

**ESTERIFICATION OF FREE FATTYACID FROM
SIMULATED WASTE COOKING OIL USING
IONIC LIQUID AS CATALYST**

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ABSTRACT

Ionic liquid is a catalyst which is homogeneous (liquid phase) catalyst. Ionic liquid has been recognize as a potential catalyst in esterification of free fatty acid from waste cooking oil which contain high amount of free fatty acid due to the triglyceride hydrolysis during frying due to its properties which is adjustable by adjusting its combination of cation and anion. It also recognize as a substitution of sulphuric acid in biodiesel synthesis.

In this project, different combination of cation and anion has been tested by four types of ionic liquid which involve the uses of pyridinium, 1-methyl-3-butylimidazolium (BMIM), 1-ethyl-3-methylimidazole (EMIM) as cation and the uses salicylate, sulphate, as an anion. The four types of catalyst can be considered as novel catalyst since no other researchers tried this combination of cation and anion. All this catalyst is characterize first using IR, CHNS and HNMR spectrometer. Then the catalytic performance test is done for all the catalyst in the esterification reaction of free fatty acid in simulated waste cooking oil. As the result of the catalytic performance only BMIM SCL showed the conversion with only 30% conversion.

ABSTRAK

Ionic liquid adalah pemangkin yang dikenali sebagai pemangkin homogen yang mana terbentuk dalam bentuk cecair. Ia juga telah dikenali sebagai pemangkin yang berpotensi dalam tindakbalas asid lemak terbebas dari minyak masak terbuang di mana mempunyai tahap asid lemak terbebas yang tinggi disebabkan berlakunya hidrolisis semasa menggoreng disebabkan sifatnya yang boleh diubah dengan mengubah kombinasi anion dan kation. Ia juga berpotensi sebagai pengganti kepada asid sulfurik dalam penghasilan biodiesel.

Di dalam projek ini, kombinasi kation dan anion yang belainan telah dicuba dengan menggunakan *pyridinium*, *1-methyl-3-butylimidazolium (BMIM)*, *1-ethyl-3-methylimidazole (EMIM)* sebagai kation dan *salicylate* dan *sulphate* sebagai anion. Keempat-empat jenis pemangkin ini boleh dikategorikan sebagai pemangkin yang baru kerana belum ada penganalisis yang menghasilkan gabungan kation dan anion ini. Kesemua pemangkin ini dikarakterkan dengan menggunakan *IR*, *CHNS* dan *HMR* spektrometer. Kemudian ujian pemangkin dilakukan ke atas kesemua pemangkin di dalam tindakbalas *esterification* daripada asid lemak terbebas yang terkandung di dalam minyak masak simulasi. Sebagai keputusannya, hanya pemangkin BMIM SCL sahaja yang menunjuk penukaran peratusan dengan hanya 30 peratus.

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	IV
STUDENT'S DECLARATION	V
Dedication	VI
ACKNOWLEDGEMENT	VII
ABSTRACT	VIII
ABSTRAK	IX
TABLE OF CONTENTS	X
LIST OF FIGURES	1
LIST OF TABLES	2
LIST OF ABBREVIATIONS	3
1 INTRODUCTION	4
1.1 Motivation and statement of problem	4
1.2 Scope of this research	5
1.3 Organisation of this thesis	5
2 LITERATURE REVIEW	7
2.1 Introduction	7
2.2 Biodiesel	7
2.3 Feedstock	8
2.4 Production of biodiesel	10
2.4.1 Transesterification reaction	11
2.4.2 Esterification reaction	12
2.5 Parameter affecting esterification reaction	13
2.5.1 Catalyst	13
2.5.2 Free fatty acid and water content	18
2.5.3 Temperature	18
2.5.4 Molar ratio of methanol with oil	19
2.5.5 Mode of stirring	20
3 MATERIALS AND METHODS	21
3.1 Materials	21
3.2 Characterization of ionic liquid	21
3.2.1 Fourier Transform Infrared (FT-IR)	21
3.2.2 Proton Nuclear Magnetic Resonance spectroscopy (H NMR)	21
3.2.3 CHNS spectroscopic	22
3.3 Simulated waste cooking oil preparation	22
3.4 Free Fatty Acid analysis	22
3.5 Catalytic activity study of ionic liquid on esterification reaction of free fatty acid	23
4 RESULT AND DISCUSSION	24
4.1 Overview	24
4.2 Characterization studies of ionic liquids	24
4.2.1 CHNS spectroscopy	24
4.2.2 Fourier transformed infrared (FTIR) spectroscopy	25
4.2.3 HNMR spectroscopy	28
4.2.4 Summary of characterization studies	33
4.3 Catalytic activity of ionic liquids	34

5	CONCLUSION AND RECOMMENDATION.....	36
5.1	Conclusion	36
5.2	Recommendation.....	36
5.3	Future research work.....	36
	REFERENCES	38
	APPENDICES	43
	APPENDICE A	43
	APPENDICE B.....	44

