thus, acid-base bifunctionalized hydrotalcite (HT) catalyst is choose to study in current paper because simultaneous transesterification and esterification reaction can be carry out without undergoing saponification. HT catalysts were synthesized using combustion method which required much shorter preparation time. Two important parameters to synthesize MgAl based HT i.e. calcination temperature (550°C–750°C) and MgAl ratio (2:1, 3:1) were particularly investigated. The surface morphology, crystallinity, structural and acid strength of the synthesized HT were studied by several characterization techniques. The effect of synthesis parameter on HTs' characteristics and catalytic performance on biodiesel production were successfully studied. The MgAl based HT catalyst prepared by calcination temperature of 650°C and Mg/Al ratio of 3:1 achieved highest FAME yield (about 68.75%) after 5 hours transesterification reaction using conventional mechanical stirring method from fresh mixed canola-sunflower cooking oil.

CHAPTER 1

INTRODUCTION

1.1. Research background

Currently, fossil fuels account for 87% of global energy consumption (Biresselioglu and Yelkenci, 2016) while the transportation is currently the second largest energy consuming sector and is increasing by an average of 1.1% per year (Avhad and Marchetti, 2015). But due to depletion in fossil fuel reservoir and its negative impacts towards the environment, alternative fuel which is more environmental friendly, sustainable, effective and ready to be used for automotive engine without further modification must be developed.

Among the available renewable energy alternatives to be used in transportation sector, biodiesel has been given a high attention as a viable substitute for petroleum diesel in a near future due to biodegradable, non-toxic, and environmentally friendly alternative diesel fuel. The major feedstock component of biodiesel is triglyceride (TG) and the rest of the composition might consist of varying amount of diglycerides (DG), monoglycerides (MG), and free fatty acids (FFAs) (Srivastava and Prasad, 2000). Production of biodiesel from the above feedstocks can carry out from two different chemical reaction: Catalytic transesterification (Marchetti et al., 2007) of the glycerides by base catalysts (TG, DG and MG) and esterification of FFA by acidic catalysts with methanol produce biodiesel (methyl esters of fatty acids (FAME)) (Liu, 1994). Normally, a two-step catalytic process is required to increase the FAME yield, where transesterification reaction come after esterification of FFA to avoid the saponification occur when FFA come contact with base catalysts (Mardhiah et al., 2017). But due to high cost, bi-functional catalyst which consists both acidic and base active sites is currently gaining attention to be studied and developed to improve efficiency and reduce cost for biodiesel production from feedstocks which might contain high amount of FFA.

1.2. Problem statement

95 % of current biodiesel production uses edible oil as feedstocks, which can concern the food industry since the food demand is getting increases every year and if there is food crisis occur in the future, the situation will become worse. Thus, non-edible oils such as waste cooking oil and non-edible vegetable oil are suggested to be used as an alternative for feedstocks to produce biodiesel. Generally, non-edible oils are cheaper if compared to edible oil, thus the use of non-edible oil will greatly reduce the biodiesel production cost. However, non-edible oils normally consist of high amount of free fatty acid (FFA) in them, which cause trouble to conventional available base-catalyzed transesterification process because FFA will cause saponification reaction to occur during the reaction and deactivates the base catalysts used. Current biodiesel productions are tended to use two-steps reaction to solve the problem, but it is time-consuming. Thus, heterogeneous acid-base bi-functionalized catalysts which are not yet popular in big scale production are gaining attention in researchers to transform the two-steps reactions into single step, which save both production time and cost.

Hydrotalcite catalyst (HT) is widely been used in various catalytic processes. HT is a predominant base catalyst but with its flexibility in tuning of its structure, acid-base properties of HT can be adjusted. One way to adjust the acid-base properties of HT is by adjusting the Mg/Al ratio during preparation. Higher Mg/Al ratio will lead to increase in basicity of HT prepare and vice versa. Thus, for feedstocks contain high amount of FFA, HT with Mg/Al ratio of 2:1 seem to be a better choice compare to Mg/Al ratio of 3:1. Many previous works had reported the suitability of HT in biodiesel production through simultaneous transesterification and esterification, by using HT prepared with Mg/Al ratio of 3:1. In contrast, HT prepared with Mg/Al ratio of 2:1 was relatively much less been reported. Combustion method is one of the methods to synthesize HT which require relatively shorter time and it has reported by many previous work on its applicability on HT synthesis. However, there was no previous work reported on the suitability of combustion method to synthesize HT with Mg/Al ratio of 2:1.

1.3. Research objectives

This research aims,

i) To synthesize and characterize the structural, physical and chemical properties of acid-base bi-functionalized hydrotalcite (HT) catalyst for biodiesel production from vegetable oil

ii) To clarify the catalytic activity of acid-base bi-functionalized hydrotalcite (HT) catalyst in FAME production

1.4. Thesis organization

This thesis consists of five main chapters. The following are the contents for each chapter in this study:

Chapter 1 (Introduction) briefly introduces the issues on depletion of fossil fuels which bring impact on researchers to search for effective energy replacement for fossil fuels. A brief introduction on possibility of biodiesel to replace fossil fuel as energy is also addressed in this chapter. Besides that, problem statement and objectives of the research are also presented in this chapter.

