

# **Sulfate and Hydroxide Supported on Zirconium Oxide Catalysts for Biodiesel Production**

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## **Abstract**

Biodiesel is currently produced by homogeneous catalysis. More recently however, heterogeneous catalysis is being considered as a cheaper alternative to the homogeneous process. In this research project, heterogeneous catalysts of zirconium oxide were produced by impregnation.

Zirconium oxide impregnation with sulfuric acid produced acidic solid catalysts. It was determined that impregnation and calcination at 550°C ( $\text{SO}_4/\text{ZrO}_2\text{-}550^\circ\text{C}$ ) produced the best catalyst for palmitic acid esterification with 10 wt % as the optimum concentration in esterification of palmitic acid.  $\text{SO}_4/\text{ZrO}_2\text{-}550^\circ\text{C}$  was successfully recycled for eight consecutive runs before permanent deactivation. Its sulfur content was 1.04 wt % using SEM-EDS and 2.05 wt % using XPS for characterization. BET surface area was 90.89  $\text{m}^2/\text{g}$ . The reaction mechanism over Brønsted acid ( $\text{SO}_4/\text{ZrO}_2\text{-}550^\circ\text{C}$ ) and Lewis acid ( $\text{Al}_2\text{O}_3$ ) catalysts obeyed Eley-Rideal kinetics with palmitic acid and methanol adsorbed on the active site respectively.

Zirconium oxide was also impregnated with sodium hydroxide to produce basic catalysts. The best catalyst was produced when zirconium oxide was impregnated with 1.5 M NaOH and calcined at 600°C. Soybean oil was completely converted to biodiesel with 10 wt % catalyst and 1:6 oil to methanol. A mixture of the base catalyst with 30 wt %  $\text{SO}_4/\text{ZrO}_2\text{-}550^\circ\text{C}$  effectively converted soybean oil containing 5% oleic acid indicating

that this mixture could be used for waste oils. The reaction was first order with respect to triglyceride and second order with respect to methanol. The activation energy was 49.35 kJ/mol and the reaction mechanism obeyed Langmuir-Hinshelwood kinetics.

## **Attribution**

The author, Nourredine Abdoulmoumine, is the major contributor and sole writer of the manuscripts in chapter three and chapter four of this thesis. The second co-author, Nuttapol Lerkkasemsan, was a graduate student in the chemical engineering department who conducted kinetic modeling for the experimental data obtained by the author. The third and fourth co-authors, Dr. Foster Agblevor and Dr. Luke Achenie are the advisor and co-advisor respectively.

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## **Dedications**

To my parents for their love, support, prayers and most importantly for dreaming for me long before I could. Any achievement in my life is a direct result of their sacrifices and a testimony to their excellent parenting.

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# **Chapter one**

## **Introduction**

### **1.0 Background**

The development of alternative fuels is at the forefront of research because of the forecasted depletion of crude oil reserves and the growing concern of irreversible environmental damage caused by green house gases. Alternative and renewable liquid fuels are particularly vital as they could replace petroleum derived fuels used by internal combustion engines in transportation (Vasudevan et al., 2005). Liquid biofuels have been identified in the national energy strategies of many developed countries and are promoted by policies in several countries and regions including the United States, Brazil, EU state members and many other in an attempt to reduce green house gas production and to prepare for potential energy shortage (Charles et al., 2007; Matsumoto et al., 2009; Pristupa et al.). It is in this environment that biodiesel has emerged as a promising renewable liquid fuel and the most likely replacement for petrodiesel.

Technically, biodiesel is monoalkyl ester of fatty acids currently produced from vegetable oil in the presence of a catalyst. The attractiveness of biodiesel emanated from its intrinsic similarity with petrodiesel allowing it to maintain virtually all the desirable properties while being biodegradable, non-toxic and most importantly carbon neutral. In fact, current diesel engine design requires minor or no modification to switch from petrodiesel to biodiesel.

Unlike many of the recently suggested alternative liquid biofuels, the fundamental chemistry of vegetable oil transesterification or esterification has been well studied and

several production facilities are operational. Currently, homogeneous base catalysis (NaOH or KOH) is preferred for the conversion of edible refined vegetable oil to biodiesel. While this approach has many merits, it unfortunately results in a final product more expensive than conventional diesel primarily because of the high cost of the feedstock and the extensive separation steps required to achieve fuel grade specifications (Zhang et al., 2003). New catalytic routes are consequently under investigation to improve the competitiveness of biodiesel.

The use of solid acids and bases as catalysts in organic reactions is well documented as indicated by the extensive reviews by Hattori (2001) and Corma (1995; 1997). Such heterogeneous catalysts however have only been recently used in biodiesel production; creating an exciting and promising research sphere in biofuels (Lotero et al., 2005; Zabati et al., 2009). The application of heterogeneous catalysis in biodiesel production is particularly attractive with the potential to simplify downstream operations and to decrease overall production cost.

Impregnation is simple and effective method of producing very active heterogeneous catalysts. The effectiveness of this method was demonstrated by Arata et al (1996) who reported the synthesis of acid impregnated metal oxide catalysts with very good catalytic activity. Consequently, investigation into the development of both acid base solid catalysts by impregnation is necessary and their application to biodiesel production could help reduce the cost of biodiesel (Hattori et al., 2000; Liu et al., 2006).

## **1.1 Objectives**

The overall goal of this research is to develop heterogeneous catalytic method for biodiesel production. The specific objectives are:

1. To develop zirconium oxide supported heterogeneous catalysts that can potentially utilize cheaper feedstock.
2. Optimize the heterogeneous catalyst design to achieve high yields comparable to those obtained using homogeneous catalysts.
3. Optimize the reaction conditions to reduce the severity of the reaction conditions.
4. Investigate the kinetics of the reaction and elucidate the reaction mechanism



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## **Chapter two**

### **Literature review**

The use of vegetable oil as fuel dates back to a century ago when the diesel engine was first invented. The use of vegetable oil as a diesel fuel production was first expressed by Rudolph Diesel, the inventor of the diesel engine, who described the use of peanut oil as a fuel to power compression ignition engines (Knothe et al., 2005a). In the earlier years of the diesel engine, vegetable oil was directly used as fuel. Despite the early success of vegetable oil, it became clear that it was not a suitable fuel for diesel engines due to several issues encountered. In addition to high viscosity, poor cold flow properties and low volatility, injector tips cooking, carbon deposition in combustion chamber, piston ring sticking, polymerization, and oxidations were all observed (Canakci and Sanli, 2008; Ma and Hanna, 1999; Singh and Singh, 2010). By 1920, the rapid development of the petroleum industry soon made petrodiesel a cheaper and quality alternative to vegetable oil (Manzanera et al., 2008). One solution to the poor fuel properties of vegetable oil was to convert it into monoalkyl esters of fatty acids by the process of transesterification and esterification. The first report of transesterification of vegetable oil to what is known today as biodiesel was detailed in a Belgium patent granted to G. Chavanne of the University of Brussels (Chavanne, 1937; Knothe, 2010). In this patent, the author described the transesterification of palm oil to its equivalent ethyl esters.

Nevertheless, biodiesel production will stagnate due to the abundance of low cost of petrodiesel. During the 1930's and throughout the World War II period, there was a moderate renewed interest in large scale production and in selected places even usage of pure transesterified vegetable oil or blends with petrodiesel. However, the major interest

in biodiesel came during the late 1970 when the OPEC oil embargo brought the focus on domestic alternative fuels (Canakci and Sanli, 2008; Knothe, 2010, 2001).

In the United States, the production of biofuels from diverse renewable sources has become increasingly important. Along with other biofuels such as bioethanol, biodiesel has attracted tremendous attention in recent years. Biodiesel is biodegradable, environmentally friendly and has lower emissions in addition to better lubricity than petrodiesel. Moreover, biodiesel will not contribute to global warming if produced sustainably because carbon dioxide is recycled in its lifecycle. Biodiesel has virtually similar properties as petrodiesel and therefore could be used as blending stock.

Traditionally, biodiesel is produced through homogeneous alkali catalysis. However, this process suffers from several shortcomings among which the expensive downstream separation and the high cost of edible refined vegetable oil have been identified as the major pitfalls. These shortcomings are translated into high manufacturing cost that hinders biodiesel economic viability. In recent years, the research frontier for biodiesel has shifted to the identification of suitable heterogeneous catalysts that could achieve high yields while reducing production cost. Essential to comprehending the current status of biodiesel research is to review what has been done since the early 1900's when vegetable oil became the first biofuel. In the following sections, a comprehensive review of biodiesel is presented.

## **2.0 Feedstock**

Alkyl fatty acid esters can be prepared from any fatty acid sources and as such biodiesel has been prepared from various feedstocks. The most popular type of feedstock for

biodiesel production are edible refined vegetable oils such as soybean, rapeseed, sunflower, palm, coconut and linseed (Singh and Singh, 2010). However, the choice of feedstock is dictated by the availability of oil crops in a particular region (Figure 1 and Figure 2). In the United States, the well developed soybean industry has made soybean oil the most common feedstock for biodiesel production whereas in Europe and tropical regions, rapeseed and palm oils are the typical sources for biodiesel production (Singh and Singh, 2010). Based on the 2009 Census of Agriculture survey by the USDA, soybean is the second most harvested crop in the United States accounting for 25% of the total harvested cropland and only passed by corn (USDA, 2009).

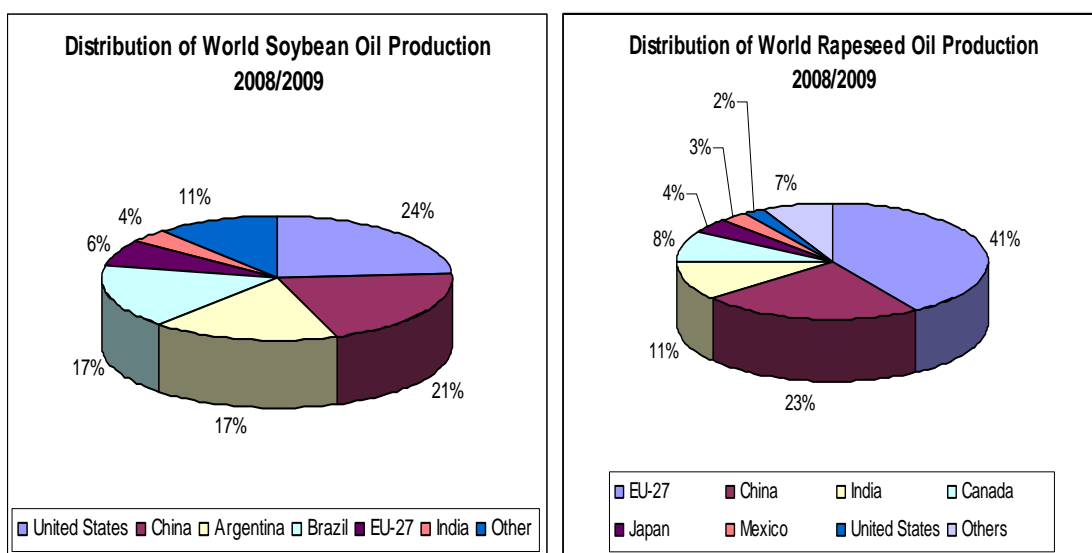


Figure 1: World production of soybean and rapeseed oil. Data retrieved from USDA Foreign Agricultural Services PSD Online database (USDA, 2010)

Lipids are a diverse group of naturally occurring organic compounds used for several biological functions such as energy storage, cellular signal transmission and membrane structural support. Vegetable oils and fats, both subgroups of lipids, are generally composed of 90 to 98% of triacylglycerols (Srivastava and Prasad, 2000). These

compounds are composed of a glycerol backbone and three esterified fatty acid groups. The fatty acids are carboxylic acids with long aliphatic chains. In plants, triacylglycerols are usually extracted from plant seeds. The biosynthesis of these compounds in the seed occurs during the development stage when acetyl-CoA, a product of glycolysis, is converted to malonyl-CoA which is further converted to free fatty acids and subsequently esterified to a glycerol backbone (Durrett et al., 2008; Lehner and Kuksis, 1996). While the role of triacylglycerols in animals differs from the plants, the biosynthesis generally resembles that described above.

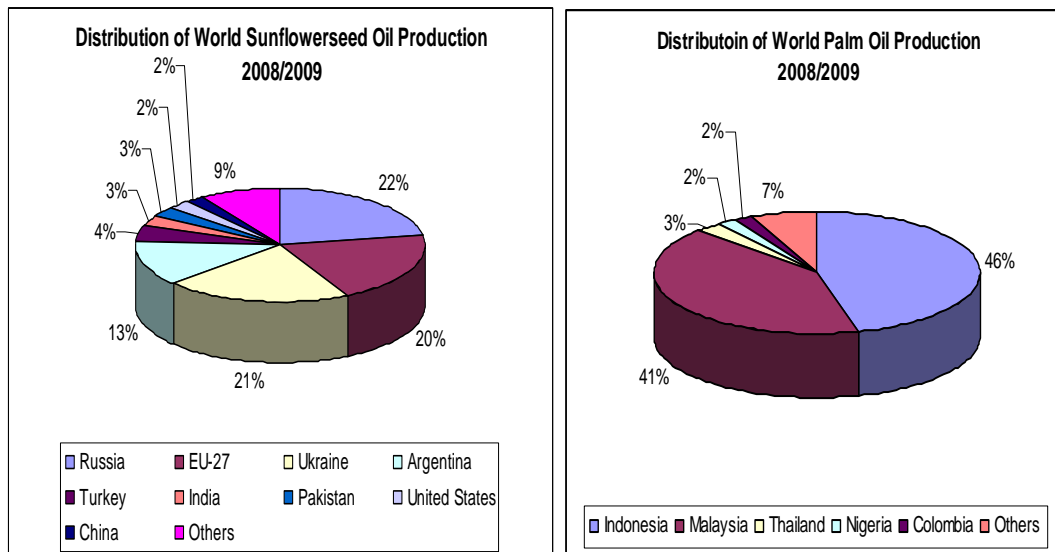


Figure 2: World production of sunflowerseed oil and palm oil. Data retrieved from USDA Foreign Agricultural Services PSD Online database (USDA, 2010).

While they are technically considered triacylglycerols, biodiesel feedstocks could be grouped in four categories: edible vegetable oil, non-edible vegetable oil, waste edible vegetable oil and waste animal fat.

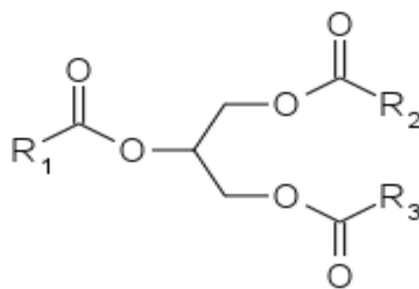


Figure 3: Chemical structure of triacylglycerol where  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are the aliphatic tails of the fatty acid groups.

