TRANSESTERIFICATION OF PALM OIL USING TUNGSTATED ZIRCONIA

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A thesis submitted in the fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineers

Faculty of Chemical and Natural Resources Engineering
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APRIL, 2010

ABSTRACT

The transesterification of unrefined oil using heterogeneous solid acid catalyst is one of the methods of producing biodiesel. Biodiesel is a non- petroleum based fuel thus it has advantages such as non- toxic, biodegradable and environmental friendly. The usage of Tungstated Zirconia will eliminate the drawbacks of using homogeneous catalyst such as corrosiveness, production of waste, and etc. The present studies aimed to determine the conversion of methyl ester produced and the optimum operating condition for the transesterification process. The research study is done in a batch reactor system. The catalyst is activated to 800^oC for it to functions at the best state. Optimum operating condition is at 95^oC with molar ratio of alcohol to oil is 9:1 and 20 wt% of oleic acid in oil. The highest conversion of methyl ester from this optimum operating condition is 93.14%.

ABSTRAK

Proses pengesteran minyak terpakai menggunakan pemangkin asid pejal yang tidak larut di dalam fasa yang sama ialah salah satu kaedah untuk menghasilkan biodiesel. Biodiesel ialah bahn api yang dihasilkan bukan dari asas petroleum, oleh itu ianya mempunyai banyak kelebihan seperti tidak toksik, bio-degradasi dan mesra alam. Penggunaan Tungstated Zirconia akan dapat melupuskan kelemahan pemangkin yang larut di dalam fasa yang sama seperti; pengaratan, penghasilan sisa dan lain- lain. Kajian terkini tertumpu kepada mencari peratusan penghasilan Metil Ester dan keadaan optima atau terbaik untuk penghasilan melalui proses pengesteran ini. Kajian ini dijalankan menggunakan sistem reaktor batch. Pemangkin diaktifkan ke suhu 800^oC untuk berfungsi pada keadaan terbaik. Dari skop kajian, dapat dibuktikan bahawa keadaan optima dapat dicapai pada suhu 95^oC dengan 9:1 nisbah molar alcohol kepada minyak dan 20 wt% penggunaan oleic acid daripada minyak. Peratusan penghasilan tertinggi metil ester melalui kaedah optima ini ialah sebanyak 93.14%.

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LIST OF ABBREVIATION/ TERMINOLOGY/ SYMBOLS

T	-	Temperature
°C	-	Degree Celcius
ml	-	Mililiter
kJ	-	KiloJoule
min	-	Minute
K	-	Kelvin
w/w	-	Weight per weight
kg	-	Kilogram
g	-	Gram
%	-	Percentage
rpm	-	Revolutions per minute
M	-	Molar (mol/dm3)
FFA	-	Free Fatty Acid
wt	-	Percentage by Weight
TG	-	Triglyceride

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CHAPTER 1

INTRODUCTION

Over the last decade and half, the escalating concerns over global warming along with the measures to reduce dependence on foreign fuel as well as reduction in emission levels has led to the development of sources other than oil for transportation. A wide range of alternatives have been developed - from hydrogen based vehicles to natural gas vehicle. However, none of them have been as effective as biofuels - ethanol and biodiesel - both from commercial as well as environmental perspective. Use of biofuels for transportation have a great potential to replace a substantial amount of petroleum worldwide in coming decades and a clear trend in that direction has already begun. In last couple of years, the production and consumption of biofuels have entered a new era of global growth, experiencing expansion both in the scale of the industry and the number of countries involved.

According to Bowman *et al*., (2006), compared to petroleum diesel, biodiesel is environmentally friendly and is government mandated. It reduces carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrocarbons (HC) and other particulate matter emissions that cause respiratory damage.

1.1 Background of the Study

Biofuel as alternative source of energy is expected to improve the present day conditions of our environment. Biofuel or also known as bioenergy is a source of renewable energy drawn from biological sources comprised of biomass and biogas and co-firing. There are several types of biofuels that often used. There are biogas, bioethanol and biodiesel. Biofuel described as renewable energy, means it has the capability to be replenished mainly because of its inexhaustible supply, ability to re-grow or to be recycled. Plant's have the ability to capture carbon in the air, reuse the carbon as fuel then simply absorbs back the carbon released through combustion. Today, biofuel represents 10% of the world's supply of energy while the three most common biofuels that are expected to be widely usable are biodiesel, bioethanol and biomethanol.