Chapter 2 (Literature Review) presents the literature review of this study. The biodiesel production is discussed in detail by reviewing its possible feedstocks, catalytic transesterification and catalytic esterification. Production of biodiesel from vegetable oil is also given attention in this chapter. Besides that, biodiesel production using conventional stirring method is discussed in detailed with the effect of reaction parameter on the performance of biodiesel production. Type of catalyst used in biodiesel production is presented in detailed on three different categories, which are acid, base and bifunctional catalysts. Preparation of HT using combustion method and the influence of Mg/Al ratio and calcination temperature are also reviewed in this chapter.

Chapter 3 (Materials and Methods) covers the experiment materials and the details of methodology used in the biodiesel production. It addresses detailly the method used for catalyst preparation and characterization. It also presents in detailed the method used for biodiesel production, analysis and quality evaluation.

Chapter 4 (Results and Discussion) covers the results and discussion on the experimental data obtained in this present study. The characteristics of HT synthesized differed by calcination temperature and Mg/Al ratio are thoroughly discussed. Besides that, the catalytic performance of HT on biodiesel production with and without effect of FFA is also presented.

Chapter 5 (Conclusions and Recommendations) covers the summary of overall research findings of the present study. It also covers some recommendations for future research work based on the knowledge generated from the biodiesel production from vegetable cooking oil using HT which synthesized through combustion method with Mg/Al ratio of 2:1.

CHAPTER 2

LITERATURE REVIEW

2.1. Biodiesel production

Diesel engine is not suitable for high viscosity, low volatility and polyunsaturated character vegetable oils to be applied directly (Srivastava and Prasad, 2000). Thus, there are many ways for biodiesel production by refining of raw feedstocks have been developed. Balat and Balat (2010) and Lin et. al (2011) had conducted reviews in comparing few of the available techniques used to produce biodiesel, including dilution, micro-emulsification, pyrolysis, transesterification (alcoholysis) and supercritical methanol. Brief descriptions of the techniques are shown in Table 2.1.

Table 2.1: Biodiesel processing techniques

Techniques	Brief description
Dilution	Diluted with diesel without any chemical reaction take place.
Micro-emulsification	Form microemulsions with immiscible liquids (methanol)
Pyrolysis (Thermal cracking)	Thermal conversion of the organic matters in the absence of oxygen and in presence of a catalyst.
Transesterification (Alcoholysis)	Chemical conversion of triglycerides to mono-ester by reacting with short chain alcohol in the presence of a catalyst.
Supercritical methanol	Transesterification of triglycerides using supercritical methanol to employ single phased methanol/oil mixtures.

Summary of the comparison of advantages and disadvantages between techniques mentioned are showed in Table 2.2 (Mahmudul et al., 2017).

Table 2.2: Comparison of biodiesel production techniques (adapted from (Mahmudul et al., 2017))

Techniques	Advantages	Disadvantages
Dilution/ Micro-emulsification	1. Simple process	1. High viscosity 2. Bad volatility 3. Bad stability
Pryolysis	1. Simple process 2. No-polluting	1. High temperature is required 2. Equipment is expensive 3. Low purity
Transesterification (Alcoholysis)	1. Fuel properties is closer to diesel 2. High conversion efficiency 3. Low cost 4. It is suitable for industrialized production	1. Low free fatty acid and water content are required (for base catalyst) 2. Pollutants will be produced because products must be neutralized and washed 3. Accompanied by side reactions 4. Difficult reaction products separation
Supercritical methanol	1. No catalyst 2. Short reaction time 3. High conversion 4. Good adaptability	1. High temperature and pressure are required 2. Equipment cost is high 3. High energy consumption

2.2. Feedstocks

Type of feedstocks selected for biodiesel production is very important since the cost of raw feedstocks alone contributes about 70-80% of the biodiesel production cost (Gui et al., 2008, Gude et al., 2013). Pre-treatment of certain raw feedstocks for biodiesel maybe required, which will lead to higher production cost and reduce net profit of the biodiesel industry. Thus, proper selection of raw feedstocks is crucial to avoid over budget production. Feedstocks can generally categorized into four different groups, which are edible vegetable oil, non-edible vegetable oil, waste or recycled oil and animal fats (Atabani et al., 2012, Atabani et al., 2013). The example for each category mentioned above are showed in Table 2.3.