Food grade vegetable oil is referred to as refined edible vegetable oil. Currently, it holds the largest share as biodiesel feedstock because of low free fatty acid and water content, both factors that affect biodiesel production as will be discussed in the next sections.

Soybean, rapeseed, sunflowerseed and palm oils are all part of this category.

The second category, non-edible vegetable oils are either by-products of industrial processes or naturally occurring non-edible oils such as jatropha seed oil. Few examples of industrial by-products are soapstock and tall oil from the vegetable oil refineries and pulp and paper industry respectively (Haas, 2005; Ragauskas et al., 2006).

Waste edible oil and waste animal fat refer mostly to oil and fat from the food processing industry. Waste edible oil is commonly called waste cooking oil (WCO). It is the second most used feedstock for biodiesel production and is increasingly being used as a low cost and alternative feedstock to edible oil despite its higher free fatty acid content (Encinar et al., 2005; Kulkarni and Dalai, 2006). In waste cooking oils, these free fatty acids are formed during the frying process by hydrolysis of the free fatty acids on the triglycerides in the presence of water from food (Arroyo et al., 1992).

The combination of animal and used cooking oil with total free fatty acid (FFA) content of less than 15% is termed “yellow grease”. When the free fatty acid content exceeds 15%, the mixture is called “brown grease” (Canakci and Sanli, 2008).

Feedstock selection is a crucial aspect to the success of biodiesel manufacturing. The chemistry of biodiesel production, the final product quality and characteristics and its competitiveness against petroleum diesel is strongly influenced by the feedstock properties. In the next sections, the chemistry and characteristics of biodiesel and the effect of feedstock type will be discussed.

## **2.1 The chemistry of biodiesel production**

Vegetable oil derived diesel fuel can be produced via dilution of vegetable oil with petrodiesel, microemulsification, thermal cracking and transesterification or esterification. Though these derived diesel fuels have been referred to as biodiesel, the term applies only to those fuels produced by transesterification and esterification.

Dilution is achieved through blending vegetable oil with petrodiesel to reduce the viscosity. A homogeneous mixture is attainable and the desirable fuel properties could be achieved by varying the blend ratios. Over the years, blends with less than 50% vegetable oil were produced. Ma et al (1999) reported that a blend of 20% vegetable and 80% diesel was successfully used by Caterpillar (Brazil) to power their engines without any modifications in. Several engine performance tests were conducted on Ford diesel engine with 25% blends of vegetable oil. While viscosity is decreased by dilution, virtually all tests reported severe long-term performance problems, ranging from carbon deposition to

lubricant contamination by vegetable oil leading to polymerization and thickening around the operational temperatures of diesel engine (Pryor et al., 1983; Schlick et al., 1988).

Microemulsion is a colloidal equilibrium dispersion formed spontaneously from two otherwise immiscible fluids and one or more amphiphiles. The nonionic emulsions are usually made of two or more alcohols, one or more vegetable oils and sometimes No. 2 diesel. Lower viscosity is obtained through this method however it suffers from the same engine performance issues faced when using dilution of vegetable oil with diesel (Ma and Hanna, 1999).

Thermal cracking or pyrolysis is the thermal conversion of organic matter in reducing environment into low molecular weight compounds. The earliest commercial pyrolysis of vegetable was reported in China in 1947 (Chang and Wan, 2002; Ma and Hanna, 1999).

The thermal cracking of vegetable oil produced mostly alkanes and alkenes as well as fatty acid esters (Alencar et al., 1983; Demirbas, 2009; Schwad et al., 1988). While diesel fuel from pyrolysis does not have engine performance problems known to other methods, it suffers from high cost of equipment. In light of recent advancement in catalytic pyrolysis, thermal cracking should be investigated again to assess its economic feasibility.

Though dilution, microemulsion and thermal cracking have been successfully used for diesel fuel production in the past, today biodiesel is produced by transesterification. In general, transesterification is a reversible chemical reaction during which the alkyl or aryl group of an ester is interchanged with the alkyl group of an alcohol. This reaction is requires a catalyst, although recently a supercritical process that does not require the addition of a catalyst was developed (Canakci and Sanli, 2008).



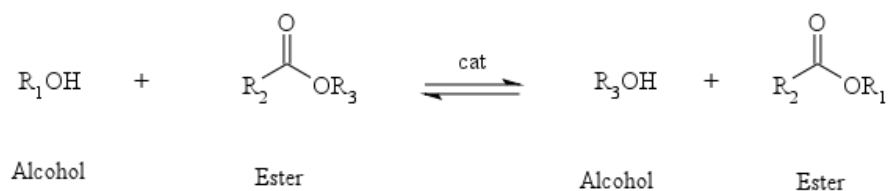


Figure 4: Transesterification reaction

For vegetable oil, the three fatty acid groups on the glycerol backbone are esterified with three methyl groups if the methanol is used to produce stoichiometrically three fatty acid alkyl monoesters and one glycerol. In several publications, transesterification has been referred to as alcoholysis to highlight the role of the alcohol alkyl group. Consequently methanolysis and ethanolysis are common terms used in the literature.

Similar to transesterification, esterification converts free fatty acids to their corresponding alkyl monoesters. Unlike transesterification where an alcohol and ester are converted to another alcohol and ester, esterification converts an alcohol and a carboxyl acid into an ester and water (see Figure 5).

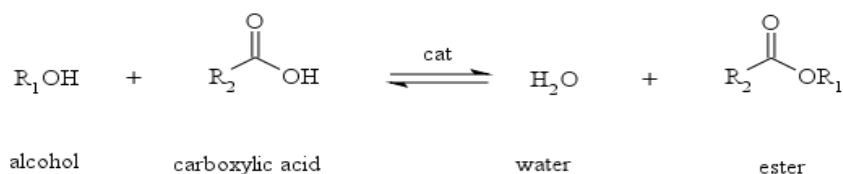


Figure 5: Esterification reaction

The difference between transesterification and esterification becomes very important when choosing feedstock and catalyst to avoid problems. Transesterification is catalyzed

by base or acid catalysts. Esterification, however, is only catalyzed by acid catalysts. In the presence of a base catalyst, the undesirable saponification reaction could take place if the feedstock contains free fatty acids, contributing to the formation of hard to remove soaps. Lotero et al., (2005a) recommends a feedstock containing less than 0.5 % wt free fatty acid when using base catalysis to avoid soap formation. Therefore, the composition of the feedstock controls the predominant chemical pathway and dictates the catalyst used for the biodiesel production. Feedstocks containing substantial amounts of free fatty acid and water must use either acid or enzyme catalysis or supercritical transesterification as the methods tolerate the presence of these constituents.

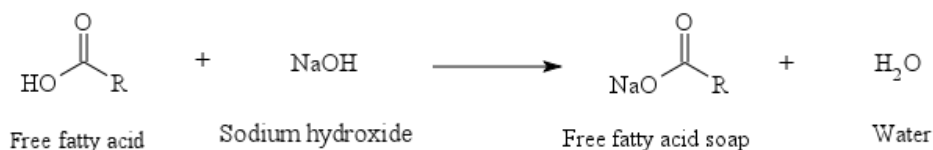


Figure 6: Free fatty acid saponification

Besides the feedstock, the alcohol and catalyst contents are also very important in the chemistry of biodiesel production. Stoichiometrically, three moles of alcohol are needed for every mole of triglyceride. However, in base catalyzed transesterification, low conversions were obtained at the stoichiometric ratio and doubling alcohol molar concentration achieved conversion greater than 93% (Freedman et al., 1984). Unlike base catalysis, acid catalysis requires even higher alcohol to oil ratios. In their pioneering work, Freedman et al (1986; 1984) investigated the kinetics of soybean oil transmethylation with sulfuric acid. The authors reported that triglyceride conversion was unsatisfactory at 1:6 and 1:20 oil to methanol molar ratios and settled on 1:30 molar ratio.

Their findings were corroborated by Canacki et al (1999) from studies of five molar ratios from 1:3.3 to 1:30 and later Crabbe et al (2001). Methanol is the most commonly used alcohol for biodiesel production although ethanol, propanol and butanol have all been used successfully (Freedman et al., 1984).

### 2.1.1 Esterification reaction

In homogeneous medium, the esterification mechanism of short chain carboxylic acids such as acetic acid is well known and covered in organic chemistry textbooks (Brown, 2000; Rönnback et al., 1997). The mechanism is illustrated in Figure 7 and like acid catalyzed transesterification, the protonation of the carbonyl group initiates the reaction.

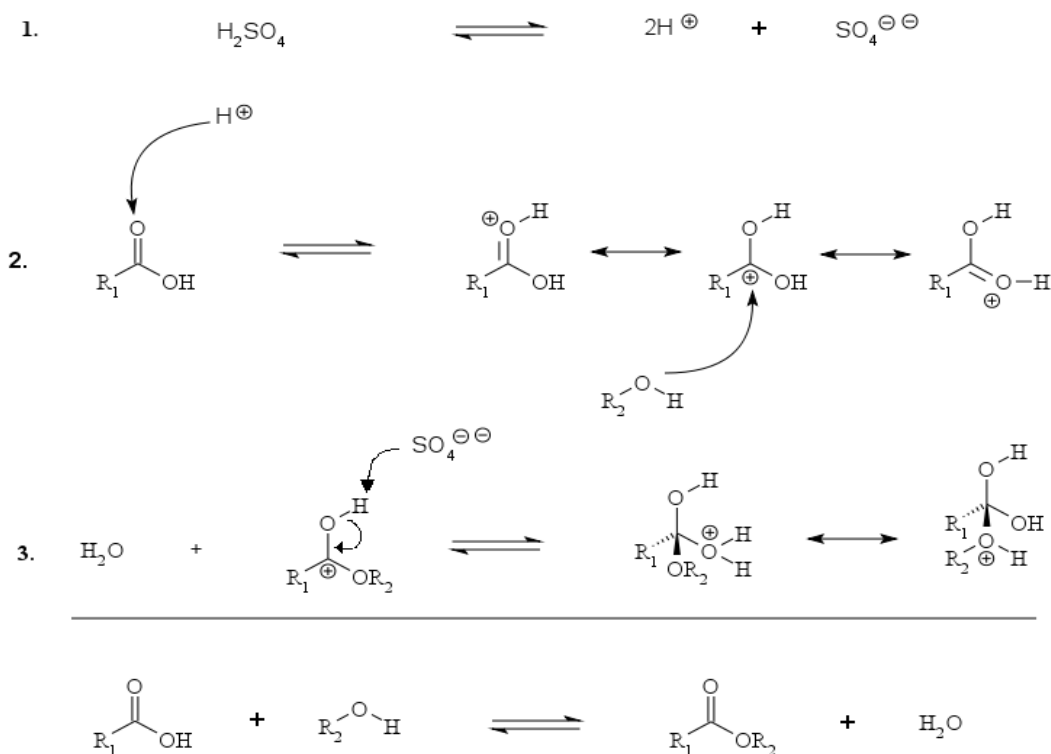


Figure 7: General mechanism of carboxylic acid esterification in homogeneous medium

### 2.1.2 Transesterification reaction

Transesterification of triglycerides by homogeneous base catalysis is perhaps the most studied aspect of biodiesel chemistry. The reactive species in homogeneous base catalyzed transesterification is the alkoxide intermediate formed when the alcohol and the base react. The very reactive alkoxide then engages in a nucleophilic attack on the carbonyl groups of the fatty acids as illustrated in Figure 8.

thus allowing a nucleophilic attack by the electronegative oxygen of the alcohol. While the intermediate steps in the reaction pathways are different for homogeneous acid and base catalyzed transesterification, both reactions proceed through a nucleophilic attack with an alcohol and an alkoxide as nucleophiles for an acid or base catalyst respectively. Since an alkoxide is much stronger nucleophile than an alcohol, it is reasonable that homogeneous base catalysis achieves much faster rate than acid catalysis in vegetable oil transesterification.

The kinetics of sunflower methanolysis was investigated by Veljković et al (2009) and Stamentović et al (2010) on CaO and Ca(OH)<sub>2</sub> respectively. Both studies assumed however that methanol adsorption on the surface and product desorption were not rate determining steps to begin and that the rate determining step was the reaction between methanol adsorbed on the surface and triacylglycerols in the bulk fluid for both CaO and Ca(OH)<sub>2</sub>. Hattori et al (2000) and later Dossin et al (2006) proposed reaction mechanisms for ethyl acetate transesterification over basic heterogeneous catalysts.