Due to the potential depletion of petroleum and environmental concerns about air pollution caused by the combustion of fossil fuels, the search for alternative fuels has gained much attention. Biodiesel (fatty acid methyl ester) derived from either the transesterification of triglycerides (vegetable oils or animal fats) or the esterification of free fatty acids (FFAs) with methanol is a potential substitute for petroleum-based diesel. Compared with conventional diesel, biodiesel has the advantages of being biodegradable, renewable, non-toxic, and low pollutant, especially SO_x emission (Peng *et al*., 2008).

Biodiesel which is recognized as 'green fuel' is one of such alternative fuel produced from vegetable oils. In spite of all the advantages such as low emissions, biodegradable, non-toxic, and better lubricity, biodiesel is not yet commercialized all over the world (Kulkarni *et al*., 2006).

Biodiesel is a nonpetroleum-based fuel that consists of alkyl esters derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with low molecular weight alcohols. The flow and combustion properties of biodiesel are similar to petroleum-based diesel and, thus, can be used either as a substitute for diesel fuel or more commonly in fuel blends.

Biodiesel advantages compared to petroleum diesel, this is include its renewable nature, superior emissions properties, good support for domestic agriculture, compatibility with existing engines, and distribution infrastructure, and ease of manufacture. Although biodiesel has experienced episodes of popularity throughout the 20th century, the most recent biodiesel revival began in Europe in the early 1990s, spurred by mandatory alternative fuel use legislation and a liquid fuel market dominated by diesel fuel (66% of on-road, liquid fuel demand).

Biodiesel is superior to conventional diesel in terms of its sulphur content, aromatic content and flash point. Conventional diesel can contain up to 500 ppm SO_2 and 20–40 wt% aromatic compounds. Biodiesel is essentially sulphur free and non-aromatic. These advantages could be a key solution to reduce the problem of urban pollution since transport sector is an important contributor of the total gas emissions. The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are it has to have a complete reaction, total removal of glycerin, catalyst and alcohol, and lastly the absence of free fatty acids.

From previous studies by Bowman *et al.* (2006) the advantages that biodiesel has over petroleum based diesel include requires of less energy. The fossil fuel energy required to produce biodiesel from soybean oil is only 30% of the energy contained in one gallon of the fuel. In other words, approximately 3.2 units of fuel energy are generated from biodiesel for every unit of fossil energy used to produce the fuel. That estimate includes the energy used in diesel farm equipment and transportation vehicles (trucks, locomotives); fossil fuels used to produce fertilizers and pesticides; fossil fuels used to produce steam and electricity; and methanol used in the manufacturing process.

To date, most of the studies on biodiesel synthesis have been focused on either base catalyzed or homogeneous acid catalyst system employing refined vegetable oils. However, if a homogeneous catalyst is used, it will cause corrosion and serious environmental related problem.

1.2 Problem Statement

A conventional operation of biodiesel usually uses strong basic or acidic solution such as NaOH, KOH and H_2SO_4 as catalyst and food- grade vegetable oils as raw material. These are homogeneous catalysts. The homogeneous catalysts are quite sensitive to FFAs and water in the oil feedstocks and alcohols because the reaction of FFAs with basic homogeneous catalyst will forms soaps. The soaps formation will complicates the glycerol separation. Therefore, heterogeneous solid acid catalyst is more frequently used since it is easier to handle and easy to be separate from products. The implementation of environmentally friendly heterogeneous (solid) catalysts in large- scale biodiesel production is preferable to eliminate the drawbacks associates with homogeneous catalysts such as corrosiveness, production of waste, excessive use of water in washing steps, and energy- intensive separation operations. Moreover, solid catalysts permit the application of continuous reaction systems that improve overall process economics. In this study, heterogeneous solid acid catalyst; tungstated zirconia are used to convert the raw material into biodiesel. The raw materials used are oleic acid (FFAs), palm oil (TGs) and methanol.

1.3 Research Objectives

The objectives of this research are:

a) To determine the conversion of oil using unrefined palm oil and tungstated zirconia.
b) To identify the optimum operating condition for the reaction.