LIST OF FIGURES

Figure 2-1: Transesterification of biodiesel from triglyceride.....	11
Figure 2-2: Esterification of free fatty acid	12
Figure 2-3: Common used anions and cations in ionic liquids.....	16
Figure 4-1: Illustration of expected Molecular structure of BMIM SCL ionic liquid with its functional group detected in IR spectra.....	26
Figure 4-2: Functional group that present in the IR spectra for PYSCL	26
Figure 4-3: Functional group that present in the IR spectra for PYSO ₄	27
Figure 4-4: Functional group that present in the IR spectra for EMIM SO ₄	28
Figure 4-5: Expected molecular structure for BMIM SCL ionic liquid	29
Figure 4-6: Expected molecular structure for PY SCL ionic liquid	31
Figure 4-7: Expected molecular structure for PYSO ₄ ionic liquid	32
Figure 4-8: Expected molecular structure for PYSO ₄ ionic liquid	33
Figure 4-9: Graph of conversion with time for esterification reaction.....	34

LIST OF TABLES

Table 4-1: CHNS elemental analysis result of ionic liquids.....	24
Table 4-2: Percentage error for each element in all ionic liquid	25
Table 4-3: FTIR spectra for BMIM SCL.....	25
Table 4-4: FTIR spectra for PYSCL ionic liquid	26
Table 4-5: IR spectra for PYSO ₄ ionic liquid.....	27
Table 4-6: IR spectra for EMIM SO ₄	27
Table 4-7: Data extracted from HNMR spectra for BMIM SCL	28
Table 4-8: Data extracted from HNMR spectra for PYSCL	30
Table 4-9: Data extracted from HNMR spectra from PYSO ₄	31
Table 4-10: Data extracted from HNMR spectra for PYSCL	32

LIST OF ABBREVIATIONS

FFA	Free fatty acid
BMIM	1- methyl-3-butylimidazolium
SCL	salicylate
EMIM	1-ethyl-3-methylimidazolium
PY	Pyridinium
IR	Infrared
HNMR	Hydrogen nuclear magnetic resonance
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur

1 INTRODUCTION

1.1 *Motivation and statement of problem*

Nowadays, biodiesel has been recognized as the best candidate for the diesel fuel substitution due to the limitation of fossil fuel sources. Biodiesel is renewable sources since it produced from the vegetable oil and animal fats. The advantages of biodiesel as diesel fuel are its availability of raw material, low engine emission and renewability.

Vegetable oil that commonly used as the raw material in biodiesel production required relatively high cost. According to S. Zullaikah (2005), the production of biodiesel from refined edible oil contributes more than 70% of overall production cost. The uses of waste oil as a substitution can lower the cost and reduce the environmental problem regarding to the waste oil disposal. It was estimated that the cost of waste cooking oil is just half of the virgin oil cost. The major constrain by using waste cooking oil as a feedstock is the high amount of free fatty acid. It is due to the hydrolysis of triglyceride during frying (Gan *et al.*, 2012).

Transesterification is the most common way in producing biodiesel from vegetable oil since the triglyceride is the main component of vegetable oil. According to Han *et al.*, (2009), the main components of waste oil are triglycerides, free fatty acid and water. From their studies, it shows that the esterification reaction is faster than transesterification reaction using waste oil as feedstock. Esterification or acid catalyzed reaction is used in producing biodiesel from waste cooking oil as a pre-treatment method to the waste oil before further reaction.

Biodiesel synthesis can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed (Zhang *et al.*, 2009). Enzyme-catalyst is rarely used since it requires a longer reaction time compared to alkali and acid catalyzed (Watanabe *et al.*, 2001). Due to the high free fatty acid in waste cooking oil, acid catalyst is commonly used instead of base catalyst. Oil and fats with high free fatty acid cannot directly used base catalyst because the conversion into ester will drop when the free fatty acid content above 2% (Naik *et al.*, 2008). The level of free fatty acid in waste cooking oil is usually greater than 2 wt% (Watanabe *et al.*, 2001). But acid-catalyzed system required longer reaction time compared to the alkali-catalyzed system. Moreover, high acidity catalyst generate many

environmental and corrosion problem to the reactor and automatically required high cost stainless steel equipment which enhance the operational cost.

In solving this problem, a presence of ionic liquid has become an alternative to solve this problem. It was define as a salt where it presence as liquid at room temperature since its melting temperature is below 100°C. The ionic liquid also offers many attractive characteristic such as negligible vapor pressure, good solubility in both organic and inorganic material and tunable for specific task and reusable. In the biodiesel synthesis, ionic liquid can be applied as a catalyst, solvent for enzyme-catalyzed transesterification, catalyst support and lipid extraction. Its usefulness in their utilization becomes more eminent. Ionic liquid can be used in variety of process by adjusting the combination of cation and anion of the ionic liquid (Fauzi and Amin., 2012)

1.1 Objectives

The following are the objectives of this research:

- To do characterization study of novel ionic liquid.
- To do catalytic performance test on different types of novel ionic liquid.

1.2 Scope of this research

The following are the scope of this research:

- i) Novel Ionic liquid with different combination of anion and cation
- ii) Catalyst characterization using FT-IR, HNMR and CHNS
- iii) Catalytic performance of catalysts on the esterification reaction of free fatty acid.