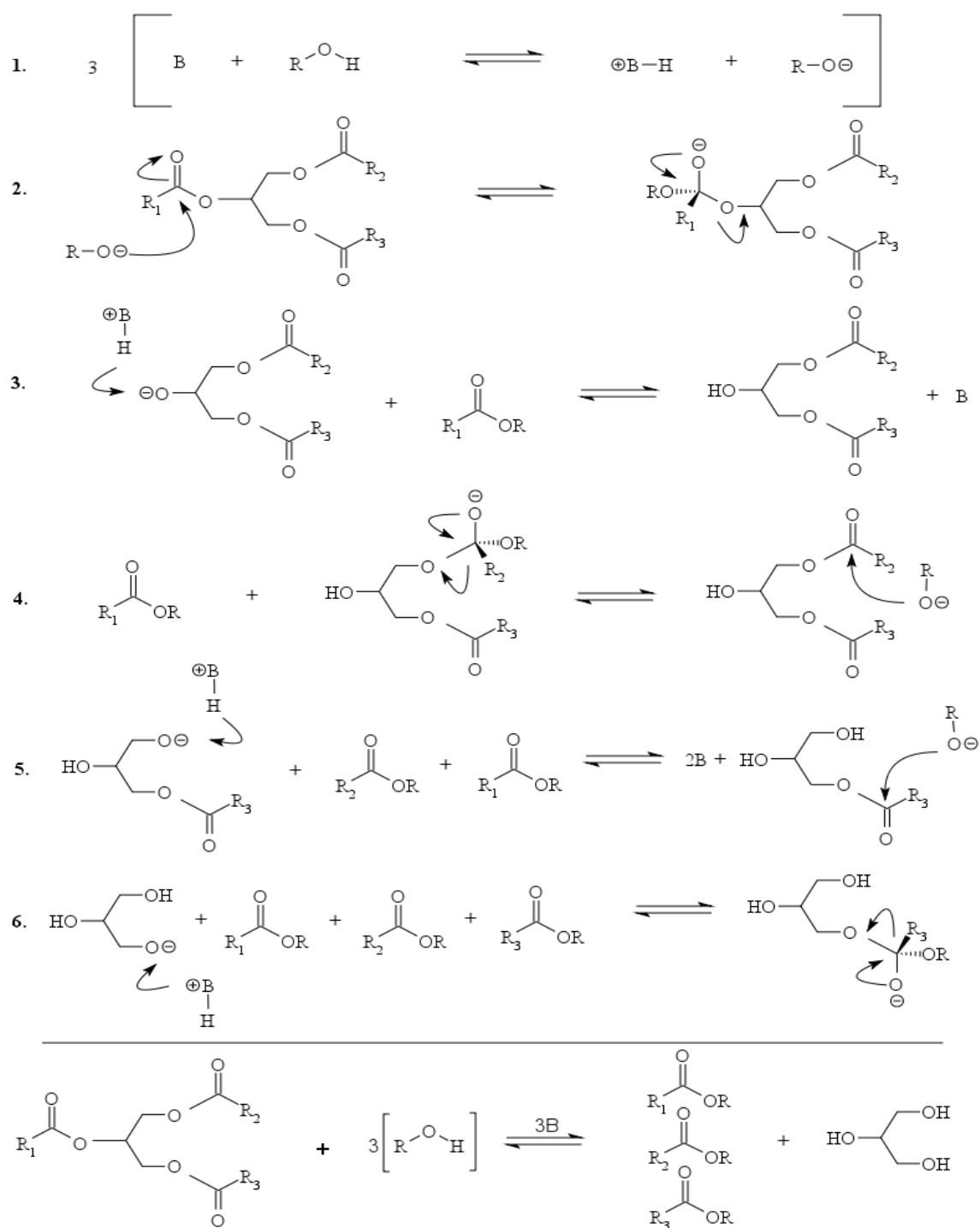


Figure 8: Reaction mechanism of homogeneous base catalyzed transesterification

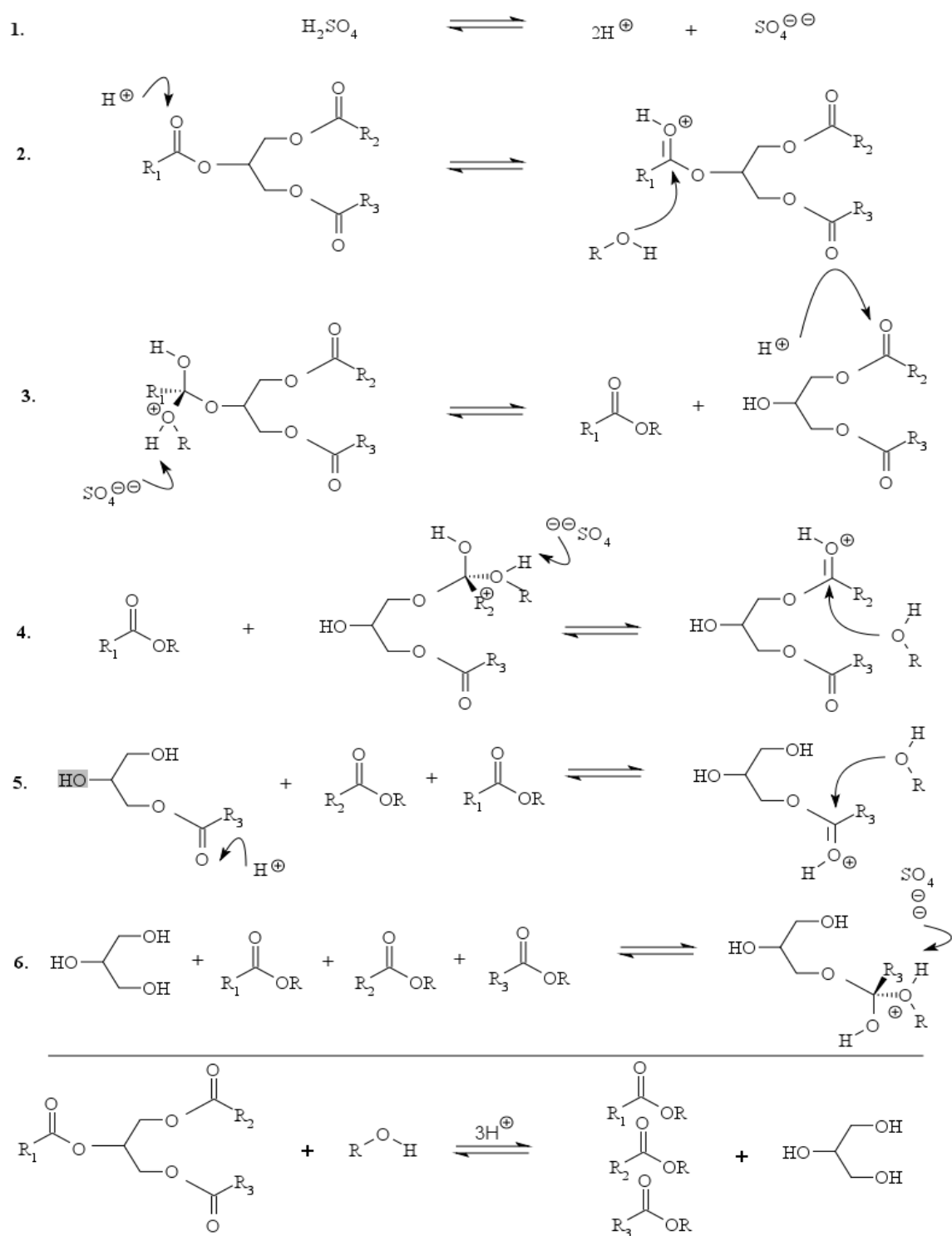


Figure 9: Reaction mechanism of homogeneous acid catalyzed transesterification  
 Transesterification is also catalyzed by acid catalysts. In homogeneous medium, the acid catalyzed reaction is initiated by the protonation of the carbonyl group (Figure 9) and

Hattori et al (2000) reported a four step reaction mechanism closely resembling mechanism derived from Langmuir-Hinshelwood (LH) kinetics. He suggested that the rate determining step was the alcohol adsorption in the presence of a weak base catalyst. However, in the presence of a strong solid base catalyst, the adsorbed alkoxide attack on the carbonyl group became the rate determining step. Though consistent with the experimental data, the proposed mechanisms were not verified by standard kinetic modeling approaches. On the other hand, Dossin et al (2006) modeled the transesterification of ethyl acetate on MgO and investigated fifteen models based on Eley-Rideal (ER) and Langmuir-Hinshelwood kinetics as well as mechanisms proposed by the previously mentioned author. It was found that the reaction between adsorbed methanol and ethyl acetate in the bulk medium best fit the experimental data indicating that the reaction obeyed Eley-Rideal kinetics.

## **2.2 Biodiesel Fuel Properties and Emission**

The inadequacy of vegetable oil fuel properties were the primary reasons for its conversion to equivalent esters. While some pure vegetable oils could be used as direct diesel fuel, it was clear since the early tests on the diesel engine that the high viscosity of vegetable oil was a problem. In the U.S. the acceptable ranges for the fuel properties of biodiesel are defined by ASTM 6751.

In general, biodiesel emission profile is significantly better than petrodiesel with lower emission across the board except for nitrogen oxide compounds (Krahl et al., 2009; Lapuerta et al., 2008). Biodiesel emission tests showed reductions of 20% in carbon monoxide, 30% in hydrocarbon, 40% in particulate matter and 50% in soot emission

relative to petrodiesel. These decreases are significant and have made it easier to promote large scale biodiesel production. For example, particulate matter and soot emissions were considered so serious that certain European cities implemented curfews on diesel truck (Durrett et al., 2008). Biodiesel is also a much better lubricant than petrodiesel and even 1% addition of biodiesel significantly improves petrodiesel lubrication properties.

Furthermore, biodiesel is sulfur free and carbon neutral if produced sustainably.

However, biodiesel exhaust analysis show an increase in NO<sub>x</sub> emission by 10-15% relative to petrodiesel. Several reasons have been cited in the literature for this increase. A review of biodiesel emission by Lapuerta et al (2008) indicated that unsaturated fatty acids promote the formation of NO<sub>x</sub>. Indeed, when methyl esters of oleic, palmitic and lauric acids were compared with conventional diesel, it was observed that the NO<sub>x</sub> content increased for methyl oleate by 6% relative to petrodiesel. Methyl esters of palmitic and lauric acids however both resulted in 4% and 5% decreases respectively in the NO<sub>x</sub> content relative to petrodiesel (Knothe et al., 2005b).

The engine exhaust emissions are crucial in determining the environmental and health hazard of fuels. While the environmental effect of petrodiesel and biodiesel are well known, their health hazard is becoming a topic of interest. Diesel engine exhaust emissions contain mutagenic and carcinogenic species on the surface of exhaust particle. The species have been determined to be polycyclic aromatic hydrocarbons or PAH (Bünger et al., 2006; Krahel et al., 2009). Krahel et al (2009) investigated the mutagenicity of petrodiesel, biodiesel and rapeseed oil as diesel fuels on *Salmonella typhimurium* mammalian microsome assay and found that rapeseed oil exhaust emission induced much higher mutation compared to petrodiesel and biodiesel. Both petrodiesel and biodiesel



induced only minor mutation. However biodiesel produced higher mutation relative to the reference petrodiesel. In contrast, Bünger and co-workers (2006) found that exhaust emission of biodiesel produced from soybean and rapeseed oils resulted in lower mutation than petrodiesel at 41, 21 and 0% engine load in the presence of an oxidative catalytic converter. When the load was increased however, the presence of an oxidative catalytic converter seemed to promote higher mutagenicity (Bünger et al., 2006). While, these findings on the health risk of biodiesel exhaust emission are noteworthy, other factors such engine type and effective load could change the emission profile thus the changing the mutagenicity of the exhaust. Several investigators have examined the health risk of biodiesel exhaust but meaningful comparison is difficult due to lack of standard methodology (Madden, 2008).

### **2.3 Economics of biodiesel production**

Economically, biodiesel is not competitive with petrodiesel (Encinar et al., 2005). Edible and cheaper and low quality waste oils are the two most common feedstock used in biodiesel production. It has been previously mentioned that low free fatty acid and water content oil is required to avoid saponification in base catalysis. The concentrations of these components are usually very low in refined edible vegetable oil. Waste oils however are richer in free fatty acids. Therefore, the competitiveness of biodiesel depends on both the feedstock cost and the type of catalyst: If fast reaction rate is desired, more expensive feedstock must be used and if a cheaper feedstock is used, the slower acid catalysis is more suitable. In the past, virtually all manufacturers opted for fast reaction rate and chose refined edible vegetable oil as the feedstock. However, refined

edible vegetable oil is expensive and has been reported to account for 75-85% of the total manufacturing cost (Apostolakou et al., 2009; Marchetti and Errazu, 2008; Zhang et al., 2003a). Recently, several investigators assessed the economic feasibility of biodiesel production from waste vegetable oil. Zhang and co-workers (2003a, b) studied the cost of biodiesel made from waste vegetable oil. They reported that the homogeneous acid process with waste vegetable oil resulted in lower total manufacturing cost compared to alkali catalyzed transesterification of pure vegetable oil. These findings were corroborated by West et al (2008) who analyzed biodiesel produced from waste vegetable oil and showed that acid catalysis was more economically feasible compared to alkali catalysis for waste vegetable oils. West et al (2008) also investigated into the economic feasibility of biodiesel production by supercritical treatment and showed that the process was limited by high equipment cost due to the need for stronger reactor capable of withstanding higher pressures. Other investigators ranked the supercritical processes as the least economically feasible technology (Marchetti and Errazu, 2008; West et al., 2008). In contrast, van Kasteren et al (2007) concluded that the supercritical process is competitive with homogeneous alkali or acid processes despite higher capital cost. The choice between homogeneous or heterogeneous catalysis is also important because it affects the cost associated with downstream separation and purification. If homogeneous catalysis is chosen, the process necessitates extensive downstream processing to remove the catalyst and to purify the end products further increasing production cost. If heterogeneous catalysis is chosen, downstream processing is reduced but high temperature and/or longer reaction time are often required. Only few studies investigated the economics of heterogeneously produced biodiesel. The lowest total capital investment

and manufacturing costs were observed when biodiesel was produced using heterogeneous instead of homogeneous catalysis (Sakai et al., 2009; West et al., 2008). In all cases, the sensitivity analysis indicated that plant size and feedstock are the most important parameters of the economic feasibility of biodiesel production (West et al., 2008; You et al., 2007; Zhang et al., 2003b).

The price of biodiesel produced by several methods is reported in Table 1. Particular attention should be paid to the plant size when comparing the price of biodiesel produced by various methods.

Table 1: Economic assessment of biodiesel methods

Reference	Van Kasteren et al (2007)	Marchetti et al (2008)	West et al (2008)				Zhang et al (2003)		
Size (tonne/year)	80000	36000	8000				8000		
Feedstock	WVO	WVO	WVO				VO	WVO	
Process	I	I	II <sup>a</sup>	III <sup>a</sup>	III <sup>b</sup>	I	II <sup>a</sup>	II <sup>a</sup>	I
Two step process	No	No	Yes	No	No	No	No	Yes	No
Price (\$/l)	0.24	0.87 <sup>c</sup>	0.58 <sup>c</sup>	0.53 <sup>c</sup>	0.43 <sup>c</sup>	0.51 <sup>c</sup>	0.76 <sup>c</sup>	0.78 <sup>c</sup>	0.57 <sup>c</sup>

<sup>a</sup> Homogeneous system, <sup>b</sup> heterogeneous system, <sup>c</sup> unit price derived from reported total production cost. WVO stands for waste vegetable oil and VO stands for vegetable oil. I = supercritical, II = alkali, III = acid

## 2.4 Catalysis for Biodiesel Production

The fundamental chemistry of converting oils into biodiesel has been well studied. The feedstock being the same, process optimization requires the most research, particularly in transesterification and esterification catalysis. Although many heterogeneous acid and base catalysts are now known and frequently used in organic chemistry, biodiesel has mostly been produced by homogeneous alkali catalysis until recently. In the following

section, the homogeneous, heterogeneous and enzymatic catalysis of biodiesel are reviewed.

### **2.4.1 Base catalysis**

Alkali metals are strong bases and can catalyze the transesterification reaction as reviewed above. It is well established that bases catalyze the transesterification of vegetable oil much faster than homogeneous acids with reaction rates 4000 times faster (Srivastava and Prasad, 2000). Consequently, alkali catalysts such as NaOH and KOH have traditionally been the most popular catalyst for biodiesel production. Typically, small amounts of alkali base (~1%) is required to effectively catalyze the reaction (Meher et al., 2006). Solid bases have been studied and used in organic synthesis as well (Hattori, 2001). More recently, several solid base catalysts were used to convert vegetable oil to biodiesel. Therefore, the next section is dedicated to the review of recent advances in application of this group of catalysts to biodiesel production.

#### **2.4.1.1 Heterogeneous base catalysis**

Solid base catalysts are typically synthesized by inorganic wet chemistry techniques such as precipitation, co-precipitation, sol-gel process, hydrothermal synthesis or impregnation (Livage, 1998). Biodiesel catalyst preparation has been carried out through any of the conventional catalyst synthesis route but wet impregnation is the dominant method perhaps due to simplicity and its ability to produce very active catalysts. Briefly, wet impregnation is the deposition of desired catalytic species on a catalyst support, often a

metal oxide. The catalyst support must meet certain criteria such as tolerance to synthesis and reaction solvents, high surface area and good catalytic properties.