Table 2.3: Example of raw feedstocks for biodiesel production

Feedstock	Examples
Edible vegetable oil	Soybeans (*Glycine max*), Rapeseed (*Brassica napus L.*), Rice bran oil (*Oryza sativum*), Barley, Wheat, Corn, Canola, Peanut, Palm and palm kernel (*Elaeis guineensis*), Sunflower (*Helianthus annuus*)
Non-edible vegetable oil	*Jatropha curcas*, Pongamia (*Pongamia pinnata*), Cotton seed (*Gossypium hirsutum*), Neem *(Azadirachta indica)*, Tobacco seed, Rubber seed tree (*Hevca brasiliensis*), Coffee ground (*Coffea arabica*)
Waste oil	Waste cooking oil
Animal fats	Pork lard, Beef tallow, Poultry fat, Fish oil, Chicken fat

2.3. Catalytic transesterification and esterification

2.3.1. Catalytic transesterification

Transesterification is a process where alcohol from an ester displace with another alcohol chain. The process is widely used in biodiesel production to reduce viscosity of triglyceride in vegetable oil by substituting long alcohol chain with a shorter alcohol chain. The principle of the reactions for biodiesel production from transesterification of triglycerides is shown in Figure 2.1. There are three consecutive reversible reactions involve in producing biodiesel (Fatty Acid Methyl Ester (FAME)). The quality and yield of biodiesel produced from transesterification is highly depends on type of feedstocks and catalyst used in the process. Transesterification process is a reversible reaction and can carry out essentially by simply mixing the reactants. However, the process can be accelerated with the presence of catalyst (Tran et al., 2017).

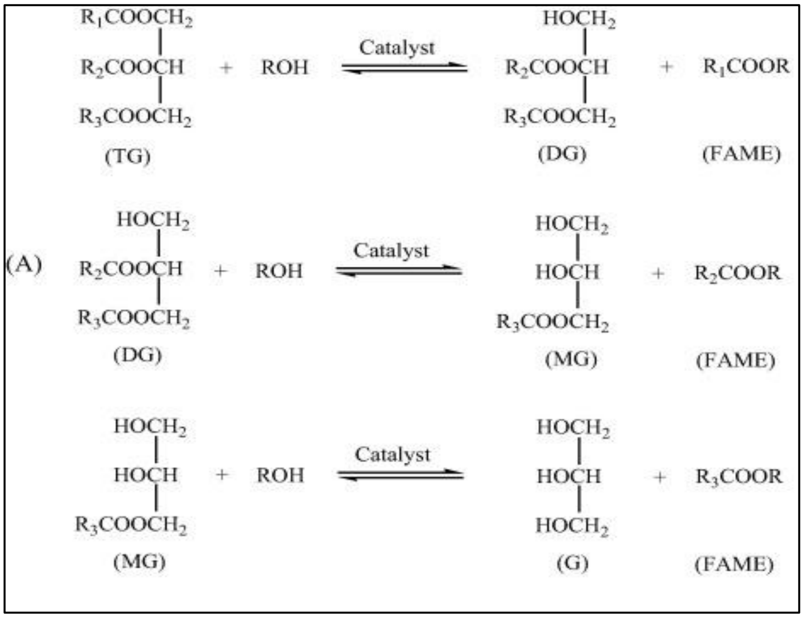

Figure 2.1: Transesterification of triglyceride with alcohol

Generally, catalytic transesterification can be categorized using two criteria; homogenous- or heterogenous-catalyzed; acid- or base-catalyzed. Homogenous-catalyzed transesterification is generally more commonly preferred in industry scale process due to its consistent product quality and kinetically faster reaction. However, much more energy and cost is required for catalyst separation, recycling and purification of products. Also, the reusability of homogenous catalyst, especially acid catalysts is complicated due to its high solubility in reaction mixture (Konwar et al., 2014). Thus, to avoid large amount of energy wastage in biodiesel production, heterogenous catalysts which can be readily separated from products at the end of process have gained more attention from researchers to develop an effective heterogenous catalysts which generally have lower reaction rate if compared to homogenous catalysts (Atadashi et al., 2013).

Both acid catalysts and base catalysts can be used in transesterification process for biodiesel production with pros and cons themselves. Base catalysts basically have higher reaction rate than acid catalysts, but with drawback that formation of undesired product and consumes catalysts by saponification reaction might occur if raw feedstocks contain high amount of free fatty acid (FFA) and water (Lotero et al., 2005). Acid catalysts are less sensitive to the quality of raw feedstocks for the process, because they can simultaneously carry out esterification of FFA to produce FAME which eliminates the formation of undesired products, but with much slower transesterification rate compared with base catalysts. Also, acid catalysts have some other drawbacks as example, require higher operating temperature during the reaction and corrosive characteristics for homogenous acid catalyst (Tran et al., 2017).

2.3.1 (a) Acid-catalyzed transesterification

As discussed previously, acid catalysts have advantages over base catalysts on faster reaction rate and prevention of soap formation which lead to catalyst inactivation. Some previous work reported are tabulated in Table 2.4. For homogeneously acid-catalyzed transesterification, sulphuric acid (H_2SO_4) is the most common used catalyst in the reaction. The FAME conversion in the presence of H_2SO_4 can reach up to 97% by using homogenous acid catalyst (Farag et al., 2011, Yustianingshi et al., 2009). Besides that, Guan et al. (2009) had reported that p-toluenesulfonic (PTSA) acid can be an option as catalyst for biodiesel production and had better performance compared to H_2SO_4 and benzenesulfonic acid (BSA) in biodiesel production using corn oil as feedstocks. The highest FAME yield was achieved after 120 min of transesterification reaction at 80^oC in the presence of dimethyl ether (DME) as co-solvent (methanol/DME = 1:1.176), alcohol-to-oil ratio at 10:1 and catalyst loading of 4 wt%.