1.3 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description and finding of former studies regarding to this thesis title. Its covers the raw material used, reaction, type of catalyst that used from the former research and parameter that effects the esterification of free fatty acid in waste cooking oil.

Chapter 3 is the material used and methodology part where all the method regarding to this thesis include the esterification reaction, catalyst preparation, catalyst characterization and free fatty acid analysis. All the procedure is stated accordingly.

Chapter 4 is devoted to gives a result and discussion of using equipment to characterization of catalyst and catalytic performance of ionic liquids in the reaction.

Chapter 5 is the overall conclusion, recommendation and the future work of this research project.

2 LITERATURE REVIEW

2.1 Introduction

Nowadays, petrochemical, coal and natural gas are the main sources of energy used worldwide. It was estimated that all of these sources will run out in less than 10 decades. Due to the limited sources of diesel from fossil fuel, biodiesel has been found as a viable alternative which are more environmental friendly.

From the history, biodiesel was first tested by Rudolph Diesel in year 1900 as a fuel for his engine and during World War II (Ghiachi *et al.*, 2010). In year 1930s and 1940s, vegetable oils were used as diesel fuels from time to time but it just in emergency situations.

With the rapidly increasing of crude oil prices due to the limitation of fossil fuel, research into sustainable alternative fuels has been highly prioritized in many countries around the world. Biodiesel was developed as substitution of diesel fuel and renewable energy sources. (Han *et al.*, 2008).

In Malaysia, renewable energy was introduced as the 5th fuel after four main energy sources in Malaysia which are oil, gas, hydropower and coal in the 8th Malaysian Plan in year 2001. According to Sulaiman *et al.*, (2011), Malaysian depends too much on fossil fuels as an energy sources. To reduce the dependency on the fossil fuel, Malaysia found palm oil as the potential energy sources due to its abundance. Palm oil acts as the feedstock to food industry in producing edible oil and oleo chemicals industry for production of soap, cosmetic and others. Nowadays, palm oil has appears as a replacement for non-renewable energy sources.

2.2 Biodiesel

Nowadays, biodiesel production becomes worldwide interest due to the relentless environmental concerns, and high demand for fossil fuel consumption. Besides, biodiesel is environmental friendly since it can eliminate or decrease engine emission such as unburned hydrocarbons (68%), particles (40%), carbon monoxide (44%), sulfur oxide (100%), and polycyclic aromatic hydrocarbons (80–90%). Moreover, it is biodegradable and technically feasible (Kiakalaieh *et al.*, 2012). The raw material used in

producing biodiesel is available from variety of sources like vegetable oil and animal fats which is renewable biological sources.

There are two constrains exist in producing biodiesel which are the cost of raw material and the cost of processing. Vegetable oil is the most used as raw material in producing biodiesel. But the uses of vegetable oil are not economic since the cost of vegetable oil relatively high. Due to this matter, waste cooking oil has been used instead of vegetable oil. Its cost was relatively low. However, the quality of waste cooking oil is bad. Waste cooking oil contains high free fatty acid and water. The presence of free fatty acid and water makes the biodiesel synthesis becomes more complicated. In order to remove the free fatty acid, pre-treatment step by using acid catalyst need to be done before undergo transesterification reaction using alkali catalyst. This pre-treatment step improved the biodiesel yield. However the multistep of producing biodiesel is not economic. High cost of processing is required since the cost of catalyst is quite high. Many studies have been made in order to find the cheaper way in utilizing of waste cooking oil in producing biodiesel including developing the catalyst that give the good performance in esterification and transesterification reaction.

2.3 Feedstock

The feedstock used in processing biodiesel can be divided into two which are edible oil and non-edible oil. Common edible oil used as a feedstock for biodiesel production is palm oil, rapeseed oil, and soybean oil. While non-edible oil that commonly used is jatropha oil and karanja oil. Soybean oil usually used as raw material in USA, jatropha oil in India, palm oil in Malaysia and rapeseed oil in European countries due to their raw material abundance (Sharma *et al.*,2008).

Biodiesel is a mono alkyl ester of fatty acid originating from vegetable oil or other fat. Vegetable oil like palm oil, rapeseed oil and soybean oil are usually used as feedstocks for biodiesel production. Vegetable oil has been used as a feedstock in the producing biodiesel by transesterification of the oil with short chain alcohol like methanol and ethanol in the presence of catalyst or enzyme (Demirbas, 2003).

In Bangladesh, rubber seed oil has been found as a potential source for biodiesel production since there is around 91.8 thousand hectare of land of Bangladesh is used for rubber plantation from where the rubber seeds can be collected. With the mechanical

press and addition of solvent, the maximum amount of oil obtain is 49% (Mahbub *et al.*, 2011).

But, the uses of vegetable oil as a raw material required high cost. It is the major obstacle in commercializing biodiesel from vegetable oil. According to Zullaikah, the production of biodiesel from refined edible oil contributes more than 70% of overall production cost.