Hak-Joo et al (2004) investigated the use of Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Na/NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a heterogeneous base catalysts for the transesterification of soybean oil to biodiesel. Na/NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to be the best catalyst at 60°C with a molar ratio of 6:1 methanol to oil. Without optimizing the reaction conditions, the conventional homogeneous transesterification yield was 20% higher than of Na/NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyzed reaction. However, after optimizing their best catalyst, Na/NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1.0g catalyst, 9:1 methanol to oil molar ratio) with the addition of hexane as a co-solvent, this heterogeneous catalyst yielded 94% biodiesel. Lingfeng and coworkers (2007) investigated the transesterification of cottonseed oil with methanol over potassium fluoride supported alumina, KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The catalyst preparation was optimized to create superbasic sites on the catalyst. When superbasicity was achieved, the reaction occurred at a lower temperature while higher temperatures were required for normal basic sites. Under optimum conditions (60°C, 3h, 12:1 methanol to oil molar ratio, 4 % wt catalyst), the yield reached 95%. The catalyst also showed good thermal stability. Soybean oil transesterification was attempted with strontium oxide or strontia, a superbase. The yield was greater than 95% at temperatures below 70°C and the catalyst had a long lifetime and a good thermal stability (Liu et al., 2007). Singh and Fernando (2007) studied the reaction kinetic of MgO, BaO, CaO, PbO and MnO<sub>2</sub> in a high pressure reactor with temperature up to 215°C and achieved 60% or more conversion in 100 min with the highest yield of 95% obtained with BaO. Though no characterization was performed on the catalysts, the authors reported that BaO and CaO had the highest yields

in the shortest time. It must however be mentioned that BaO is highly soluble in methanol thus raising a question about the nature of the catalysis. Calcium methoxides,  $\text{Ca}(\text{OCH}_3)_2$ , and calcium oxide CaO have both been successfully used as heterogeneous catalysts for biodiesel production with yields of 95% under optimum conditions (Liu et al., 2008a; Liu et al., 2008b). Several investigators noted moderate dissolution of CaO in alcohol and reported partial homogeneous catalysis of the dissolved CaO (Granados et al., 2009; Granados et al., 2007; Kouzu et al., 2009). Rare earth oxide catalysts were also evaluated (Rusbueldt and Hoelderich, 2010). Among many rare earth aluminates, titanates and zirconates,  $\text{La}_2\text{O}_3$ , 20%  $\text{La}_2\text{O}_3$  on  $\gamma\text{-Al}_2\text{O}_3$  and 10%  $\text{La}_2\text{O}_3$  on  $\text{ZrO}_2$  achieved fatty acid methyl ester yields greater than 90% at 250°C.  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$  however showed poor activity in the transesterification of refined palm oil. Zirconium oxide modified by cesium cation exchange was prepared and reported to effectively catalyze the methanolysis and ethanolysis of rapeseed oil (Hamad et al., 2010). Conversions of 100% and 64% were reported at 60°C and 79°C for the methanolysis and ethanolysis respectively. NaOH/  $\gamma\text{-Al}_2\text{O}_3$  catalysts were prepared by impregnation (Arzamendi et al., 2007). Under optimum conditions, the most active catalyst achieved nearly 100% conversion. The authors analyzed the alkali leaching and reported that only 5% of the total NaOH leached into the reaction medium. Due to this low percentage, they concluded the homogeneous catalysis was insignificant. KF, LiF and CsF supported on  $\text{Al}_2\text{O}_3$  were tested in the transesterification of vegetable oils using conventional heating, microwave and ultrasound irradiation (Verziu et al., 2009). Stable catalysts were obtained and greater than 90% conversion was achieved by microwave heating.

## **2.4.2 Acid catalysis**

Acids catalyze transesterification of triglycerides as well as esterification of free fatty acids, unlike homogenous or heterogeneous base catalysts. Strong liquid acid catalysts have been used but slower reaction rates necessitate higher temperature and/or longer reaction time. Harsher reaction conditions, corrosion, and environmental problems are the main disadvantages of homogeneous acid catalysis (Lotero et al., 2005b). Consequently, solid acid catalysis has been intensively investigated as a replacement for liquid acid catalysis. Heterogeneous acid catalysis presents several advantages over homogeneous catalysis such as, reduction of corrosion, ease of separation from reaction mixture and lesser environmental issues.

### **2.4.2.1 Heterogeneous acid catalysis**

Zeolites are tridimensional aluminosilicates and are industrially among the most important group of catalysts (Coma, 1995). Zeolites are natural occurring minerals but they are often engineered to impart on them desired catalytic properties such as selectivity, purity and high acidity (Coma, 1995; Weitkamp, 2000). Zeolites are among the strongest and most synthesized solid acid catalyst, so it is not surprising that they were used to catalyze esterification. This group of catalyst is particularly interesting as it could be engineered for various pore sizes, proton exchange ability and acid strength. However, as pointed out by Lotero et al. (2005b) and later established by Rothenberg et al. (2005) mass transfer is a limiting factor because of the microporous nature of zeolites and the large molecular size of triglycerides and free fatty acids. This limitation in diffusion slows down the catalysis. Rothenberg et al. (2005) showed that zeolites only

showed a minor increase in yield (1-4%) compared to the uncatalyzed reaction. As mentioned by the authors, a lower ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3$  increases the acidity of the catalyst and its hydrophilicity. In a later study, a different group tested zeolites and found that zeolites loaded with basic groups leached significantly and hypothesized that the improved yield was due to the homogeneous catalysis of the basic acetate groups that leached into the solution (Ramos et al., 2008).

While zeolite synthesis has been known since the 1950's, sulfated metal oxides have only been synthesized much later. A sulfated metal oxide is a metal oxide impregnated with sulfuric acid enhancing its acidity and thus its reactivity. The treatment is believed to impart superacidity to the metal oxides and yielding both Brönsted and Lewis acid sites as illustrated in Figure 10 (Coma, 1995).

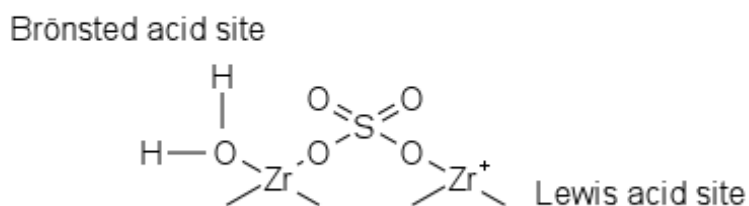


Figure 10: Sulfated zirconium oxide and its acid sites

Arata and coworkers (1996, 1990) have reported the synthesis of various superacid materials for the last 20 years as well as developed procedures to engineer solid superacids of extreme acidity on several catalyst supports that included metal oxides. These superacids are acids that have an acidity level greater than 100% sulfuric acid.



Sulfated zirconia ( $\text{SO}_4/\text{ZrO}_2$ ) and sulfated tin oxide ( $\text{SO}_4/\text{SnO}_2$ ) have been used successfully, the latter showing superior activity to the former (Lotero et al., 2005b). The sulfated zirconia was prepared by impregnation of zirconium oxide with sulfuric acid solution followed by calcinations for 3h at 650°C. While in general the yield improved by increasing the catalyst loading % (w/w) in reaction, the temperature, and/or the reaction time, the maximum yield, 90%, was reported for the following conditions: 1% (w/w) of catalyst, 150°C and 200 minutes. The catalyst activity was 90% of the original after five consecutive runs and calcination reactivated the catalyst again. No leaching of sulfonic groups was observed and the formation of side products was absent, indicating good selectivity.

Silica molecular sieves, doped with aluminum, zirconium, titanium or tin to enhance acidic strength, were thought to be strong acid catalysts. In reality, they behaved more like a weak acid. Sulfated silica mesoporous materials have also been reported.

Unsurprisingly, the pore size played a significant role on diffusion of the mesoporous materials. At 50 Å, benzenesulfonic acid catalysts activities were comparable to sulfuric acid.

Transesterification over metal oxide superacid catalysts was also reported. Tungstated zirconia-alumina, sulfated tin and zirconium oxides were investigated by Furuta et al (2004). Tungstated zirconia-alumina produced the maximum yield of 90% at a temperature above 250°C. As for the two other superacids, sulfated tin and zirconium oxides, their yield never exceeded 80% even at 300°C. Other researchers investigated tungstophosphoric acid (TPA) doped catalysts (Kulkarni et al., 2006). TPA was impregnated on zirconia, silica, alumina and activated carbon. The resulting highly acidic

catalysts were tested for activity in vegetable oil transesterification. Although all four catalysts were proven very efficient at optimum conditions, zirconia supported TPA was the most promising. The superacid  $\text{SO}_4/\text{Fe}_2\text{O}_3$  was also tested for the methanolysis of rapeseed oil. The catalyst had the best activity when the sulfate deposition was carried out in an iced water bath followed by calcination at  $500^\circ\text{C}$ . The optimum transesterification condition was achieved at 2% wt catalyst based on rapeseed oil, 12:1 methanol to oil molar ratio,  $220^\circ\text{C}$  reaction temperature and 8 h reaction time. The yield under these optimum conditions was 80%. The catalyst produced 70% yield even after 40 h usage (Wang et al., 2007).

Heteropolyacids (HPA) supported on MCM-41, mesoporous silica sieves were successfully employed in the esterification of acetic acid using butanol as the alcohol in the esterification reaction. Similarly, Chai et al. (2007) investigated the transesterification of vegetable oil using the heteropolyacid  $\text{Cs}_{2.5}\text{H}_{0.5}\text{Pw}_{12}\text{O}_{40}$ . They obtained a yield comparable to that obtained using homogeneous base catalysis under mild reaction conditions. Under minimal methanol to oil ratio (1:5.3), mild reaction temperature ( $55^\circ\text{C}$ ) and less than 0.2 wt catalyst, the conversion was greater than 99% in 45min. The efficiency of this catalyst was significantly improved through the use of tetrahydrofuran (THF), a co-solvent used to bring the reaction mixture from three phases to a single phase, effectively creating a homogeneous mixture. At the end of the reaction, both the methanol and THF could be co-distilled and recycled while the catalyst would precipitate out and deposit in the bottom layer of glycerol. The catalyst was stable and reusable for at least six times without a loss in activity. In addition,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{Pw}_{12}\text{O}_{40}$  showed good water tolerance. In an earlier study, the same authors reported that  $\text{Cs}_{2.5}\text{H}_{0.5}\text{Pw}_{12}\text{O}_{40}$  was more

active than zeolite H-ZSM5 for the esterification of acetic acid. However,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is soluble in methanol and acts more like a homogeneous catalyst under reaction conditions. The same authors produced biodiesel from waste frying oil, methanol, and a heteropolyacid,  $\text{PW}_{12}$ , a known good esterification agent. Like the previous catalyst,  $\text{PW}_{12}$  is a solid acid but it is soluble in methanol. Therefore, the authors used this property by first preparing a homogeneous methanol- $\text{PW}_{12}$  mixture then performing the transesterification reaction. At the end of the reaction, the methanol was evaporated, resulting in the precipitation of the catalyst, which was decanted with the lower glycerol phase of the product solution.  $\text{PW}_{12}$  proved to be an excellent esterification agent and achieved a maximum conversion of 97% at 65°C for 12 h at a methanol to free fatty acid ratio of 2.5:1 (Cao et al., 2008). As expected, an increase in temperature, catalyst loading, and reaction time produced higher yields. However, beyond 65°C, product yield decreased due to the side reaction of fatty acid methyl ester degradation, as speculated by the authors. To prevent fouling of  $\text{PW}_{12}$ , zeolites were added to absorb the water present in the frying oil. A conversion of 87% was achieved at 65°C. However, high alcohol to oil ratio (1:70) and long reaction time (14 h) was required at 65°C.

### **2.4.3 Enzyme catalysis**

Enzymatic conversion of lipids was demonstrated with various lipases and as early as 1990. Mittelbach (1990) reported enzymatic transesterification of sunflower oil with methanol and two lipases: *Mucor miehei* and *Candida antarctica*. Today, most enzymatic transesterification processes utilize immobilized enzymes to reduce downstream

processing, increase reusability and improve the economics. Still, however, synthesis of biodiesel via enzyme catalyzed reaction is not economical because of the high cost of enzymes and the inhibitory effect of alcohols like methanol (Ranganathan et al., 2008).

In recent years, several lipolytic enzymes from extremophilic microorganisms have been discovered and characterized. Lipases and esterases derived from these aerobic thermoacidophiles and thermoalkilophiles could be potential biocatalyst for biodiesel production. Generally, lipases are more selective towards water insoluble long fatty acid esters chains ( $> C_9$ ) while esterases prefer shorter chain substrates ( $< C_{10}$ ) (Antranikian et al., 2008).

Antranikian and co-workers (2008) identified, cloned and expressed in *E. coli* two esterase genes from the genome of *Picrophilus torridus*, which thrives at the extremely harsh conditions of pH 0.7 and 60°C. Enzyme activity was detected from 10 to 90°C and pH 4-9. The esterases were compatible with various alcohols like ethanol, methanol and toluol. In general, higher concentration of these alcohols had an inhibitory effect on one of the two esterases.

Two thermoalkilophiles were characterized and expressed from *sulfolobus solfataricus*, a thermoacidophile. Two research groups have independently purified, characterized and expressed *sulfolobus solfataricus* P<sub>1</sub> and *sulfolobus solfataricus* P<sub>2</sub> in *E. coli* (Kim and Lee, 2004). The esterases showed broad ester substrates activity for C<sub>2</sub> to C<sub>16</sub> chains with an optimum pH and temperature of 8.0 and 85°C and 7.4 and 80°C respectively for P<sub>1</sub> and P<sub>2</sub>. Esterases should be capable of hydrolyzing fatty acid esters. Esterases from *sulfolobus solfataricus* P<sub>2</sub> showed no inhibitory effect with ethanol while methanol, 1-

propanol, 2-propanol, 1-butanol and 2-butanol strongly reduce their activity. To the best of our knowledge, no extremophiles has been used in biodiesel production.

## **2.5 Kinetics of biodiesel production**

One aspect that is increasingly being investigated is the kinetics of biodiesel production. The importance of kinetic studies is expected to grow particularly as newer heterogeneous catalysts are developed. In this section, the kinetics of esterification and transesterification are reviewed and summarized.