1.4 Scope of Research

The scope has been identified for this study in order to achieve the objective. The scopes of research are listed as below:

- Study of the effect of free fatty acid content on oil product.
- Study of the effect of molar ratio of alcohol to oil.
- Study of the effect of temperature.

1.5 Significance of the Study

The rationales and significances of this study are:

- Creating a new development technology in biodiesel.
- Maximizing the utilities of heterogeneous solid acid catalyst.
- Utilized unrefined oils as raw material to produce high quality biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Petroleum is the largest single source of energy consumed by the world's population, exceeding coal, natural gas, nuclear, hydro, and renewable. Global demand for petroleum is predicted to increase 40% by 2025. Concerns about oil supply and energy security have motivated many countries to consider alternatives to imported petroleum. Liquid biofuels, renewable fuels derived from biomass, are arguably one of the best options to lead the transition away from petroleum fuels in the near-term and have made a recent resurgence in response to rising oil prices. However, biofuels present resource and environmental challenges depending on where, how, and from which feedstocks they are developed. The current issue about crude oil petroleum that we often heard is regarding its price.

Biodiesel is the biofuels of focus in our study due the diesel engine's wide range of applications, the diesel-cycle's inherent combustion efficiency advantage over otto-cycle engines (powered by gasoline), and diesel fuel's dominant position in the refined petroleum products market, accounting for 27.0% of worldwide refined petroleum consumption vs. 25.6% for motor gasoline. As biodiesel is nontoxic, renewable and beneficial for environmental protection, it is considered as an alternative fuel to traditional petroleum-based fuels.

2.2 Esterification

Esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing the water that is formed. Esters can also be formed by various other reactions. These include the reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-O-COR'). Early studies into the chemical mechanism of esterification, concluded that the ester product (R-CO-OR') is the union of the acyl group (R-C=O-) from the acid, *RCO*-OH, with the alkoxide group (R'O-) from the alcohol, *R'-O*H rather than other possible combinations.

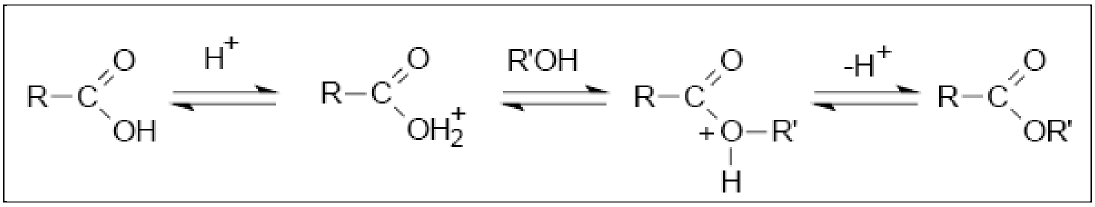


Figure 2.1: Acid catalyzed esterification of fatty acid.

Kuriakose *et al*. (2004) says that selective esterification of bifunctional carboxylic acids in the presence of aromatic alcohol is a useful organic synthesis reaction. The esters thus obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics

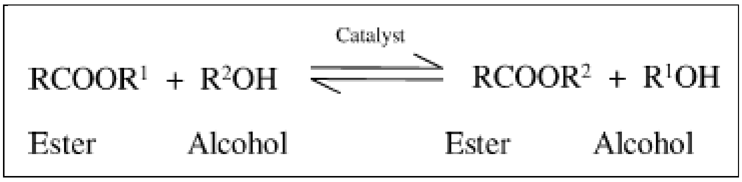
From previous studies by Marchetti *et al*. (2007), the direct esterification reaction of triglycerides to biodiesel was studied and the effects of the main variables involved in the process, reaction temperature, amount of catalyst, initial amount of free fatty acid and the molar ratio alcohol/oil, were analyzed. It was found that ethanol and sulfuric acid were suitable to perform not only the transesterification reaction but also the direct esterification reaction to increase biodiesel production of the process.

According to Bhorodwaj *et al*. (2010), compared to primary alcohols, esterification of a secondary alcohol is much more difficult to achieve. The steric effect of these substrates and the lower nucleophilicity of the oxygen atom hinder the formation of the corresponding ester. Conversions are also limited by slow reaction rates and reversible reactions.