Due to that, waste cooking oil has been recognized to be attractive and economic alternative way instead of using vegetable oil as a raw material since it is cheaper and environmental friendly alternative feedstock for biodiesel production. It was estimated that waste cooking oil price is about half of the virgin vegetable oil. It was extremely large amount of waste cooking oil generated from restaurant, food processing and industries which usually not properly disposed into the sewer system. This practice affects the environmental and human health as it can contribute to the pollution of rivers, lakes, seas and underground water (Boffitto *et al.*, 2012). The uses of waste cooking oil as a feedstock in biodiesel production will help to solve the waste cooking oil disposal problem.

Shin *et al.*, (2012) used the waste lard as their biodiesel feedstock. This idea comes up since Korea country has high consumption of this type of animal fat. In Korea, there is enormously popular cuisine called *samgyeopsal* (pork belly). A survey conducted by Agricultural Cooperatives found that 85% of Korean adult favourite food is *samgyeopsal*.

From Gehard and Kevin (2009) studies, they found that the feedstock from the waste cooking oil gives different profile of fatty acid in difference sources. It is influenced by the different increase in degrees of saturation in that oil and fats. It's acid value and viscosity will consistently increase with the use. However, in the same sources of waste cooking oil, there is some consistency in their properties. But for some cases, there is possibility that the different in properties biodiesel produce from the waste oil is wide if they used different kind of vegetable oil.

According to the Shashikant *et al.*, it is about 20% and 17% of free fatty acid in the recycled or waste oil and by product from refining of vegetable oils, some non-edible oils, animal fats and oil.

2.4 Production of biodiesel

In producing biodiesel there are four primary ways which are, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification (Fangrui and Hannab, 1999).

Direct use of vegetable oil as a fuel has been tested by Rudolf diesel without any changes to the engine. The properties of vegetable oil which has high viscosity lead to a problem when run in a long time. The problems that occur are carbon deposited caused by difficulty in atomization of vegetable oil, choking and trumpet formation on the injector and oil ring sticking.

Due to the high viscosity of vegetable oil, microemulsion step has been introduced. Microemulsion is defines as the colloidal dispersion of fluid microstructure in solvent producing two immiscible liquids. Solvent that commonly used are methanol, ethanol, and 1-butanol. Less viscosity make the atomization of vegetable oil becomes easier.

Pyrolysis or thermal cracking is the method where one substance is converted into another substance using heat with the aid of catalyst to speed up the reaction. Vegetable oil, animal fat, natural fatty acid and methyl esters of fatty acid can be used as material in pyrolysis. Pyrolytic chemistry becomes difficult because same material can produce different products depending on the path of reaction. In pyrolysis process, it produce some low materials, sometimes, it produce more gasoline than diesel fuel.

Transesterification is the most used method in biodiesel synthesis of vegetable oil and animal fat. Waste cooking oil contains significant amount of free fatty acid. Direct used of base-catalyst is prohibited because reaction of free fatty acid with alkali catalyst forming soap and water. Saponification process will form a stable emulsion which causes difficulties in separation (ester and glycerol) and (water washing) reutilization of catalyst.

Regarding to that matter, two synthesis steps of biodiesel has been found to achieve high yield. The first step is pretreatment step. In this step, it used acid catalyst to reduce the amount of free fatty acid in feedstock. Then finally goes to the transesterification reaction as a second step using alkali catalyst since the reaction using alkali catalyst is quicker than using acid catalyst.

Supercritical alcohol technology is the technology that has been introduced with non-catalytic process by using high ratio of methanol with oil. This process can eliminate all the tedious separation and purification step to remove side product like unreacted

catalyst. According to Demirbas (2002), without catalyst this method minimize the time of reaction to achieve a significant yield of biodiesel. High yield of biodiesel obtain in the short period. Although this technology offers a lot of advantage but the disadvantage of this technology is its required high temperature and pressure. Cao *et al.*, (2005) report the good yield obtain in 6 minutes reaction time at temperature of 350°C and 400°C with pressure of 450 and 650 bar using methanol/oil molar ratio of 42.

2.4.1 Transesterification reaction

Transesterification is the most popular method used in producing biodiesel. The reaction converted triglycerides into the mixture of ester and glycerine with the presence of catalyst and alcohol (Abidin *et al.*, 2012). Triglyceride is highly found in vegetable oil and some animal fats.

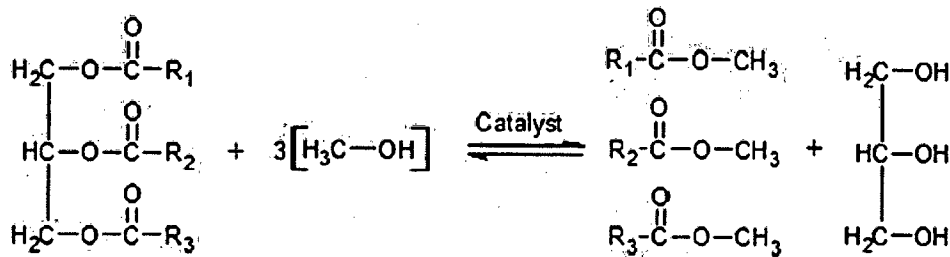


Figure 2-1: Transesterification of biodiesel from triglyceride

According to the Sendzikiene *et al.*, (2004), the overall chemical reaction process is a series of three consecutive and reversible reactions which forming di- and monoacylglycerols as intermediates. In the other way, triglycerides can be transform by hydrolysis into free fatty acids with acid or bases depend on the reactivity order of different position of carbon in glycerol structure (Gan *et al.*, 2012). Several oil raw materials with different compositions and a high content of fatty acids can employ this alternative method for direct transesterification process (Freedman *et al.*, 1986).