### **2.5.1 Kinetics of esterification**

Several authors have reported the kinetics of free fatty acid esterification in homogeneous systems. Berrios et al (2007) reported the kinetic study of free fatty acids in sunflower oil with sulfuric acid as the homogeneous catalyst and modeled the reaction with pseudo-homogeneous first order for the forward reaction and second order for the reverse reaction. Similarly, Tesser et al (2009) described the esterification of oleic acid over an ion-exchange sulfonic resin by a pseudo-second order kinetic model. Meunier and coworkers (2007) investigated the esterification of palmitic acid in sunflower oil over a silica-supported Nafion® resin and compared its activity with sulfated zirconium oxide.  $\text{SnCl}_2$  was successfully used for the esterification of oleic acid in soybean oil using ethanol and the catalyst was found to yield comparable result with homogeneous  $\text{H}_2\text{SO}_4$  catalyzed reactions (Cardoso et al., 2008). Despite the recent surge in research with regards to heterogeneously produced biodiesel, fewer publications dealt with the kinetics of esterification and even less attempted to investigate the reaction mechanism.

### **2.5.2 Kinetics of transesterification**

The early work on the kinetics of transesterification dealt with homogeneous catalysis, in particular homogeneous base catalysis. The kinetics of homogeneous base catalyzed transesterification of edible and non-edible oils has been investigated by several authors (Freedman et al., 1986; Nouredini, 1997; Singh and Fernando, 2007; Stamenkovic et al., 2010; Veljkovic et al., 2009). Freedman et al (1986) studied the transesterification of soybean oil by sodium butoxide and concluded that the forward reaction was a pseudo-first order when the oil to alcohol ratio was larger (1:30) or second order for lower ratio (1:6). They also observed that the reverse reaction was second order. Nourreddini et al (1997) also studied the kinetics of soybean oil transesterification by sodium hydroxide and reported activation energy values consistent with the findings of the previous authors. The kinetics of heterogeneously catalyzed vegetable oil transesterification has also generated interest in recent years. Singh et al (2007) studied the kinetics of soybean oil transesterification by MgO, CaO, BaO, PbO and MnO<sub>2</sub> in a high pressure reactor to determine the overall rate constant and the reaction order. The reaction order was first order for all catalysts except for BaO which had a third order.

## Conclusion

It is evident from the literature review that biodiesel is an attractive alternative to petrodiesel. In addition to the four traditional methods used to produce biodiesel, supercritical transesterification and enzymatic processes have been successfully used recently. Still, transesterification appears to be the preferred method of production. In particular, heterogeneous catalysis for biodiesel production is a promising approach as evidenced by the surge in related publications in recent years.

Many catalysts have been reported for the conversion of vegetable oil to biodiesel. Among the acid catalysts, mixed and sulfated metal oxides and heteropolyacids have been investigated and could effectively carry out both transesterification and esterification reactions. However, high temperature and often longer reaction times are required. Solid base catalysts on the other hand were proven to effectively catalyze the reaction under mild conditions near the boiling point of methanol. Unfortunately, they are limited to vegetable oil with very low free fatty acid content.

Economic assessment studies of biodiesel production have repeatedly highlighted the impact of feedstock cost on the final price of biodiesel. In this regard, non-edible cheaper feedstock is better than edible expensive feedstock. The production method is also crucial and it has been shown that biodiesel heterogeneously produced is cheaper than that homogeneously produced.

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## Chapter three

### Production of biodiesel from sulfated zirconium oxide

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#### Abstract

Biodiesel can be produced by homogeneous or heterogeneous catalysis. While homogeneous base catalysis has been traditionally used, heterogeneous acid catalysis is generating interest because of its potential superior promise of catalyzing both the conversion of free fatty acids and triglycerides into fatty acid alkyl esters. Solid acid catalysts such as zirconium oxide are being investigated for their potential in biodiesel production due to their fast reaction rate and their ability to esterify cheaper but high free fatty acid content oil. In this chapter, the potential of sulfated zirconium oxide as both an esterification and transesterification catalyst is investigated.

The catalyst support, zirconium oxide, was subjected to three treatments ( $\text{H}_2\text{SO}_4$  impregnation ( $\text{SO}_4/\text{ZrO}_2$ ),  $\text{H}_2\text{SO}_4$  impregnation and calcination at  $550^\circ\text{C}$  ( $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$ ) and  $650^\circ\text{C}$  ( $\text{SO}_4/\text{ZrO}_2-650^\circ\text{C}$ ) and their physiochemical properties determined by SEM-EDS, XPS and BET surface area. The sulfur content were respectively 1.22% wt, 1.04 wt %, and 1.01 wt % for  $\text{SO}_4/\text{ZrO}_2$ ,  $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$  and  $\text{SO}_4/\text{ZrO}_2-650^\circ\text{C}$  when SEM-EDS was used and 2.98 wt %, 2.05 wt %, 2.72 wt % when XPS was used for the same catalysts. BET surface area was determined to be 80.44, 90.89 and 79.87  $\text{m}^2/\text{g}$  for  $\text{SO}_4/\text{ZrO}_2$ ,  $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$  and  $\text{SO}_4/\text{ZrO}_2-650^\circ\text{C}$  respectively.

The effect of the treatments on the catalyst activity toward the esterification of free fatty acid as well as the optimum catalyst concentration was determined.  $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$  was the best catalyst and 10 % (w/w) was the optimum catalyst concentration. Furthermore,  $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$  was successfully recycled for eight consecutive runs before permanently losing its activity. The three catalysts showed low catalytic activity in the transesterification of soybean oil. The ester yields were 31.39%, 25.82% and 25.04% for  $\text{SO}_4/\text{ZrO}_2$ ,  $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$  and  $\text{SO}_4/\text{ZrO}_2-650^\circ\text{C}$  respectively at  $98^\circ\text{C}$ .

The mechanism of the reaction over the Bronsted acid catalyst ( $\text{SO}_4/\text{ZrO}_2-550^\circ\text{C}$ ) was shown to obey Eley-Rideal kinetics in which the palmitic acid was initially adsorbed on the active site. Although the Lewis acid catalyst ( $\text{Al}_2\text{O}_3$ ) also followed Eley-Rideal mechanism, methanol was adsorbed first instead of palmitic acid.

**Keywords:** Palmitic acid, sulfated zirconium oxide, esterification, Eley-Rideal mechanism, biodiesel

### 3.1 Introduction

Biodiesel can be produced by the transesterification of triglycerides through acid or base catalysis (Figure 11) or esterification of free fatty acids by acid catalysis (Figure 12). Homogeneous base catalysis has been the preferred method of biodiesel production traditionally due to the faster reaction rate. When alkali bases are used for biodiesel production, feedstock selection is crucial to the success and economic feasibility of biodiesel production.

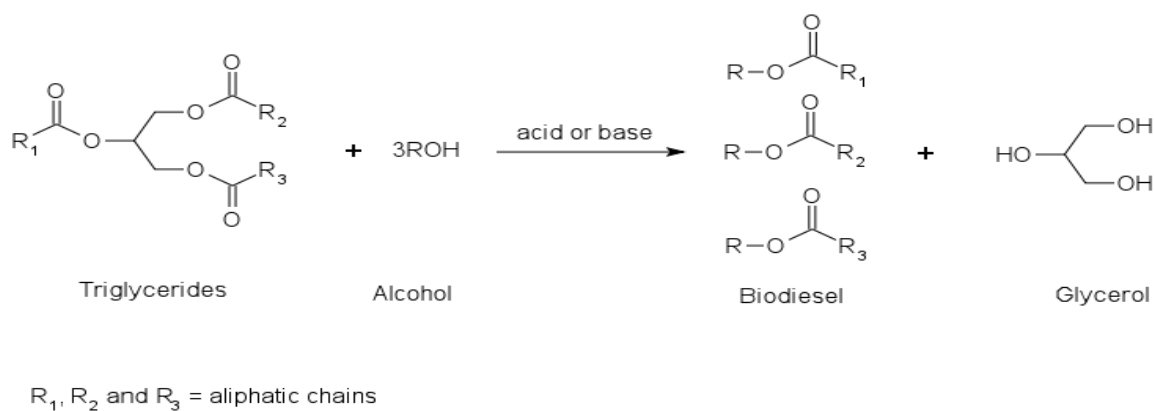


Figure 11: Transesterification of triacylglycerol to produce three fatty acid alkyl esters (biodiesel) and glycerol by acid or base catalysis

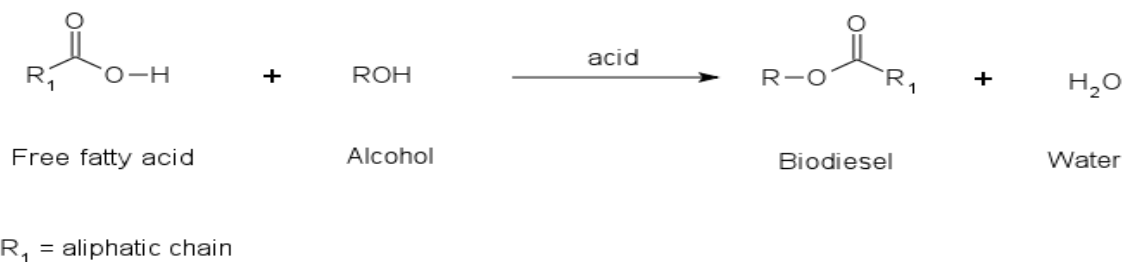


Figure 12: Esterification of a free fatty acid to an alkyl fatty acid ester catalyzed by acid c



Both water and free fatty acid contents are detrimental to the process and their concentrations must be minimized to prevent side reactions such as saponification and ester hydrolysis (Freedman et al., 1984). In the presence of water, triglycerides could hydrolyze, leading to the formation of additional free fatty acids (Arroyo et al., 1992). Free fatty acids react with base catalysts to form soaps through saponification (Figure 13).

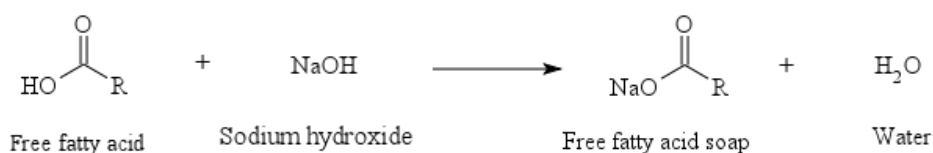


Figure 13: Free fatty acid saponification

According to Lotero et al., (2005a) the free fatty acid contents in the oil should be no more than 0.5 % wt beyond which the downstream separation process is hindered by excessive soap formation due to the saponification side reaction. Furthermore, it is estimated that the majority of the production cost of biodiesel is associated with the cost of refined vegetable oil the price of which is already comparable to the selling price of petrodiesel (Apostolakou et al., 2009; Di Serio et al., 2007; Encinar et al., 2005). Consequently, while homogeneous base catalysis achieves high biodiesel yields in shorter time, it limits the choice of feedstock to refined oils due to its limitation by the criteria described above. This feedstock limitation hinders the competitiveness of biodiesel with petrodiesel.

Several economic cost analysis studies revealed that biodiesel is more competitive when produced from cheaper feedstock such as waste vegetable oil and animal fat

(Apostolakou et al., 2009; Marchetti and Errazu, 2008; van Kasteren and Nisworo, 2007; West et al., 2008; You et al., 2007; Zhang et al., 2003). However, the free fatty acid content in such feedstocks often exceeds the tolerable limit mentioned above thus requiring a solution for handling the free fatty acids. For oils with high free fatty acid content, Canacki and Gerpen (2001) proposed a two-step process where free fatty acids are first converted by homogeneous acid catalysis via esterification followed by homogeneous base catalysis when the free fatty acid content was reduced to an acceptable level. This approach unfortunately increases the chemical consumption since the acid catalyst used in the first stage must be neutralized before the second stage resulting in an increase in chemical usage. Heterogeneous acid catalysis is an attractive alternative that promote catalyst reusability and to simplify downstream separation while simultaneously converting free fatty acids and triglycerides to biodiesel.

Many heterogeneous acid catalysts have been employed for biodiesel production (Cao et al., 2008; Furuta et al., 2004; Kiss et al., 2006; Kulkarni et al., 2006; Lotero et al., 2005b; Ramos et al., 2008; Rothenberg et al., 2005).

In this chapter, the esterification of free fatty acids and the transesterification of soybean oil on sulfated zirconium oxide were investigated. The kinetics of free fatty acid esterification on sulfated zirconia and  $\text{Al}_2\text{O}_3$  were studied and compared to elucidate the reaction mechanism.

## **3.2 Materials and Methods**

Zirconium oxide, silicon dioxide and activated acidic alumina were obtained from Alfa Aesar (Alfa Aesar, Ward Hill, MA). The two HZSM5 catalysts were obtained from

BASF (BASF Inc., Florham Park, NJ) and Süd-chemie (Süd-chemie Inc., Colton, CA). Palmitic acid was purchased from Sigma Aldrich (St. Louis, MO). Methanol, n-hexane and acetonitrile were purchased from Fischer Scientific (Fair Lawn, NJ) as analytical grade solvents and used as received. Kroger brand soybean oil was purchased from the local Kroger grocery store (South Main St Kroger Store, Blacksburg, VA).

### **3.2.1 Catalyst preparation**

Prior to sulfation, the metal oxide pellets ( $\text{ZrO}_2$  and  $\text{SiO}_2$ ) as well as the Süd-chemie HZSM5 were ground to pass through a 20 mesh screen. The catalysts were subjected to two types of treatments: surface acidification and temperature activation. For surface acidification, 1g of each catalyst support was impregnated with 15ml of 0.5M  $\text{H}_2\text{SO}_4$  under constant stirring for 24 h followed by overnight drying in a gravity oven at  $100^\circ\text{C}$  and then ground again to pass through a 20 mesh screen again (Arata, 1996a; Arata and Hino, 1990). The catalysts obtained after this treatment were referred to as  $\text{SO}_4/\text{ZrO}_2$ ,  $\text{SO}_4/\text{SiO}_2$ ,  $\text{SO}_4/\text{B-HZSM5}$  and  $\text{SO}_4/\text{S-HZSM5}$  for the catalyst supports  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , BASF HZSM5 and Süd-chemie HZSM5 respectively. The dried catalysts were then calcined in a muffler furnace under air at  $550^\circ\text{C}$  or  $650^\circ\text{C}$  for at least six hours and sealed in a container until use.

### **3.2.2 Esterification of free fatty acids**

The esterification of palmitic acid was carried out in a batch reactor. The reaction mixture was placed in a 250 ml flask when the reaction temperature was below methanol boiling temperature or a crimp top glass bottle fitted with a rubber stopper and aluminum

seal when the reaction temperature was above the boiling point of methanol. The reaction container was placed in a shaker bath (Precision Scientific, Model 25, Chicago, Illinois) at the appropriate temperature and shake speed of 170 rpm. All experiments were carried out with 0.01mol free fatty acid and 1mol of methanol (1:100 fatty acid to methanol molar ratio). The reaction was monitored using an HPLC analysis. The analytical instrument was a Shimadzu HPLC 10 AVP (Shimadzu Scientific, Columbia, MD) equipped with an evaporative light scattering detector (ELSD-LT) and a HAISIL 300 C18 5µm column (Higgins Analytical, Mtn View, CA). The analysis was carried out in the isocratic mode and the mobile phase consisted of 100% acetonitrile (mobile phase A) and 99.9% water/0.1% acetic acid (mobile phase B). The total flow rate was 1.0ml/min with 85% phase A and 15% phase B. Calibration standards with concentrations of 1.5mg/ml, 3.25mg/ml and 7.5mg/ml were prepared by dissolving palmitic acid in hexane. The change in palmitic acid area and the palmitic acid calibration curve were used to calculate the final concentration of palmitic acid which was then used to determine the palmitic acid conversion according to the equation below.

$$Conversion, \% = \frac{(C_{FFA,0} - C_{FFA,F})}{C_{FFA,0}} \times 100$$

where

$C_{FFA,0}$  = Initial palmitic acid concentration, mg/ml

$C_{FFA,F}$  = Final palmitic acid concentration, mg/ml

All aliquots were centrifuged to remove any fine catalyst particles at the bottom of the eppendorf then diluted and filtered through a 0.2 µm syringe filter into a vial for analysis.