2.3 Transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides.

The transesterification reaction is represented by the Figure 2.2 below:



$$\underset{\text{Ester}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{RCOOR^2} + \underset{\text{Alcohol}}{R^1OH}$$

Figure 2.2: General equation of transesterification process.

Samios *et al.* (2008), says that the transesterification process has two different forms. First is the ideal transesterification with the primary alcohol is given by the overall reaction. The second is the real transesterification process. It also stated that in reality, there is no such thing as ideal transesterification. Transesterification never occurs in ideal form. The main feature of this reaction is the transformation of the triglyceride to glycerol and three ester molecules. These esters constitute the components of the biodiesel. The reaction includes at least a catalytic component.

Figure 2.3 shows the ideal process of transesterification:

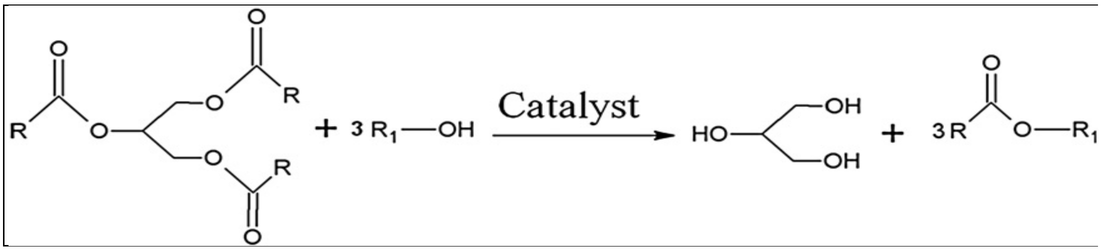


Figure 2.3: Ideal process of transesterification.

In reality, the transesterification process occurs when the chemical agents and products are present without consideration of stoichiometric parameters. There is no evidence of transesterification with 100% conversion efficiency. There are presence of triglycerides, diglycerides, monoglycerides, biodiesel esters, glycerol, alcohol and catalytic component.

Figure 2.4 shows the real transesterification process.

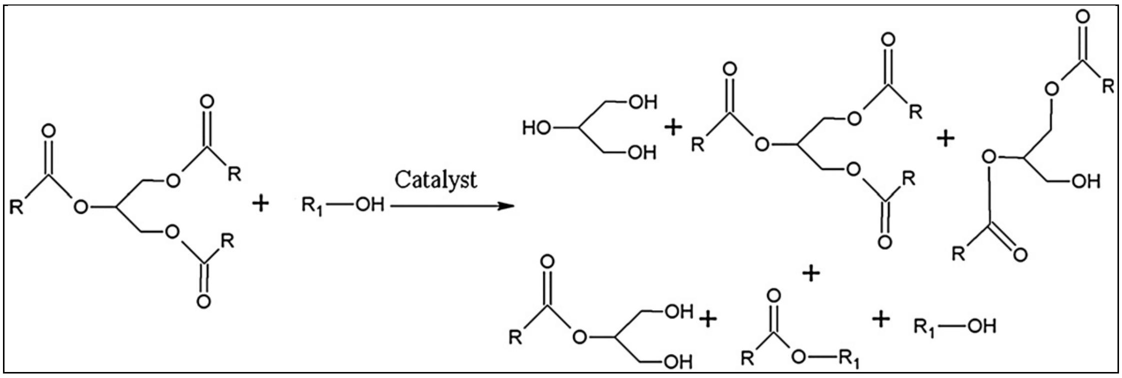


Figure 2.4: Real transesterification process

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. In this research, a simultaneous free fatty acid and triglyceride transesterification using a solid acid catalyst will be studied

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According to Meher *et al.* (2004), a transesterification can be catalyzed by Brownsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters but these reactions are slow, requiring typically temperature above 100^{o}C and more than 3 hour to complete the conversion. However, it can be extended to di- and tri- glycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.

The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2.6 and Figure 2.5 shows the transesterification of triglyceride with alcohol.