Darnoko and Cheryan (2000) studied that the conversion of triglyceride, diglycerides and monoglycerides was second order from the transesterification of palm oil with methanol at 60°C. Reaction rate constants for the hydrolysis reactions were higher for the monoglycerides reaction than for triglycerides hydrolysis.

Waste cooking oil contains high free fatty acid and water. According to Fangrui and Hannab (1999), there is a significant effect on the transesterification of glycerides with

alcohol using alkaline and acid catalyst with the present of free fatty acid and water. It also disturbed the separation of fatty acid ester and glycerol. Commercially acid-catalyzed transesterification is slower than alkali-catalyzed transesterification.

According to Sharma and Singh (2011), there are several factors that effect transesterification reaction which are the presence of free fatty acid and water content, molar ratio of alcohol to oil, catalyst type and loading, reaction temperature and stirring rate. Transesterification can be divided into three categories which is alkali-catalyzed, acid catalyzed or enzyme catalyzed. Enzyme-catalyst is rarely used since it requires a longer reaction time compared to alkali and acid catalyzed (Watanabe *et al.*, 2001). Alkali catalyst that commonly used is sodium hydroxide and potassium hydroxide. Alcohol that was commonly used in the process study is methanol since it is low cost. Large amount of methanol used to shift the equilibrium far to the right (Zhang *et al.*, 2009)

2.4.2 Esterification reaction

Esterification is a reaction where an organic acid and an alcohol combine usually in the presence of acid catalyst producing an ester with water.

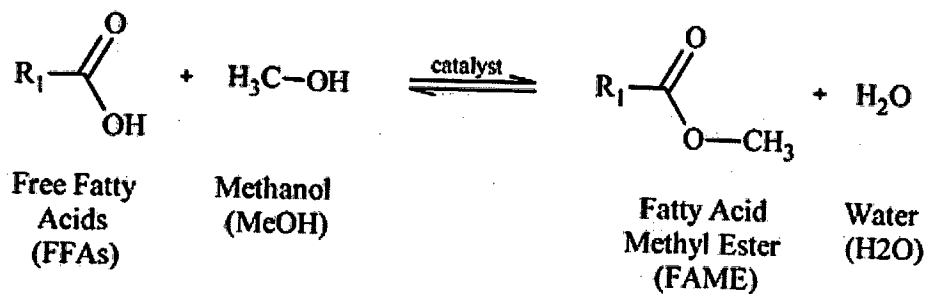


Figure 2-2: Esterification of free fatty acid

Alcohol that commonly used in the esterification reaction is a short chain alcohol. The common alcohol used is methanol. According to Jeenpadiphat *et al.*, (2014), the yield of methyl ester is low using ethanol compared to methanol. It is due to the sterical hindrance of ethanol which limit the active site of reactant (Stavarache *et al.*, 2005).

Waste cooking oil contained high free fatty acid. Free fatty acid in the other name is uncombined fatty acid which their fatty acid that is not attached to the other molecule. It is the breakdown of triglyceride. With the high free fatty acid content, transesterification

reaction is not compatible with the using of waste cooking oil as a feedstock. Transesterification reaction is commonly used in biodiesel synthesis using vegetable oil and animal fats as feedstock which its constituent is triglyceride.

According to the Han *et al.*, (2009), the main components of waste cooking oil are fatty acid and triglycerides. With the increasing number of fatty acid, its acid number of waste oil will also increase. From their studies, they conclude that, esterification reaction of fatty acid with methanol is quicker than transesterification of triglycerides with methanol since the fatty acid of waste oil is more which can easily converted into biodiesel (Fatty Acid Methyl Ester) by using Bronsted acidic ionic liquid as catalyst.

In the traditional way, the reaction was carried out under batch conditions in homogeneous liquid phase (Caetano *et al.*, 2013). Usually homogeneous acid catalyst is used in conducting esterification process in chemical industries. However, homogeneous acid catalyzed reaction caused many environmental and corrosion problem. Hence, heterogeneous catalyzed reaction getting intention in esterification reaction (Kamath *et al.*, 2011)

According to Naik *et al.*, (2008), there is a significant drop of ester conversion when the free fatty acid content is above 2% using alkali catalyzed transesterification. Homogeneous alkali catalyst is saponified free fatty acid caused catalyst depletion increased the cost of purification (Shu *et al.*, 2007)

2.5 Parameter affecting esterification reaction

There are 5 primary parameter that evaluate in esterification reaction in biodiesel synthesis which are catalyst, amount of free fatty acid and water content, temperature of reaction, molar ratio of methanol with oil and lastly mode of stirring.