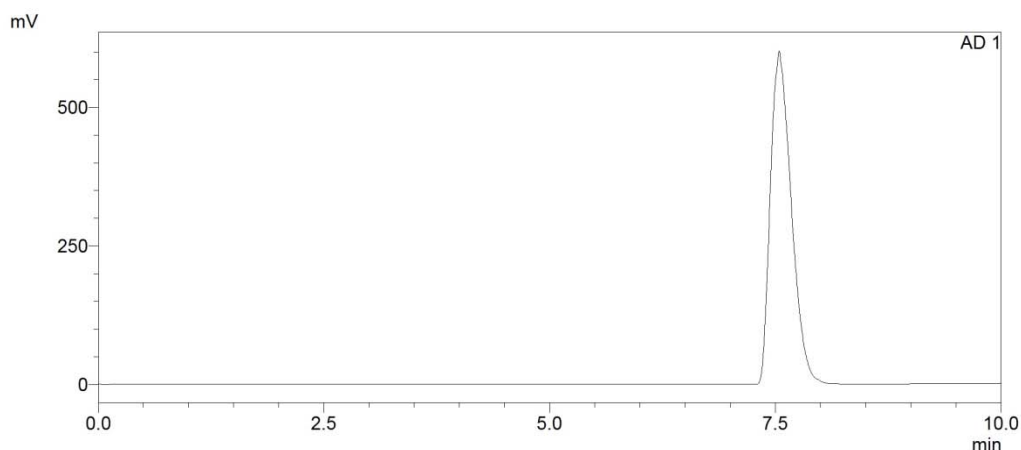


Figure 14: Typical HPLC chromatogram for palmitic acid

### 3.2.3 Transesterification of soybean oil

$\text{SO}_4/\text{ZrO}_2$ ,  $\text{SO}_4/\text{ZrO}_2$ -550°C and  $\text{SO}_4/\text{ZrO}_2$ -650°C were investigated for the transesterification of soybean oil. The reaction was carried out in the shaker bath described previously at 98°C and 170 rpm. The reaction mixture was placed in a crimp top glass bottle fitted with a rubber stopper and an aluminum seal. The European standard, EN14103, was used to monitor the reaction progress. The methyl ester peaks identified by comparing their retention times to that of authentic standards obtained from Restek (Restek, Bellefonte, PA). The ester content, expressed as a mass fraction in percent, is given by the equation below:

$$C = \frac{(\sum A)}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$

Where

$C$  is mass fraction of fatty acid ester, in %, in sample

$\sum A$  is the total peak area from the methyl esters

$A_{EI}$  is the peak area of the palmitic acid

$C_{EI}$  is the concentration, in milligrams per milliliter, of palmitic acid

$V_{EI}$  is the volume, in milliliter, of palmitic acid solution

m is the mass, in milligrams, of sample

A typical fatty acid methyl ester chromatograph of soybean oil is shown below.

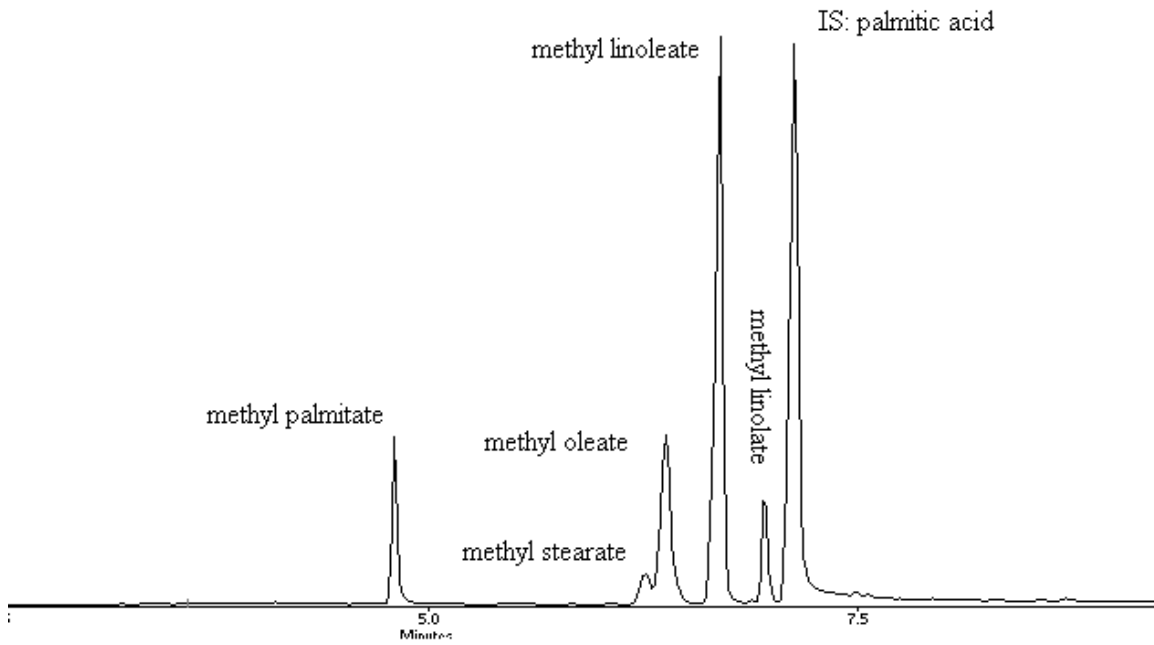


Figure 15: Typical soybean biodiesel chromatogram depicting five fatty acid methyl ester and the internal standard

The gas chromatographic instrument was a Shimadzu GC-14A (Shimadzu, Columbia, MD) equipped with a flame ionization detector or FID and a FAME column (Rtx-225, 30m, 0.25mm, 0.25um, Restek, Bellefonte, PA). The GC inlet and detector temperature were maintained at 220°C and 300°C respectively.

### **3.2.4 Catalyst evaluation**

As three catalysts were prepared for every catalyst support, twenty catalysts were screened at a reaction temperature of 55°C and 50% wt catalyst for one hour in the preliminary phase. The discrimination between the twenty catalysts was done on the bases of the palmitic acid conversion and the potential reusability of the catalyst.

Catalysts that showed significant reduction in activity after the first use were first eliminated and from the remaining pool, the catalyst with the highest conversion was chosen for subsequent studies.

The best catalyst from the later investigation was used in the evaluation of the effect of the catalyst amount on the conversion. Six catalyst concentrations, 5%, 10%, 25%, 50%, 75% and 100% by weight of palmitic acid, were evaluated.

### **3.2.5 Catalyst characterization**

The group of catalysts selected from the previous step was characterized by scanning electron microscopy on a FEI Quanta 600 FEG ESEM equipped with an energy dispersive x-ray detector (Physical Electronics, Chanhassen, MN) to determine the elemental composition of the catalysts. In addition, the zirconium oxide catalysts were also characterized by x-ray photoelectron spectroscopy on a PHI Quantera SXM (Physical Electronics, Chanhassen, MN).

The catalysts BET surface area were determined by a surface area and porosity analyzer (ASAP 2000, Micromeritics Norcross, GA) in nitrogen at 77K.

The acidity of the catalysts was measured by colorimetric titration. For each titration, 1g of the catalyst was dissolved in 10ml of deionized water and stirred for one hour. The

slurry was then titrated with 0.01M NaOH with phenolphthalein indicator. The acidity was reported as mmol NaOH per g catalyst.

The effects of calcination temperature (550°C and 650°C) on mean wt % sulfur adsorbed on ZrO<sub>2</sub> and mean acidity (mmol NaOH/g catalyst) were studied by a one-factor analysis of variance of a balanced design. The statistical analysis software, JMP, was used to perform the analysis (JMP, 2008). If necessary, Tukey-Kramer HSD was used for multiple comparisons (Sall et al., 2001).

### **3.2.6 Vegetable oil characterization**

The Kroger brand soybean oil was first analyzed for acid number using ASTM D664.

The moisture content was determined by Karl Fischer titration using a Metrohm 701KF Titrino titrator and 703 titration stand (Brinkmann Instruments Inc., New York, NY). The fatty acid composition of the soybean oil was determined by gas chromatography on Shimadzu GC-14A previously described.

### **3.2.7 Catalyst life**

In order to determine the catalyst life, SO<sub>4</sub>/ZrO<sub>2</sub>-550°C was reused consecutively. The reaction was carried out as described before for one hour at 60°C. At the end of the reaction, the catalyst was filtered out, washed with 10 ml of hexane and dried at 80°C in a vacuum oven for one hour. The washed catalyst was reused and both the amounts of palmitic acid and methanol were adjusted accordingly to ensure a constant catalyst concentration. Since some catalyst was lost in between runs, 100 % catalyst by weight of palmitic acid was used to ensure that enough catalyst was recovered for several



consecutive runs. The analytical procedure for determining the conversion of palmitic acid was described in section 3.2.1. For very low conversion, a sample of the reaction mixture was analyzed by gas chromatograph to confirm that the absence of palmitic acid methyl ester. The reaction was repeated until the conversion of palmitic acid was near zero at which point the catalyst was washed with 10 ml of hexane and calcined at 500°C in furnace for 3 h before reuse. If activity was restored, the cycle was repeated until the catalyst was permanently deactivated.

### **3.2.8 Kinetics of palmitic acid esterification**

The kinetic data of palmitic acid esterification was obtained by carrying out the reaction at 40°C, 60°C and 80°C with 10% sulfated zirconium oxide ( $\text{SO}_4/\text{ZrO}_2$ -550°C) and 100% activated acidic alumina ( $\text{AcAl}_2\text{O}_3$ ) by weight of palmitic acid.  $\text{AcAl}_2\text{O}_3$  was used a model Lewis solid acid to investigate the difference, if any, between Brønsted and Lewis heterogeneous catalysts in the esterification of palmitic acid. For temperature below the boiling point of methanol, such as 40°C and 60°C, about 1ml of the reaction mixture was collected from the flask at time intervals of 10 min or 20 min up to 180 min. Above the methanol boiling point, the reaction was stopped and cooled before removing the aluminum seal on the sealed bottle to prevent loose of methanol vapors.

Twenty two models based on Langmuir-Hinshelwood (Figure 17) and Eley-Rideal (Figure 16) kinetics were investigated for sulfate zirconium oxide and acid alumina.

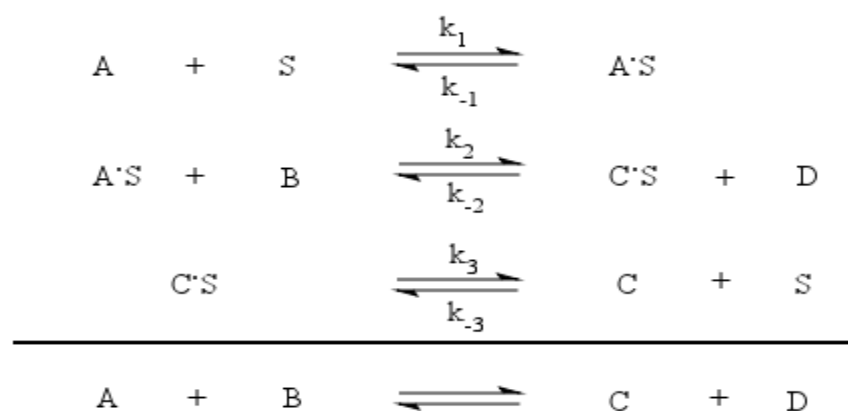


Figure 16: Bimolecular Eley-Rideal mechanism

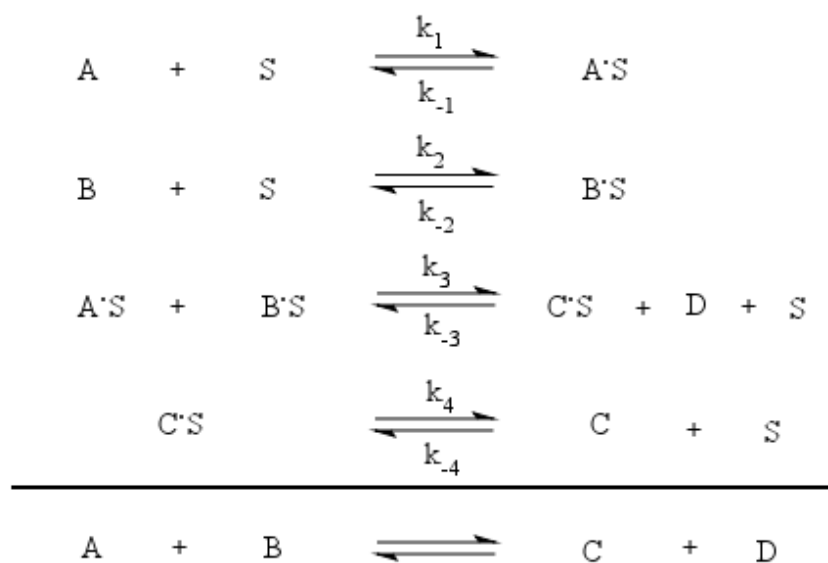


Figure 17: Bimolecular Langmuir-Hinshelwood mechanism

### 3.2.8.1 SO<sub>4</sub>/ZrO<sub>2</sub>-550°C deterministic kinetic model

The rate law that best fitted the experimental results of palmitic acid esterification on sulfated zirconia assumed that the reaction obeyed Eley-Rideal kinetics. The reaction consisted of three elementary reactions as described in Figure 16 where A is palmitic acid, S is a vacant active site on the surface, B is methanol, C is palmitic acid methyl ester and D is water. Both A·S and C·S are adsorbed intermediates. The kinetic model was derived based on the following assumptions:

1. The rate of the non-catalyzed reactions is negligible compared to the catalyzed reaction.
2. The diffusion rate of reactants and products to and from the surface are negligible.
3. There are no differences in the activity and accessibility of sites on catalyst surface.
4. The surface reaction was the rate determining step (RDS) and the adsorption and desorption are quasi-equilibrated (QE).
5. There was no palmitic acid methyl ester and water before the reaction.