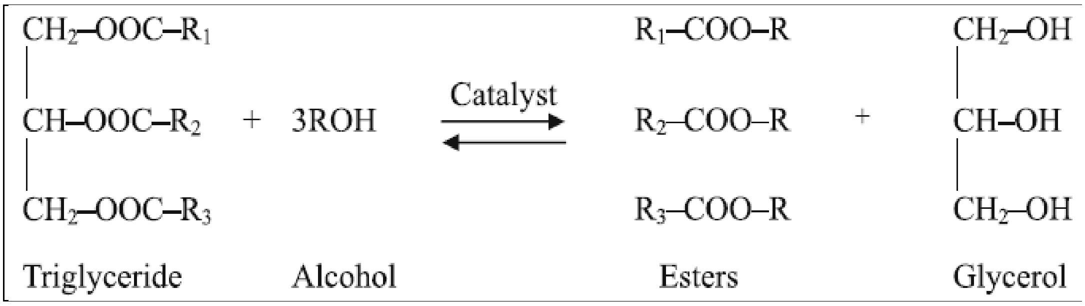

Figure 2.5: Transesterification of triglycerides with alcohol.

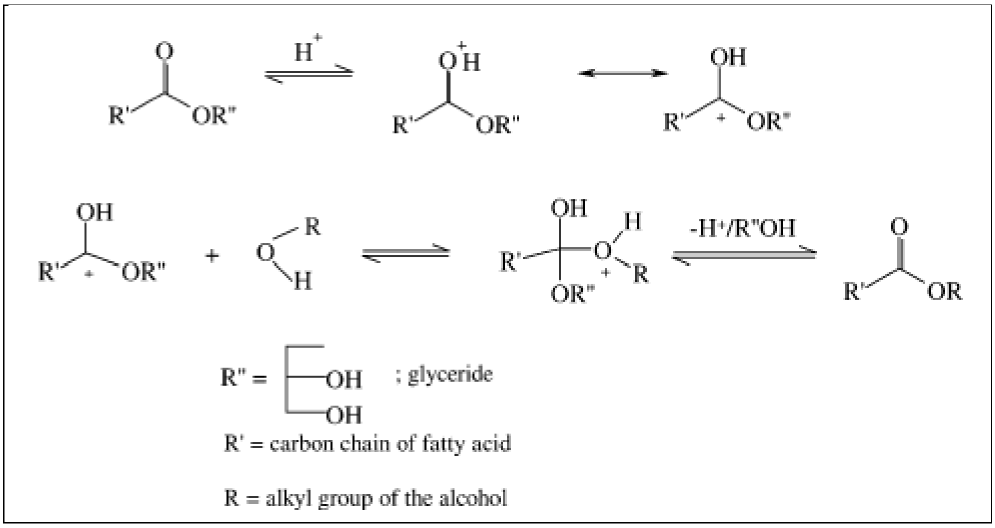

Figure 2.6: Mechanism of acid catalyzed transesterification.

Yusuke Asukuma *et al.* (2008) studied the effect of chain length of triglyceride on activation energy says that the transesterification of a triglyceride with exclusively straight chains was considered because saturated fatty acids form straight chains shows the relationship between the chain length of the triglyceride and the activation energy. Because of the similar activation energy values for all of the transesterification reactions in this calculation, the decomposition behavior seems to be similar, even if the triglyceride chain length is different. This differs from other researchers who have shown that the reaction rate of triglycerides with larger fatty acids is slower. This might be caused by a mixture property because the co- solvent of triglycerides with varying fatty acid sizes and methanol shows differences in a vapor– liquid–liquid three phase equilibrium.

Lotero *et al.* (2009) conducted a study on simultaneous free fatty acid esterification and triglyceride transesterification using a solid acid catalyst with in situ removal of water and unreacted methanol. A heterogeneous solid acid catalyst is used in this experiment. The continuous three- phase alcoholysis reaction of 0- 25 wt% lauric acid (HLa) in tricaprylin (TCp) catalyzed by a commercial tungstated zirconia (WZ) was investigated in a well- stirred semibatch Parr reactor at 130^{o}C and atmospheric pressure. WZ effectively catalyzed both esterification and transesterification, achieving 85% HLa conversion and 22% TCp conversion after 2 hour of reaction under the reaction conditions used for a model 25 wt% HLa- TCp mixture.