2.5.1 Catalyst

In synthesis of biodiesel, there are two types of catalyst that commonly used which is homogeneous catalyst and heterogeneous catalyst. The two types of catalyst can be either acid catalyst or base catalyst. Due to the high free fatty acid in waste cooking oil, acid catalyst is commonly used instead of base catalyst. Oil and fats with high free fatty acid cannot directly used base catalyst because the conversion into ester will drop when the free fatty acid content above 2% (Naik *et al.*, 2008).

Homogeneous catalyst that commonly used in the production of biodiesel is sulfuric acid. Chia *et al.*, (2013) studied the effect of catalyst loading on esterification reaction catalyzed by hydrochloric acid with 0.1-1M. He found that as the catalyst loading increase, the conversion of FFAs in waste cooking oil was also increased at a temperature of 303.15 K and methanol/FFA molar ratio of 5:1.

According to Deshmane *et al.*, (2009), high catalyst loading faster the reaction rates because hydrochloric acid makes protons available in FFA in sufficient quantity to catalyze the reaction at a reasonable rate. The same result also reported from former research under acid catalyzed reaction (Berrios *et al.*, 2007; Deshmane *et al.*, 2009)

Sulfuric acid has high acidity and very suitable for the reaction since waste cooking oil has high free fatty acid and water. But, due to the high acidity, it generate many environmental and corrosion problem to the reactor and automatically required high cost stainless steel equipment which enhance the operational cost. Homogeneous catalyst is not environmental friendly since it cannot be reused, generated more byproduct which requiring high cost of separation and purification. Due to the drawbacks of the homogeneous catalyst, former research developed heterogeneous catalyst in the synthesis of biodiesel.

It has been proved that heterogeneous catalyst can simplify the production and purification processes because they can be easily separated from the reaction mixture without requirement of washing. Then, it can directly reduce the waste and environmental impact. Heterogeneous catalysts have a unique advantage in esterification and transesterification reactions which enhances the use of high acid value oil to be used as feedstock for synthesis of biodiesel. According to the Yogesh C. Sharma and Bhaskar Singh (2010), there are two type of heterogeneous which is solid base and solid acid.

Solid base catalysts include a wide group of compounds in the category of alkaline earth metal hydroxides, hydrotalcites/layered double hydroxides, alumina loaded with various compounds, zeolites, and various other compounds. It shows high conversion and yield of biodiesel obtained. But, they are sensitive to the presence of free fatty acid.

Thus, solid acid shows better performance in the biodiesel synthesis from waste cooking oil which has high free fatty acid content. The advantages of solid acid are it have high stability, strong acid site, large pores, hydrophobic surface and economically viable. According to the Gan *et al.*, (2009) studies, as the amount of catalyst increase the FFA

of waste cooking oil conversion was also increase until 98% of optimum conversion with 0-7.5% of catalyst mass percent at $T= 368.95K$ with molar ratio of methanol /FFA 18:1 using ferric sulfate /active carbon as a solid acid catalyst.

Hence, instead of two stage synthesis of biodiesel which acid value is reduce at the first stage followed by the conversion of oil into biodiesel for second stage, it is replaced by single step process when solid acid as a catalyst adopted. Various solid acid catalysts such as resins, tungstated and sulfated zirconia, polyaniline sulfate, heteropoly acid, metal complexes, sulfated tin oxide, zeolite, acidic ionic liquid, and others have been explored as potential heterogeneous catalysts. (Yogesh C. Sharma and Bhaskar Singh, 2010). Solid acid as a catalyst can reduce many problems related to homogeneous acid catalyst in technological and environmental aspects. To achieved high conversion using solid acid, the reaction need to be carried out at long reaction times and high temperature.

Solid acidic ionic liquid polymer is a catalyst which ionic liquid is copolymerized with polymeric support like polystyrene, divinylbenzene (DVB), silica and zeolite. It was known as a molten salt at room temperature. The term of ionic liquid is used for the salt which is melting point lower than $100\text{ }^{\circ}C$. Ionic liquid is emerging as a green reaction media which is as catalyst and solvent at the same time (Adnan *et al.*, 2008). Ionic liquid cost is quite expensive compared to conventional solvents but it has an ability to be reused by recycling. Some method can be applied in order to recover ionic liquid from reactants. Recycled ionic liquid is able to maintain its performance based on the yield and selectivity of product. The presence of alkyl sulfonic group which maintain it connection to imidazole ring by covalent bond is main factor of good reusability of ionic liquid (Li *et al.*, 2009).

In the biodiesel synthesis, ionic liquid can be applied as a catalyst, solvent for enzyme-catalyzed transesterification, catalyst support and lipid extraction. Its usefulness in their utilization becomes more eminent (Fauzi and Amin, 2012).

Ionic liquid is form from different combinations of cations and anions. The ions used influence its physicochemical and thermal properties of ionic liquid. In produce task-specific ionic liquids (TSILs) for different application, manipulation of ionic liquid functional group can be done. It also has tunable properties depends on it's the organic cation and inorganic anion. The solubility, density and the viscosity of the liquids is determined by the organic cation. For lewis acid of ionic liquid, it's properties depend

on the metal halide chosen and the ratio of the metal halide with the organic base. (Valkenberg *et al.*, 2001).