Based on the assumptions above, the following kinetic rate law was derived:

$$rate = \frac{\alpha \left( K_1 C_A C_B - \left( \frac{C_D C_C}{K_3 K_2} \right) \right)}{1 + K_1 C_A + \frac{C_C}{K_3}}$$

Where  $K_1$ ,  $K_2$ ,  $K_3$  represent the equilibrium constants of adsorption of palmitic acid on SO<sub>4</sub>/ZrO<sub>2</sub>-550°C, surface reaction of adsorbed palmitic acid with methanol and desorption of palmitic acid methyl ester,  $\alpha = Lk_2$ ,  $k_2$  is the forward reaction rate constant of rate determining step and  $L$  is the active site density.

The concentration of the reactants and products can be expressed as

$$C_A = C_{A_0}(1 - X)$$

$$C_B = C_{A_0}(100 - X)$$

$$C_C = C_{A_0}X$$

$$C_D = C_{A_0}X$$

Therefore, the rate law can be expressed as:

$$\text{rate} = \frac{\alpha \left( K_1 C_{A_0}^2 (1 - X)(100 - X) - \left( \frac{C_{A_0}^2 X^2}{K_3 K_2} \right) \right)}{1 + K_1 C_{A_0} (1 - X) + \frac{C_{A_0} X}{K_3}}$$

### 3.2.8.2 AcAl<sub>2</sub>O<sub>3</sub> deterministic kinetic model

Similarly, the reaction mechanism of palmitic acid esterification on AcAl<sub>2</sub>O<sub>3</sub> was assumed to follow the Eley Rideal mechanism. The mechanism consisted of 3 elementary reactions as described below as illustrated in Figure 16 where here A is methanol, S is a vacant active site on the surface, B is palmitic acid, C is water and D is palmitic acid methyl ester. Both A'S and C'S are adsorbed intermediates. The kinetic model, derived based on the same assumptions described previously, is shown below:

$$\text{rate} = \frac{\alpha \left( C_A - \frac{C_C C_D}{K_3 K_2 K_1 C_B} \right)}{1 + \frac{C_C C_D}{K_3 K_2 C_B} + \frac{C_D}{K_3}}$$

The concentration of the reactants and products can be expressed as

$$C_B = C_{B_0}(1 - X)$$

$$C_A = C_{B_0}(100 - X)$$

$$C_C = C_{B_0}X$$

$$C_D = C_{B_0}X$$

Therefore, the rate law can be expressed as

$$rate = \frac{\alpha \left( C_{B_0}(100 - X) - \frac{C_{B_0}X^2}{K_1K_2K_3} \right)}{1 + \frac{C_{B_0}X^2}{K_2K_3(1 - X)} + \frac{C_{B_0}X}{K_3}}$$

### 3.3 Results and discussion

Sulfated zirconium oxide has long been known to have superior catalytic properties compared to its equivalent unsulfated metal oxide. The superior properties are attributed the increase in acidity that occurs when sulfate groups are adsorbed on the catalyst surface. The acidity of sulfated zirconium oxide has often been compared to that of aluminosilicates and zeolites used in petrochemical industry. The ability of sulfated zirconium oxide to catalyze reactions that are typically catalyzed by strong acids such the dehydration of ethanol or the conversion of butane to isobutane and propane has lead to their classification as superacid catalysts (Arata, 1990).

#### 3.3.1 Catalyst evaluation

For all catalysts, sulfation and calcination increased the catalyst activity as illustrated by the increase in conversion from untreated to treated catalysts (Figure 18).

The HZSM5 catalysts had low conversion despite their known high acidity. Normally, high acidity results in esterification conversion, hence the use of sulfuric acid in homogeneously catalyzed esterification. However, in the case of zeolites, the internal diffusion limitations combined with loss of structural integrity are believed to negatively

affect the conversion of palmitic acid. When HZSM5 catalysts were immersed in the sulfuric acid solution, a powdery material was collected after drying as a result of the dissolution of the binder used to manufacture the catalyst. Treatment improved its activity perhaps as a result of adsorbed sulfate groups (Figure 18). The low conversion observed for the HZSM5 zeolite catalysts is consistent with reports by Lotero et al (2005b) as well as Rothenberg et al (2005).

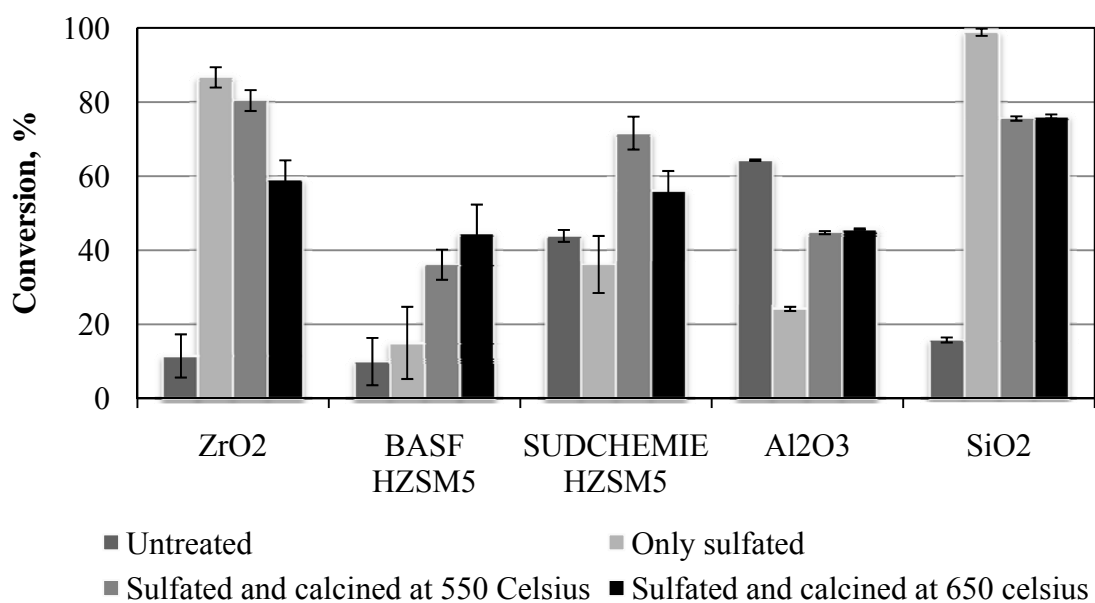


Figure 18: The effect of sulfation and calcination on the activity of twenty acid catalysts.

In the case of activated aluminum oxide ( $\text{Al}_2\text{O}_3$ ), the untreated catalyst had the highest conversion, contrary to all other catalysts produced where the treated catalysts usually had higher conversions than the untreated ones. Like the zeolite catalysts, the acidic activated alumina catalyst became powdery upon sulfation and lost some activity as illustrated by the decrease in conversion after sulfation. It is well known that aluminum

oxide reacts with sulfuric acid to generate aluminum sulfate according to the reaction illustrated in Figure 19.

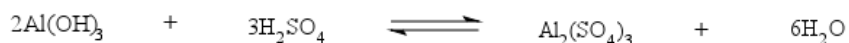


Figure 19: Aluminum oxide reaction with sulfuric acid

Aluminum sulfate that have been shown to catalyze the esterification of oleic acid (Álvarez et al., 2009). Therefore, it is believed that the loss of structural integrity had a significant role on the reduction of the catalyst activity.

Silicon dioxide as a support was included in this study because of its well established catalytic role as a component in zeolites and other catalysts. As illustrated in Figure 18, silica supported catalysts came close to sulfated zirconia in activity. The sulfated but not calcined silica in particular had the highest conversion of 99%. However, only 3% of the original conversion was obtained after the first time use. It was consequently concluded that this activity was due to unadsorbed sulfate groups on the surface that leached into the reaction mixture. Calcination improved the reusability of this catalyst: sulfated silica catalysts calcined at 550°C and 650°C achieved 89% and 95% of the original conversion after the first time use respectively.

After the initial screening stage, sulfated zirconium oxide calcined at 550°C was selected for further experimentation because it had a high conversion and retained 98% of its original conversion. The optimum catalyst concentration was determined and it appeared that 10 wt % was the limit beyond which an increase in catalyst concentration did not significantly increase the conversion (Figure 20).

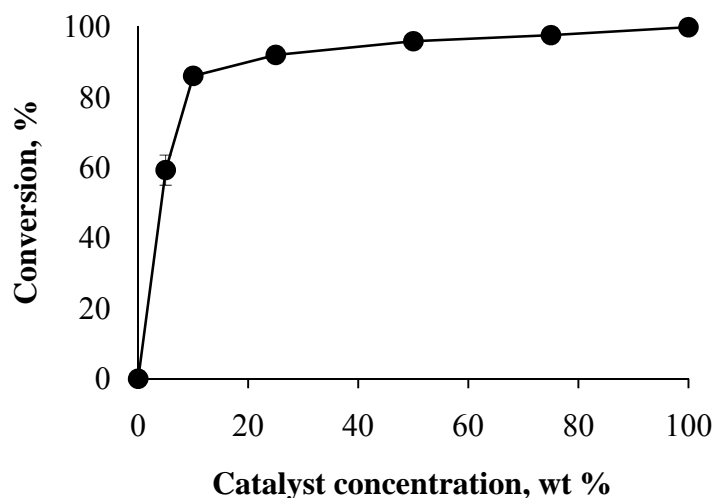


Figure 20: Effect of catalyst concentration on palmitic acid esterification yield

### 3.3.2 Catalyst characterization

The physical properties of zirconium oxide catalyst were measured to gain better understanding of the effects of treatments. The influence of sulfuric acid impregnation on BET surface area is shown in Table 2.

Table 2: The BET surface areas of the control and treated catalysts

	ZrO <sub>2</sub>	SO <sub>4</sub> /ZrO <sub>2</sub>	SO <sub>4</sub> /ZrO <sub>2</sub> -550°C	SO <sub>4</sub> /ZrO <sub>2</sub> -650°C
Surface area (m <sup>2</sup> /g)	81.70	80.44	90.89	79.87

The increase in calcination temperature resulted in increase in the BET surface area first followed by a decrease at higher temperature. Sulfuric acid impregnation and calcination was known to increase the surface area of metal oxide catalysts (Arata, 1990; Corma, 1995). Crystallization of zirconium oxide occurs around 450°C (Srinivasan et al., 1992). However, it has been observed that the crystallization of zirconium oxide occurred at higher temperature for sulfated metal oxides (Corma, 1995). It has also known that



calcination in air of amorphous metal oxides decreased the surface area due to increase in crystallinity (Kondo and Domen, 2007). Therefore, calcination at 550°C probably produced a predominantly amorphous catalyst resulting in higher surface area.

Calcination at 650°C however produced a crystalline catalyst resulting in the decrease in surface area. These results are in good agreement with previously reported findings on sulfated metal oxide catalyst properties (Arata, 1996b, 1990; Corma, 1995). The extent of sulfate adsorption was determined by examining the wt % sulfur content measured by SEM-EDS (See Table 3).

.There was statistically significant evidence that the mean wt % sulfur measured by SEM-EDS were not all equal  $F(3,11)=14.21$ ,  $MS=0.53$ ,  $P=0.001$ . The calcination explained 84% of the total variation while 16% was unexplained indicating that the effects of calcination temperature were indeed statistically significant.

Table 3: Elemental composition of sulfated zirconium oxide by SEM-EDS

	<b>ZrO<sub>2</sub><sup>a</sup></b>	<b>ZrO<sub>2</sub>-SO<sub>4</sub><sup>b</sup></b>	<b>ZrO<sub>2</sub>-SO<sub>4</sub>-550°C<sup>b</sup></b>	<b>ZrO<sub>2</sub>-SO<sub>4</sub>-650°C<sup>b</sup></b>
<b>Zr</b>	72.82 ± 3.21	73.21 ± 2.67	74.31 ± 9.39	67.35 ± 2.61
<b>O</b>	22.44 ± 4.63	22.88 ± 2.36	20.99 ± 8.81	27.13 ± 0.74
<b>C</b>	4.47 ± 1.37	2.70 ± 0.24	3.66 ± 1.55	4.53 ± 2.61
<b>S</b>	0.26 ± 0.05	1.22 ± 0.14	1.04 ± 0.25	1.01 ± 0.25

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)

It is evident that the sulfur content increased with sulfation as indicated by the significant difference between ZrO<sub>2</sub> and the sulfated and calcined catalysts. The sulfated and uncalcined catalyst, SO<sub>4</sub>/ZrO<sub>2</sub>, had the highest sulfur content. The sulfur content of

uncalcined and calcined catalysts at 550°C and 650°C were not significantly different based on Tukey-Kramer multiple comparison (Sall et al., 2001).

The x-ray photoelectron spectroscopic analysis was also conducted on sulfated zirconium oxide catalysts. The biggest difference between these two analytical techniques is the penetration depth. XPS typically scans the surface with a penetration depth between 1.5 to 5 nm whereas SEM-EDS scans deeper with a penetration depth around 1  $\mu$ m.

Therefore, XPS results reflect the surface composition whereas as SEM-EDS results more accurately reflect the bulk composition. When compared to the SEM-EDS results, XPS analysis produced higher carbon and oxygen content. The source of carbon on these catalysts is attributed to adsorbed atmospheric carbon dioxide. Since XPS is more surface sensitive than SEM-EDS and carbon dioxide is adsorbed on the surface, higher carbon and oxygen contents would be expected with XPS (See Table 4).

Table 4: Surface composition of sulfated zirconium oxide by XPS

	<b>ZrO<sub>2</sub><sup>a</sup></b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub><sup>b</sup></b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub>-550°C<sup>b</sup></b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub>-650°C<sup>b</sup></b>
<b>Zr</b>	20.18 ± 4.44	18.55 ± 2.36	15.07 ± 3.27	25.03 ± 1.34
<b>O</b>	53.41 ± 5.46	57.77 ± 7.08	48.86 ± 3.79	65.30 ± 5.92
<b>C</b>	26.39 ± 1.91	20.69 ± 0.73	34.01 ± 4.07	7.75 ± 1.05
<b>S</b>	0.02 ± 0.05	2.98 ± 0.71	2.05 ± 0.29	2.72 ± 0.50

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)

The catalysts used for the reaction were kept sealed in a dessicator after activation, the high carbon content is probably due to the adsorption of CO<sub>2</sub> during the sample preparation for XPS analysis.

A one factor analysis of variance revealed that there was statistically significant evidence that the mean % wt sulfur measured by XPS were all equal  $F(2,8)=2.48$ ,  $MS=0.69$ ,  $P=0.164$ . Calcination temperature only explained 45% of the total variation.