Yan *et al*. (2008), also have a successful experiment using the heterogeneous catalyst. In this experiment, they are using series of heterogeneous zinc and lanthanum mixed oxide. The effects of metal oxide molar ratio, free fatty acids (FFA) and water content in feedstock, molar ratio of methanol and oil, and reaction temperature on the yield of biodiesel were investigated. As conclusion, they found that the use of this class of catalysts. Which is relatively inexpensive because of low raw materials and manufacturing cost, significantly simplifies the oil pretreatment process and product purification process, and greatly decreases the production cost of biodiesel.

2.4 Cracking Process

Cracking is a petroleum refining process in which heavy-molecular weight hydrocarbons are broken up into light hydrocarbon molecules by the application of heat and pressure, with or without the use of catalysts, to derive a variety of fuel products. Cracking is one of the principal ways in which crude oil is converted into useful fuels such as motor gasoline, jet fuel, and home heating oil. In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of any catalysts. Cracking, also referred to as pyrolysis, is the breakdown of a large alkane into smaller, more useful alkanes and an alkene. There are two most common cracking methods that are used in the industries. They are catalytic cracking and thermal cracking.

2.4.1 Catalytic Cracking

Catalytic cracking, with a worldwide processing capacity of over 500 million tones of oil per year, is one of the most important processes applied in modern oil refineries and the prime method for making petrol from oil. It is an important way of producing diesel blends and valuable products such as propene and butene. Researchers have used various kinds of catalysts in order to find out the best catalyst for catalytic cracking process.

According to Kulkarni *et al*. (2006), a 1, 2- tungstophosphoric acid (TPA) was used as the catalyst. It says that, the hydrous zirconia supported TPA was found to be most promising catalyst exhibiting the highest ester yield (~77%). This experiment is an attempt to develop a strong solid acid catalyst that can simultaneously catalyze esterification as well as transesterification reactions.

From previous studies by Kuriakose et al. (2004), the liquid phase esterification reaction between salicylic acid and phenol in the presence of hydrated oxides (alumina, silica and zirconia) and zeolites (Y, ZSM5 and β) and the sulfated forms of oxides and protonated forms of zeolites as catalysts yield salol with 100% selectivity. Of all the catalysts used H-β and sulfated zirconia exhibited good conversion of salicylic acid, 70 and 59%, respectively. It is also noticed that β zeolite catalyst can be reused to get good selectivity and activity.

2.5 Solid Acid Catalyst

The production of biodiesel from low quality oils is challenging due to the presence of undesirable components especially free fatty acids (FFAs) and water. Usage of homogeneous base catalyst for transesterification of such feedstock suffers from serious limitation of formation of undesirable side reaction such as saponification which creates serious problem of product separation and ultimately lowers the ester yield substantially. Homogeneous acid catalysts have the potential to replace base catalysts since they do not show measurable susceptibility to FFAs and can catalyze esterification and transesterification simultaneously. However, requirement of high temperature, high molar ratio of oil and alcohol, separation of the catalyst, serious environmental and corrosion related problems make their use non-practical for biodiesel production. Solid acid catalysts have the strong potential to replace liquid acids, eliminating separation, corrosion and environmental problems. Recently a review is published that elaborates the importance of solid acids for biodiesel production. Solid acids having interconnected system of large pores, a moderate to strong acid sites and a hydrophobic surface would be ideal for biodiesel preparation. In this research, I will be using heterogeneous solid acid catalyst. By implementing the environment friendly heterogeneous solid catalyst, it will help to eliminate the drawbacks associated with the homogeneous catalyst such as corrosiveness, production of waste, excessive use of water in washing steps, and energy intensive separation operations.

Homogeneous catalysts, although effective, lead to serious contamination problems that make essential the implementation of good separation and product purification protocols, which translate into higher production costs. To be economically viable and to compete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve continuous processing in a flow system, have as few reaction steps as possible, limit the number of separation processes, and ideally use a robust heterogeneous (solid) catalyst. The appropriate solid catalysts could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation (Lotero *et al.*, 2005).

The chemical industry has been benefited tremendously. Further advances in the development of more efficient, highly selective and cost-effective catalysts that help minimize or eliminate adverse effect on environment are the need of the hour and are bound to draw increasing attention of the concerned scientists.