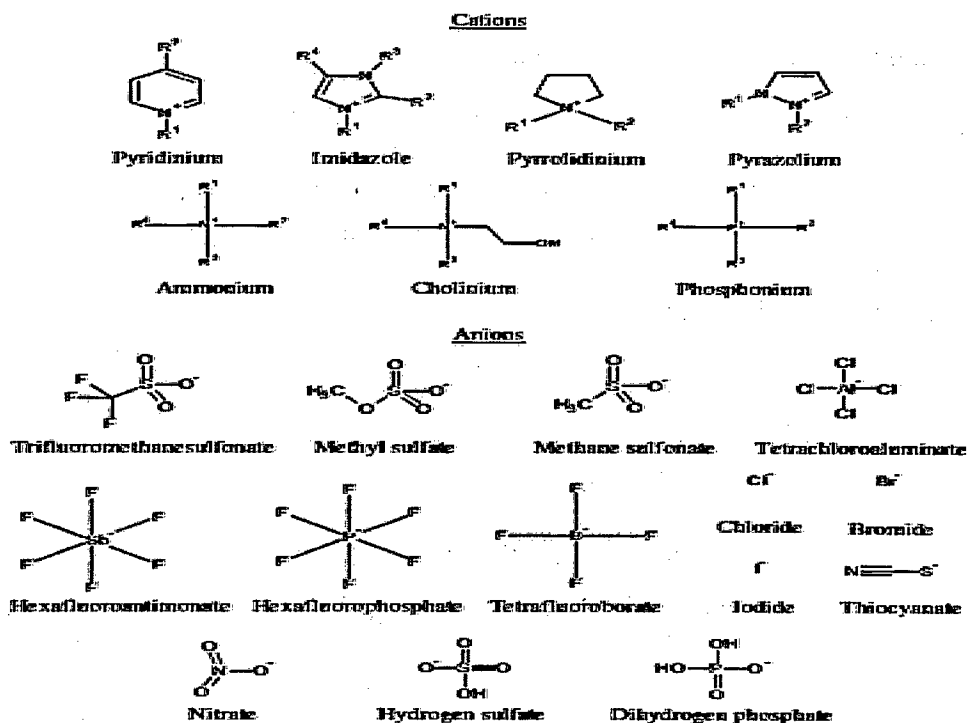


Figure 2-3: Common used anions and cations in ionic liquids.

Instead act as a catalyst, ionic liquid can also act as catalyst support in the biodiesel production. The presence of support provides sites for the reaction to occur. Supports which have high surface area enhance the reaction. In the catalytic reaction, support can be either inert or participation (Fauzi and Amin, 2012). Common solid catalyst that has been use before were alumina, silica and zeolite.

According to Liang *et al.*, (2009), there are some drawbacks of ionic liquid. Catalyst loss of ionic liquid happens at certain solubility with some organic compound which can also cause difficulty in separation. Their industrial application will also limit due to the high viscosity which increase the mass transfer resistance. Much attempt was made to solve the problems including adjusting the molecular structure and melt point. Former research found immobilization of ionic liquid by implant supports and linkage cover up the problem. Support that can be used to immobilization of ionic liquid is zeolite, polystyrene and silica. In order to immobilized the ionic liquid different method can be applied such as, simple impregnation, sol-gel method, grafting or polymerization (Eero *et al.*, 2013). According to Xu *et al.*, (2010), the immobilization of ionic liquid gives

many advantages such as separation, reusability and the ability to provide practical convenience in a continuous system.

Zeolite is performed by different proportion of SiO₄ and AlO₄-tetrahedra interconnected by the O atom (Weitkamp, 2000). It has ordered porous system, large surface area, and tuneable acidity gives the better performance on the immobilization of the catalyst. Many cation and small particle found absorbed by the porous material inside the pores and cavities. According to the Campos *et al.*, (2012), zeolite provides dense networks of regular pores, not limited to particle interstices and crack compared to the silicas and aluminosilicas. The adjustable dimension of zeolites pores may change the behavior of the active center, reactivity of the monomers and the microstructure of the final products which may originate interesting confinement effect.

According to Xu *et al.*, (2010), the immobilization of polystyrene on acidic ionic liquid by using different coupling agent, shows high synthesis of homoallylic alcohol and esterification. Liang studied that ionic liquid with polystyrene support shows high activities for esterification with the average yield of 96%. In 2010, Xu studied the efficiency of polystyrene-supported acidic ionic liquid catalyst for Esterifications which are PS-CH₂Cl and PS-CH₂-[SO₃H-pIM][HSO₄]. From the study, PS-CH₂-[SO₃H-pIM][HSO₄] catalyst showed a better thermal stability than that of PS-CH₂Cl support.

J. Miao *et al.*, (2011) and Amaraseka *et al.*, (2010) studied that immobilization of ionic liquid on silica performs high activities for acetalization and hydrolysis of cellulose since silica have high surface and hydroxyl group that fastened ionic liquid. According to Xu, with supported ionic liquid catalyst, it can make the separation process easier, reusability and provide practical conveniences in continuous system.