However, heterogeneous acid catalysts are gaining more and more attention as corrosiveness of homogeneous acid catalysts and difficult separation from the products. Narkhede and Patel (2013) had carried out research on catalytic activity of 12-tungstosilicic acid supported in zeolite-Hβ for soybean oil as feedstocks and was reported that acid strength of catalysts was increased by the incorporation of 12-tungstosilicic acid on the zeolite surface. 95 % conversion of soybean oil was achieved after reaction at 65^oC for 8 hours. Alhassan et al. (2013) and Ayodele and Dawodu (2014) also reported heterogeneously acid-catalyzed transesterification achieved FAME yield up to 99 %. Notice that heterogeneously-catalyzed reaction required higher operating temperature and longer reaction time in order for FAME conversion to achieve up to 95 %.

Table 2.4 Performance of acid-catalyzed transesterification

Catalyst	Feedstock	Reaction condition				FAME yield (%)	Reference
		Alcohol to oil ratio	Catalyst loading	Operating temperature (^{o}C)	Reaction time (h)		
Sulphuric acid (H2SO4)	Soybean oil	6:1	2.5 %wt	60	1	96.6	(Farag et al., 2011)
Sulphuric acid (H2SO4)	Rice Bran	SS[a] ratio: 10 ml/g	12.5 %wt	60	4	89.2-96.3	(Yustianingshi et al., 2009)
p-toluenesulfonic acid	Corn oil	10:1	4 %wt	80	2	97.1	(Guan et al., 2009)
30%Tungstosicic acid/zeolite Hβ	Soybean oil	4:1	200 mg	65	8	95	(Narkhede and Patel, 2013)
Fe(HSO4)3	Waste oil	15:1	1 %wt	205	4	94.5	(Alhassan et al., 2013)
Sulfated PAHs	Calophyllum inophyllum	15:1	5 wt%	180	4	99	(Ayodele and Dawodu, 2014)

a: Solvent to solid ratio

2.3.1 (b) Base-catalyzed transesterification

Many papers had been reported on the research of base-catalyzed transesterification due to its desired properties where carry out transesterification process at higher rate and lower operating condition which can help in reduce the cost of biodiesel production. For homogeneously base-catalyzed transesterification, Fadhil and Ali (2013) and Uzun et al. (2012) had reported the use of KOH and NaOH respectively as base catalysts for transesterification to achieve FAME yield of 96%. Chen et al. (2012) had reported the performance of $NaOCH_3$ for transesterification of waste cooking oil to produce biodiesel with the aid of microwave. It was found that microwave can greatly shorten the reaction time from 90 min to only 3 min to achieve FAME yield above 96% due to absorption of microwave radiation cause the excitation of -OH group to exceed activation energy require for the reaction.

For heterogeneously-base catalyzed transesterification, Teo et al. (2014) had reported the use of CaO-NiO as base catalyst to achieve 86.3% FAME yield from *Jatropha curcas* and can be used repeatedly without loss in activity. Correia et al. (2014) had investigated the use of egg shells and crab shells as source foe CaO catalyst for biodiesel production from sunflower oil. The CaO derived from egg shell was found to possessed good activity because of its high basicity and achieved FAME yield of 94.73 % after 180 min of reaction performed at 60^oC with methanol to oil ratio of 9:1 and 3 wt% catalyst loading. Lee et al. (2013) had carried out research on mixed oxide catalyst (MgO-ZnO) on biodiesel production and achieve 83% FAME yield from *Jatropha curcas*. Again, the mixed oxide showed excellent reusability with only slight decrease in catalytic activity in each repetition.

Table 2.5: Performance of base-catalyzed transesterification

Catalyst	Feedstock	Reaction condition				FAME yield (%)	Reference
		Alcohol to oil ratio	Catalyst loading (wt%)	Operating temperature (^{o}C)	Reaction time (min)		
KOH	Heckel fish oil	6:1	0.5	32	60	96.0	(Fadhil and Ali, 2013)
NaOH	Waste frying oil	7.5:1	0.5	50	30	96.0	(Uzun et al., 2012)
$NaOCH_3$	Waste cooking oil	6:1	0.75	65	90 3 (microwave)	96.6 97.9	(Chen et al., 2012)
CaO-NiO	*Jatropha curcas*	15:1	5	65	360	86.3	(Teo et al., 2014)
CaO (egg shell)	Soybean oil	9:1	3	60	180	94.73	(Correia et al., 2014)
MgO-ZnO	*Jatropha curcas*	25:1	3	120	180	83.0	(Lee et al., 2013)

2.3.2. Catalytic transesterification mechanism

Transesterification process can be a base-catalyzed process or acid-catalyzed process. As discuss earlier, base-catalyzed transesterification has a higher reaction rate whereas acid-catalyzed transesterification is less sensitive to quality of feedstocks. The mechanism of catalytic transesterification is simple and easily to be understood.