There are two types of catalytic cracking; homogenous and heterogeneous catalytic cracking. Heterogeneous catalytic cracking occurs when the reactants and the catalyst are in different phases (Siregar, 2005). Theoretically, a heterogeneous catalytic reaction consists of five successive steps:

i. Transport of reactants from homogenous (gas or liquid) phase to the surface of the catalyst.
ii. Balanced sorption of the reactants on specific sites of this surface, to create the intermediate chemisorbed species.
iii. Chemical reactions in the adsorbed phase between these intermediate species.
iv. Desorption of the reaction products.
v. Removal of the reactions products into the homogenous phase.

Figure 2.7 shows the reaction occurring in heterogeneous cracking:

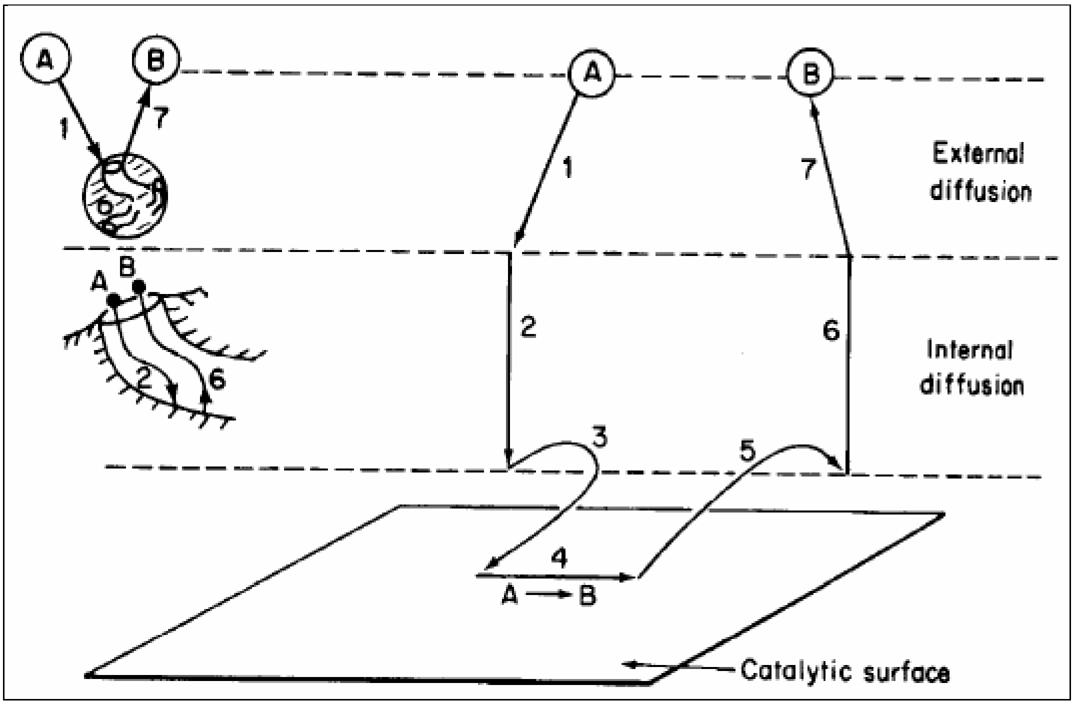

Figure 2.7: The reaction occurring in heterogeneous cracking (Fogler, 1999).

Almost all the reactions involving heterogeneous catalytic reaction occur at the interface between the solid catalyst and the fluid or gas phase. The reactions are catalyzed in seven stages:

i. Diffusion of the reactants to the external surface of the catalyst.
ii. Diffusion of the reactants from the pore mouth through the catalyst pores to the immediate vicinity of internal catalytic surface.
iii. Adsorption of the reactants on the catalyst surface.
iv. Reaction of the adsorbed reactants species in which it is converted to a product molecule.
v. Desorption of the products from the catalyst surface.
vi. Diffusion of the products from the interior of the catalyst to the pore mouth at the external surface.
vii. Mass transfer of the products from the external surface into the bulk of the process stream.

Table 2.1 shows the past studies of biodiesel production via esterification and transesterification process using homogeneous and heterogeneous catalyst.