Liang *et al.*, (2013) studied the effect of catalyst amount on the yield of methyl ester using novel solid acidic polymer ionic liquid. From the studies it was found that as the amount of catalyst increase from 0.01-0.05/g the yield increase to 99% but, as the amount reach to the 0.07/g the yield got no change at T= 70°C for 12 hour. Finally at 0.09 catalyst amount/g the yield decreased to 98.5%. From this finding it can be conclude that too much of catalyst may alter or converse the reaction.

One property of ionic liquid polymer is reusability. The solid catalyst from the reaction product can be recovered by simple filtration method. The previous report shows the polystyrene-supported ionic liquid only decrease 7.3% yield after reused for 13 times for esterification reaction (Xu *et al.*, 2010). Former research test the reusability of DVB-

supported ionic liquid found that the performance of the recycled catalyst show high performance. Although the catalyst recycled for 6 times, the catalyst yield is 99% (Liang *et al.*, 2013).

According to the Decastro *et al.*, (2000), ionic liquid as a catalyst were not reactive in the second run. He found that there are two factors that influenced the catalyst deactivation. The first factor is the presence of water from the moisture residue in the filter during recovering the catalyst. It can be avoided by careful drying of the starting material. The second factor is the adsorption of reactant on catalyst surface which blocking the active site of catalyst preventing the reaction.

2.5.2 Free fatty acid and water content

Waste cooking oil contains high free fatty acid and water. The presence of free fatty acid and water are the main constrain in the biodiesel synthesis since they inhibit the transesterification reaction. With an acid catalyst, free fatty acid in the oil can be converted to alkyl ester then followed by standard alkali-catalyzed transesterification to convert the triglycerides. But the reaction rates are too slow. The presence of water in the waste oil esterification can cause soap formation. The formation of soap increased the viscosity of the product. It can consume the catalyst and reduced catalyst efficiency hence the separation of glycerol with ester will be difficult.

From the Liang (2013) studies, it is found about 22wt% of free fatty acid found in the waste oil. With the uses of novel solid acidic ionic liquid polymer, the yield of the reaction is over 99%. Liang stated that high acidity and stability is the key feature of the process.

In cases of rubber seed oil as a biodiesel feedstock, the free fatty acid and water content will change due to the storage time of the seed. Mahbub *et al.*, (2011) studied the effect of time on the percentage of free fatty acid. They found that FFA content increases from 2 wt.% (fresh seed) to 45 wt.% after 2 months of storage at room temperature.

2.5.3 Temperature

Temperature significantly influenced the reaction rate and yield of ester. According to the Han *et al.*, (2009), Fatty Acid Methyl Ester (biodiesel) content increase with an increase in reaction temperature every 20°C from 80 to 180°C but the result shows that the effect of reaction temperature on the reaction becomes smaller when temperature

increase. The optimum temperature from the studies is between 170 and 180°C by using Bronsted acidic ionic liquid as a catalyst.

From Zhang studies, conversion of oleic acid increased as temperature increased for biodiesel synthesis using Bronsted acidic ionic liquid as catalyst. Esterification yield increased reaching the maximum of 95% in 8 hour at 70°C. Oleic acid is the major component in waste oil for biodiesel production.

Zakaria *et al.*, (2013) found that at reaction temperature of 120-170°C the conversion of free fatty acid increase from 20% to 82.1% using Bronsted ammonium ionic liquid from crude palm oil. Beyond to that temperature there is no increase in FFA conversion. The esterification reaction was carried out under the same operational parameter. It can be conclude that 170°C is the optimum reaction temperature.

2.5.4 Molar ratio of methanol with oil

As the molar ratio of methanol to oil increase the biodiesel production will also increase. Increasing amount of methanol is beneficial in forward reactions since esterification and transesterification reaction are reversible. High amount of methanol use avoid the backward direction of reaction from occurring. Ionic liquid which is used as a catalyst in the reaction is soluble in methanol will increase the amount of methanol. As the amount increase the contact area between catalysts with the oil will be bigger resulting higher rate of reaction. But, as the molar ratio of methanol increased more than 12:1, the concentration of catalyst will greatly dilute which increase the rate of reaction. Large amount of methanol with oil will cause more methanol needed to be separated from ionic liquid during recycling. Hence the optimum amount of methanol with oil is 12:1 (Han *et al.*, 2009)

According to the Man *et al.*, (2013), at the same operating condition, the conversion of free fatty acid increase as the amount of methanol increased from crude palm oil. The maximum conversion of free fatty acid obtained is at the molar ratio of 15:1. Beyond this molar ratio there is no increase in free fatty acid conversion. Same thing goes to the Jolius *et al.*, (2013) studied. They found that at the beginning of the reaction, increasing amount of methanol increase the conversion of FFA but as the molar ratio of methanol with water increase from 5:1 to 6:1 the conversion start to decline. It may be caused by the reversible reaction has been initiate thus reduce the reaction conversion.