For base-catalyzed transesterification, the mechanism had been proposed by Eckey (1956) and Sridharan and Mathai (1974). Several steps involve in the reaction are shown in Figure 2.2. The reaction starts with the formation of alkoxide ions from an alcohol molecule by transferring a proton molecule from alcohol molecule to hydroxide ion to from a water molecule and an alkoxide ion (Pre-step). The alkoxide ion formed is then attack carbonyl carbon of the triglyceride molecule and form a tetrahedral intermediate (Step 1). The reaction of tetrahedral molecule with an alcohol molecule form an alkoxide ion by deprotonation of the alcohol molecule (Step 2). Lastly, the intermediate undergo rearrangement and produce an ester and a diglyceride (Step 3).

For acid-catalyzed transesterification, the mechanism has been review by Schuchardt et al. (1998). The reaction can be carry out in the presence of Brownsted acid. Mechanism of the reaction is shown in Figure 2.3. It starts with the protonation of carbonyl group of triglycerides by a proton molecule provide from Brownsted acid catalyst and lead to formation of carbocation (Step 1). Nucleophilic attack of an alcohol molecule to carbocation formed a tetrahedral intermediate (Step 2). The intermediate then eliminates glycerol to produce an ester molecule and regenerate a proton molecule (Step 3).

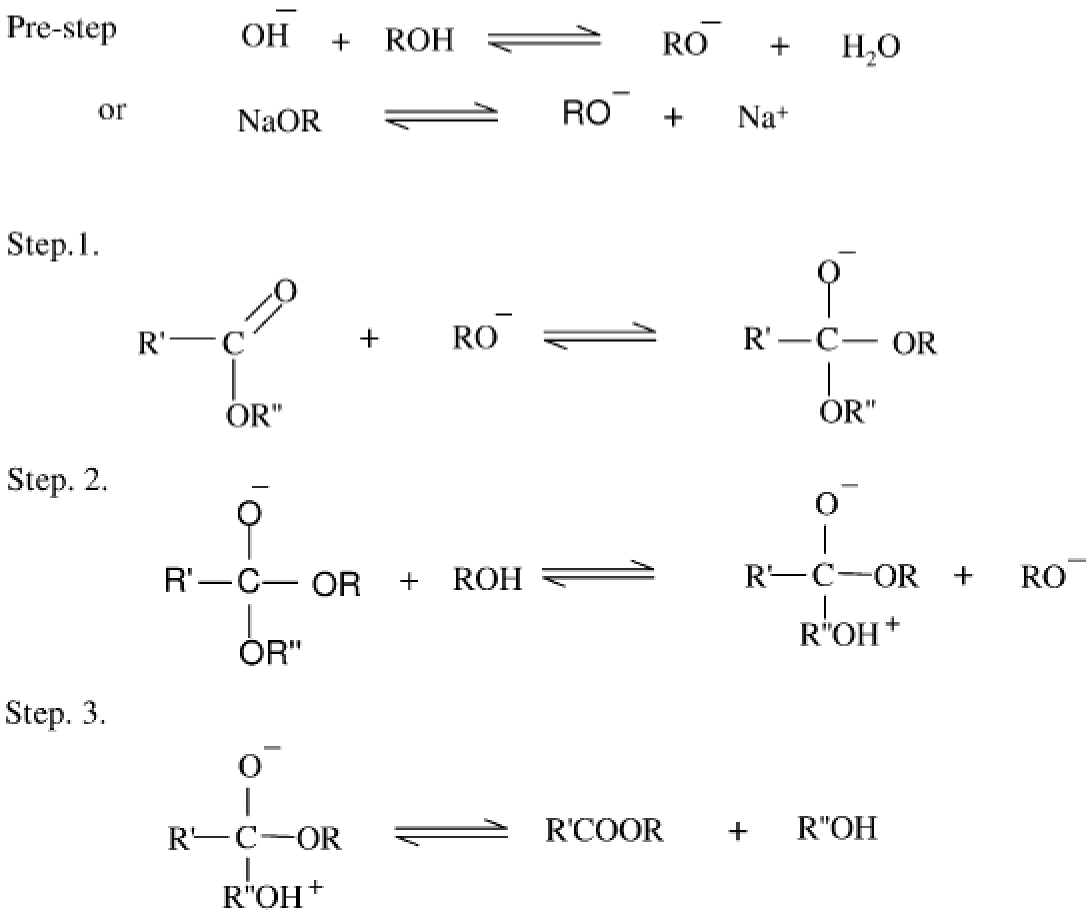

Figure 2.2: Mechanism of base-catalyzed transesterification (Eckey, 1956)

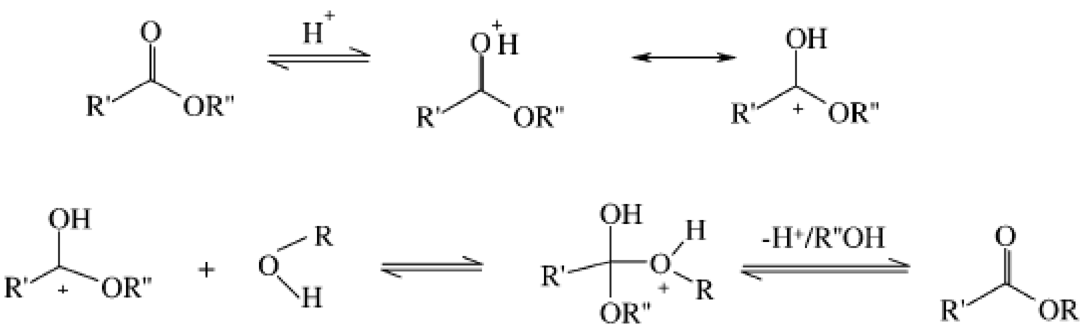

Figure 2.3: Mechanism of acid-catalyzed transesterification (Schuchardt et al., 1998)

2.3.3. Catalytic esterification

There is wide variety of lower cost high free fatty acid (FFA) oil available in large quantities which are unsuitable for human consumption and mainly used for making low-cost soap. FFA content in these oils can be utilized for biodiesel production through catalytic esterification reaction of FFA with alcohol. The principle of esterification of FFA is described in the following equation:

$$R_1 - COOH + R_2 - OH \rightarrow R_1 - COO - R_2 + H_2O$$

Biodiesel production from high FFA oils is generally not suitable to use the commercially available base catalyst. Thus, the process is normally carried out in the presence of homogenous acid catalysts such as H_2SO_4, HF, H_3PO_4, HCl and p-toluene sulfonic acid (Carmo Jr. et al., 2009). However, the use of these catalysts is dangerous because they are hazardous and corrosive liquid acids. Also, recovery of the homogenous catalyst is typically difficult and catalysts cannot be reused. Therefore, acid heterogeneous catalysts can be considered as an alternative to minimize environmental damage and reduce biodiesel cost. It is also found that water content will reduce FAME conversion from FFA. Thus, pretreatment to remove moisture from feedstocks might needed in order to increase the biodiesel production efficiency from FFA conversion (Park et al., 2010b).

Table 2.6 shows some of the previous work done for catalytic esterification to produce biodiesel. Lokman et al. (2014) reported the used of sulphuric acid as catalyst to convert palm fatty acid distillate (PFAD) through microwave-assisted esterification and achieved FAME yield up to 97.5 % with only 15 mins reaction performed at alcohol to oil ratio of 9:1, 1 wt% of catalyst loading and operating temperature of 55^oC. In contrast, Metre and Nath (2015) reported the used of superphosphoric acid for esterification of PFAD with much poorer performance, which required a much longer reaction time (300 mins) and higher operating temperature (70^{o}C) for the FAME yield to reach up to 95 %. However, superphosphoric acid was way less corrosive compared to sulphuric acid, thus made it to become another option for the use of homogeneous acid catalyst in biodiesel production to reduce maintenance work required.

For heterogeneously-catalyzed esterification process, Doyle et al. (2016) reported the used of zeolite Y prepared using Iraqi kaolin can achieve FAME yield up to 85 % from oleic acid after 60 mins reaction. Catalytic activity of the catalyst was believed to be provided by high density of acid sites due to low Si/Al ratio in the catalyst. Sheikh et al. (2013) reported the used of cesium-doped heteropoly tungstate (CsHPW) for esterification of oleic acid-soybean mixture and achieve FAME yield of 90.4 %. However, the reaction required relatively higher operating temperature (200^{o}C) and longer reaction time (10 h), which shows the CsHPW catalyst was not that active. Soltani et al. (2016) reported the used of sulfonated $ZnAl_2O_4$ for esterification of PFAD could achieve maximum FAME yield of 94.7 % after 60 mins of reaction performed at 100^{o}C, alcohol to oil ratio of 9:1 and 1 wt% of catalyst loading. The catalyst showed good stability on reusability test even after 8 reaction cycles, at which FAME yield can still maintain at 67.3 %.

Table 2.6: Performance of catalytic esterification for biodiesel production

Catalyst	Feedstock	Reaction condition				FAME yield (%)	Reference
		Alcohol to oil ratio	Catalyst loading (wt%)	Operating temperature (°C)	Reaction time (min)		
Sulphuric acid	Palm fatty acid distillate	9:1	1.0	55	15	99.5	(Lokman et al., 2014)
Superphosporic acid	Palm fatty acid distillate	12:1	9.0	70	300	95.0	(Metre and Nath, 2015)
Zeolite Y	Oleic acid	6:1	5.0	70	60	85.0	(Doyle et al., 2016)
CsHPW	Oleic acid-Soybean mixture	20:1	3.0	200	600	90.4	(Sheikh et al., 2013)
Sulfonated $ZnAl_2O_4$	Palm fatty acid distillate	9:1	1	100	60	94.7	(Soltani et al., 2016)

2.3.4. Catalytic esterification mechanism

Catalytic esterification is generally acid-catalyzed reaction, thus only the acid-catalyzes esterification is discussed here. The mechanism of acid-catalyzed esterification is shown in Figure 2.4 (Clark, 2004, Foreman, 2012). The reaction starts with protonation of carboxylic acid, where the proton molecule provided by acid catalyst attached to oxygen which is double-bonded to the carbon. Rearrangement of molecule is then lead to formation of carbocation (Step 1). Then, nucleophilic attack by an alcohol molecule to the carbocation produce tetrahedral intermediate, and rearrangement of intermediate by transferring a proton molecule intramolecularly occurred (Step 2). Lastly, the intermediate eliminates a water molecule and regenerate proton molecule (Step 3).

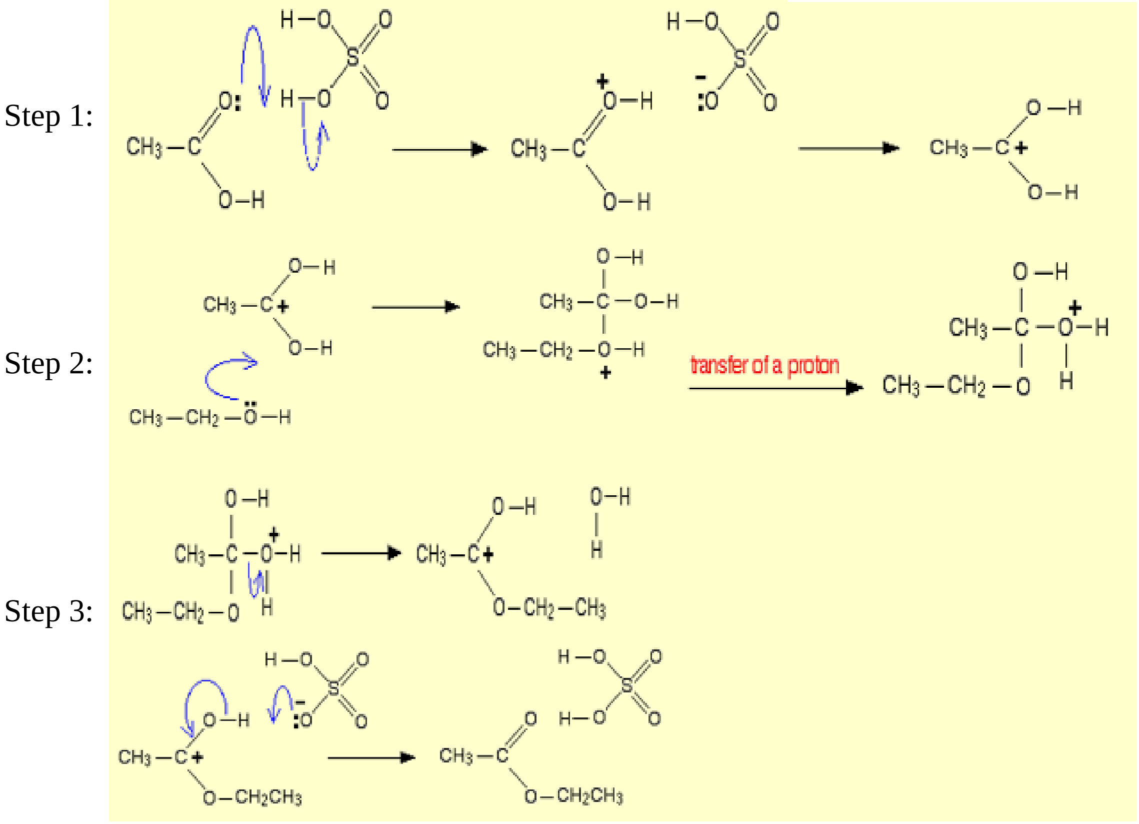

Figure 2.4: Mechanism of acid-catalyzed esterification (adapted from Clark (2004))

2.3.5. Simultaneous catalytic transesterification and esterification

Like what mentioned previously, cost of biodiesel production is mainly based on the type of feedstocks used in the process. Thus, to reduce the cost of biodiesel production, low cost feedstocks like non-edible oils, waste or recycled oil and animal fats are chosen for biodiesel production. However, the main problem of using low cost feedstocks is that high amount of FFA content in oils which cannot undergo transesterification process and will cause deactivation of base catalysts. Consequently, FFA contained in low cost feedstocks can be either removed or converted to FAME through esterification process prior to undergo transesterification process (Park et al., 2010b).

However, to increase FAME yield and cost saving, it is preferred that FFA content in the feedstocks is also converted to FAME. Generally, two steps reaction are required, where the feedstocks are first undergoing catalytic esterification of FFA using acid catalyst, then follow by catalytic transesterification of triglyceride in the presence of base catalyst. However, the process is quite time-consuming. Thus, simultaneous catalytic transesterification and esterification in the presence of acid-base bi-functionalized catalysts is beneficial for biodiesel production from low cost feedstocks. Bi-functionalized catalyst is a catalyst that comprising both acidic and basic sites which can perform one-step simultaneous transesterification and esterification reaction. The use of bi-functional catalyst would not only eliminate the time-consuming two-steps process, but also reduce the need of high cost equipment. The acid and base sites on a single catalyst surface could be generated through synthesis procedure or by addition of heterospecies (Mardhiah et al., 2017). Some of the recent work is summarized in the Table 2.5.

Table 2.7: Examples of the bifunctional catalyst reported in past 5 years

Catalyst	Feedstock	Reaction condition				FAME yield (%)	Reference
		Alcohol to oil ratio	Catalyst loading (wt%)	Operating temperature (^{o}C)	Reaction time (min)		
Bi_2O_3-La_2O_3	*Jatropha curcas*	15:1	2.0	150	240	93.0	(Rabiah Nizah et al., 2014)
CaO-La_2O_3	*Jatropha curcas*	25:1	3.0	160	180	98.8	(Lee et al., 2015)
$CaFe2O_4$-$Ca_2Fe_2O_5$	*Jatropha curcas*	15:1	4.0	~100	30	78.2	(Xue et al., 2014)
Mo–Mn/γ-Al_2O_3–MgO	Waste cooking oil	27:1	5.0	95	240	91.4	(Farooq et al., 2013)
Quitininte-3T	Coffee oil	12:1	10.0	75	240	96.6	(Kondamudi et al., 2011)
Hydrotalcite	Waste cooking oil	15:1	8.0	57	60	76.5	(Anuar and Abdullah, 2016)
Hydrotalcite	Sunflower mixture	9-12:1	2.5	60-65	240	97.1	(Gomes et al., 2011)

Rabiah Nizah et al. (2014) had reported a bifunctional catalyst, bismuth (III) oxide (Bi_2O_3) supported on lanthanum oxide (La_2O_3) catalyst can be used for simultaneous transesterification and esterification reaction for biodiesel production and achieved FAME yield up to 93% when reaction performed at methanol to oil ratio of 15:1, 2 wt% of catalyst loading and operating temperature of 150^{o}C for 240 mins. Reusability test had been carried out and the FAME yield up to 87% was recorded after 3 cycles, shows that the catalyst was high in stability and consisted strong acid-base strength.

Lee et al. (2015) reported that better result can be obtained if calcium oxide (CaO) was loaded with La_2O_3 catalyst instead of Bi_2O_3. The CaO-La_2O_3 catalyst prepared by precipitation method achieved up to 98.8% FAME yield for the biodiesel production from *Jatropha curcas* oil. However, weak reusability was observed for the catalyst upon second cycles, although it remained stable after 4 consecutive cycles with significant drop in catalytic activity. It discussed that the result was because leaching of active Ca^{2+} occur at the first run, thus lead to saponification of calcium which reduce the catalytic activity of the catalyst.

Xue et al. (2014) reported on the suitability of CaFe2O_4-$Ca_2Fe_2O_5$ catalyst as acid-base bi-functionalized catalyzed for biodiesel production. FAME yield of 78.2% was reported when reaction performed with methanol to oil ratio of 15:1, 4 wt% of catalyst loading and operating temperature of 99.85^{o}C for 30 mins. The FAME yield was not as high as catalyst made up of transition metal oxides and silica-supported mixed metal oxide, but it can be reused up to 3 cycles with minimal loss of catalytic activity, shows very excellent in catalyst stability.

Study on biodiesel production from waste cooking oil had been carried out by Farooq et al. (2013) and Anuar and Abdullah (2016) using Mo–Mn/γ-Al_2O_3–MgO and HT as acid-base bi-functionalized catalyst respectively. FAME yield of 91.4 % and 76.5 % had been recorded for HT and Mo–Mn/γ-Al_2O_3–MgO catalyst, respectively. HT catalyst showed a good stability with only slight decreased in catalytic activity after reused for 3 cycles while Mo–Mn/γ-Al_2O_3–MgO catalyst showed even better stability with no major loss of activity after reused for 8 cycles.

Kondamudi et al. (2011) reported on the suitability of Quintinite-3T catalyst as bi-functionalized heterogeneous catalyst for biodiesel production from feedstocks with vary FFA content. Coffee oil with high FFA content (33 wt%) was one of the feedstock used, and 96.6% FAME yield was achieved when the simultaneous transesterification and esterification was performed at methanol to oil ratio of 12:1, 10 wt% of catalyst loading and operating temperature at 75^{o}C for 4 h reaction time.

Gomes et al. (2011) also reported the used of HT as catalyst to carry out simultaneous transesterification and esterification reaction. The effect of Mg/Al ratio on the characteristics of HT synthesized and catalytic performance of biodiesel production from sunflower mixture had been investigated. The results showed that Mg/Al ratio with 2:1 had the best performance in biodiesel production which achieved FAME yield of 97.1 %. However, stability of the catalyst tested showed significant drop in catalytic activity after 3 cycles, with only 34.7 % of FAME yield achieved. XRD revealed that the catalyst deactivation might due to leaching of Na compounds in the structure since the Na compounds on the structure surface were disappeared after first reaction cycle.