The acidity of the catalysts increased with sulfation (Table 5). The increase in calcination temperature however resulted in a decrease in acidity. Sulfate groups on sulfated metal oxides are known to decompose at higher temperature (Corma, 1995). Therefore, the gradual decrease in acidity with increase in calcination temperature was attributed to this decomposition. The statistical analysis revealed there was statistically significant difference between the mean acidity (mmol NaOH/g catalyst)  $F(2,8) = 56.20$ ,  $MS = 0.18$ ,  $P < 0.001$ . Furthermore, calcination temperature explained 95% of the total variation. Tukey-Kramer HSD analysis showed that the acidity of uncalcined and calcined catalysts were statistically different at the 0.05 level. However, catalysts calcined at 550°C and 650°C were not statistically different at the same level.

Table 5: Acidity of sulfated zirconium oxide catalysts

	<b>ZrO<sub>2</sub></b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub></b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub>-550°C</b>	<b>SO<sub>4</sub>/ZrO<sub>2</sub>-650°C</b>
<b>Acidity, mmol NaOH/g catalyst</b>	0 ± 0	1.044 ± 0.058	0.620 ± 0.071	0.549 ± 0.036

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)

### 3.3.3 Soybean oil characterization

The Kroger brand soybean oil had very low free fatty acid and water content (Table 6).

The GC analysis revealed that Kroger brand soybean oil was composed of 84%

unsaturated fatty acid. Our results are consistent with results published by various authors (Table 7).

Table 6: Properties of Kroger brand soybean oil

<i>Property</i>	<i>Mean</i>	<i>Standard deviation</i>
Acid number, mg KOH/g	0.314	0.046
Moisture content, % wt	0.147	0.0207

Table 7: Fatty acid composition in soybean oil

<i>Fatty acids, %</i>	<i>Canacki et al, 2001</i>	<i>Brown, 2000</i>	<i>This work</i>
<b>Palmitic acid, C16:0</b>	10.6	9.8	12.1
<b>Stearic acid, C18:0</b>	6.4	2.4	4.2
<b>Oleic acid, C18:1</b>	22.5	28.9	22.9
<b>Linoleic acid, C18:2</b>	52.3	50.7	53.1
<b>Linolenic acid, C18:3</b>	8.2	8.2	7.7

### 3.3.4 Catalyst life

Catalyst lifetime is perhaps one of the most important criteria in determining the industrial potential of heterogeneous catalysts. This is an important facet of biodiesel heterogeneous catalysis that is unfortunately rarely covered in published work. The lack of this information renders many of the published works incomplete for the purposes of determining which catalyst might be more suitable for industrial use.  $\text{SO}_4/\text{ZrO}_2$ -550°C was successfully used in seven consecutive runs before losing complete activity in the eighth run (Figure 21). After regeneration at 500°C for 6 hours, the catalyst did not catalyze the reaction and was therefore concluded permanently deactivated. Titration of

the deactivated catalyst revealed that it lost its acidity indicating that the sulfate groups might have gradually desorbed from the catalyst support. However, it was previously shown that even pure zirconium oxide modestly catalyzed the reaction. Since the regenerated catalyst did not catalyze the reaction at all, irreversible catalyst poisoning occurred and was probably the dominating deactivation mechanism.

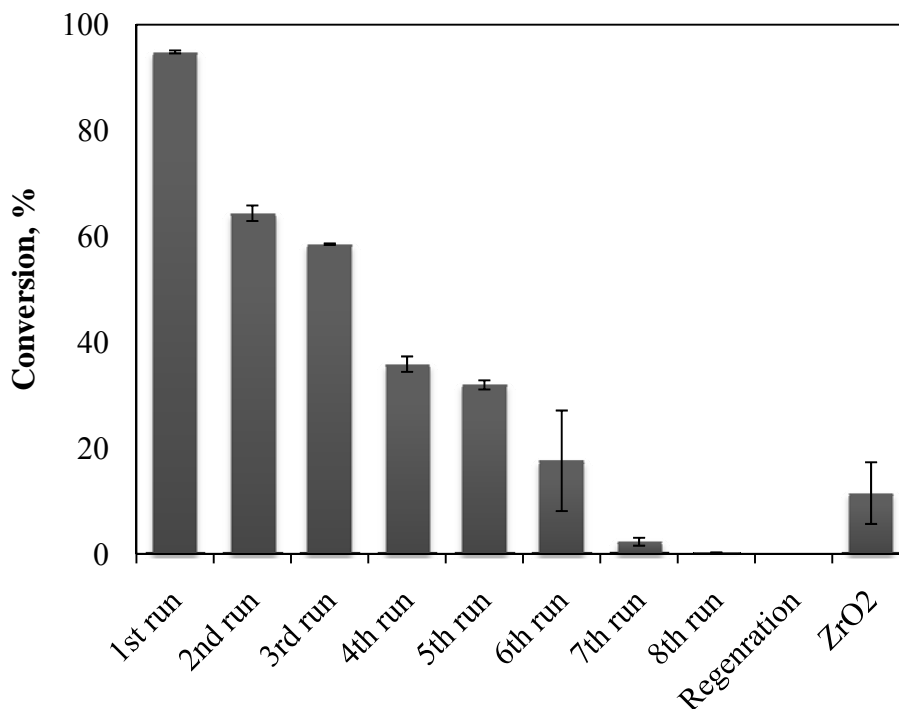


Figure 21: Reusability of sulfated zirconium oxide

### 3.3.5 Kinetics of palmitic acid esterification

Free fatty acids can be esterified by Brønsted or Lewis acids (Brown, 2000; Cardoso et al., 2008). A Brønsted acid is by definition a proton donor whereas a Lewis acid is an electron pair acceptor. It is known that the reaction mechanism of esterification in homogeneous systems is initiated by the protonation of the carbonyl group. However, to

the best of our knowledge, the reaction mechanism of esterification on Brønsted and Lewis solid acids has not been reported. Our results revealed that there are fundamental differences in the reaction mechanism over Brønsted and Lewis acids.

### 3.3.5.1 Kinetics of palmitic acid esterification on SO<sub>4</sub>/ZrO<sub>2</sub>-550°C

The esterification of palmitic acid with methanol on SO<sub>4</sub>/ZrO<sub>2</sub>-550°C obeyed Eley-Rideal kinetics as mentioned earlier. The reaction of adsorbed palmitic acid with methanol in the bulk fluid was the rate determining step indicating that the adsorption and desorption reactions were at equilibrium. The coefficients of determination for the model were 0.98, 0.99 and 0.99 for SO<sub>4</sub>/ZrO<sub>2</sub>-550°C at 40°C, 60°C and 80°C respectively. Estimates of the kinetic parameters were determined and included in Table 8. Predictions of the palmitic acid conversions at 210min and 240min for 40°C, 60°C and 80°C were in good agreement with the experimental data indicating that the model is indeed valid (Figure 22).

Table 8: Estimates of kinetic parameters for SO<sub>4</sub>/ZrO<sub>2</sub>-550°C

Temperature	$\alpha \times 10^{-4}$	$K_1 \times 10^{-2}$	$K_3$	$K_2 \times 10^{-3}$
40°C	3.78	59.75	2.01	4.21
60°C	16.12	26.74	2.01	19.38
80°C	51.10	13.38	9.08	92.41

The efficiency of the catalysts was evaluated by determining the activation energy. The reaction rate constant is related to the reaction temperature through the Arrhenius equation. Therefore, the overall reaction activation energy can be calculated from equation 1 using the reaction rate constant of the rate determining step  $K_2$ .

$$K_2 = A \exp\left(-\frac{Ea}{RT}\right)$$

The activation energy of the catalyst was determined by reformulating the equation above and plotting  $\ln K_2$  vs  $1/T$ . Based on the Arrhenius activation energy plot in Figure 23, the activation energy  $E_a$  and the pre-exponential factor  $A$  were 70.90 kJ/mol and  $2.73 \times 10^{15}$  respectively.

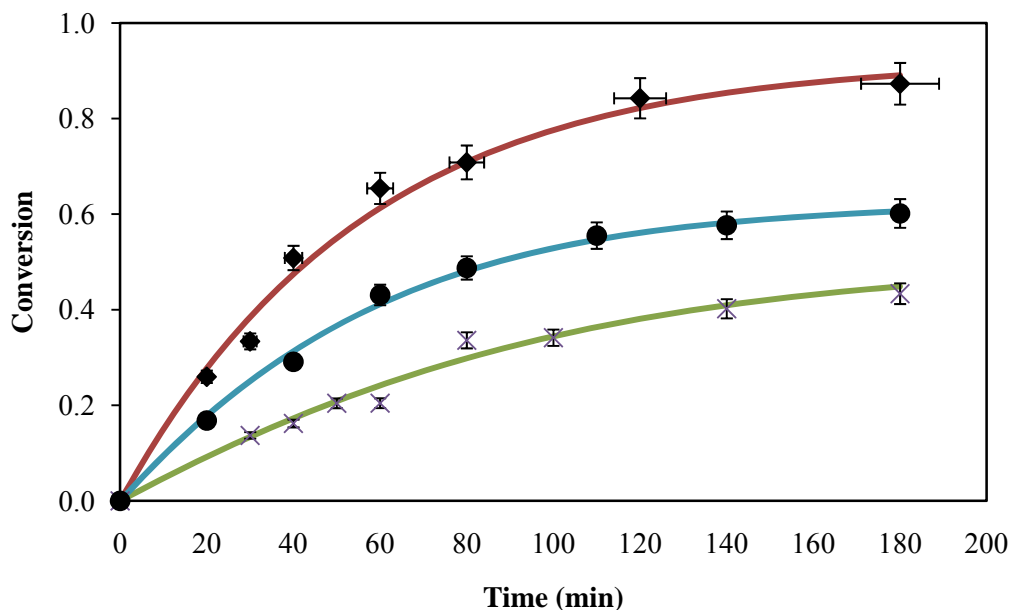


Figure 22: Conversion of palmitic acid over  $\text{SO}_4/\text{ZrO}_2$ -550°C. Experimental ( $\times$ ,  $\bullet$ ,  $\diamond$ ) and model simulation (—, —, —) at 40°C, 60°C and 80°C respectively.

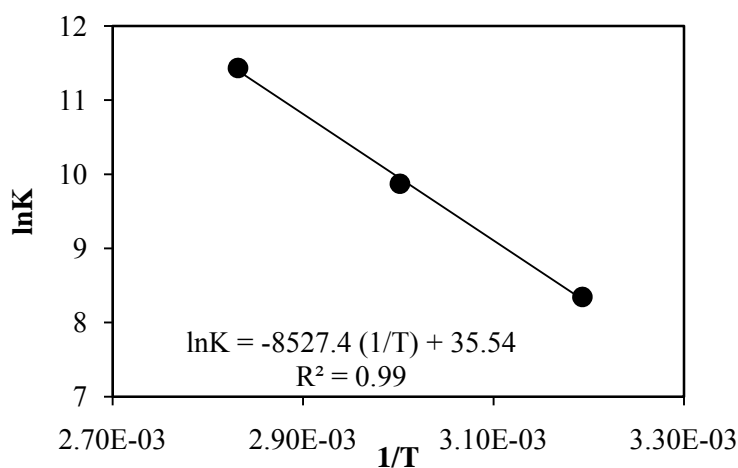


Figure 23: Arrhenius activation energy plot for  $\text{SO}_4/\text{ZrO}_2$ -550°C

Based on the elementary reactions, the reaction mechanism is depicted in Figure 24.

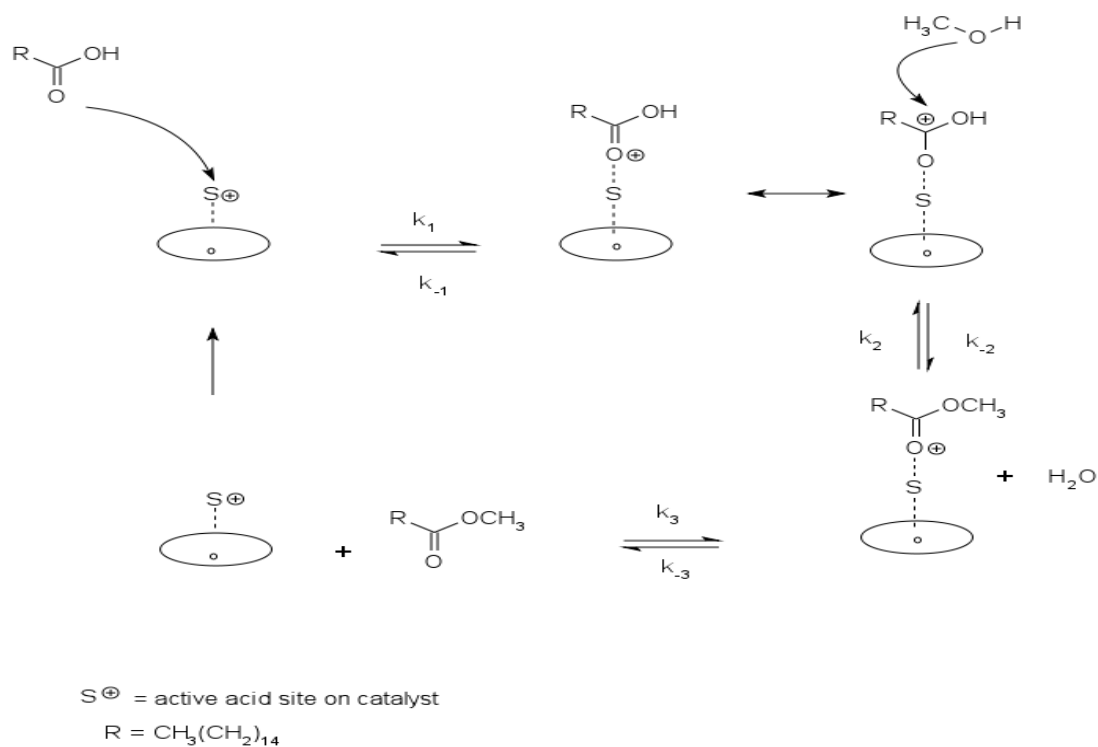


Figure 24 Illustration of palmitic acid esterification over  $SO_4/ZrO_2-550^{\circ}C$

### 3.3.5.2 Kinetics of palmitic acid esterification on $AcAl_2O_3$

In contrast to  $SO_4/ZrO_2-550^{\circ}C$ , the adsorption of methanol on an active site on the catalyst was the rate-limiting step in  $AcAl_2O_3$  indicating that the surface reaction and the desorption reactions were at equilibrium. The coefficients of determination for the model were 0.99, 0.96 and 0.98 for  $AcAl_2O_3$  at  $40^{\circ}C$ ,  $60^{\circ}C$  and  $80^{\circ}C$  respectively. Estimates of the kinetic parameters were determined and included in Table 9. Predictions of the palmitic acid conversions at 210 min and 240 min for  $40^{\circ}C$ ,  $60^{\circ}C$  and  $80^{\circ}C$  were in good agreement with the experimental data indicating that the model is indeed valid (Figure 25).



Table 9: Estimates of kinetic parameters for  $\text{AcAl}_2\text{O}_3$

Temperature	$\alpha \times 10^{-4}$	$K_1$	$K_3$	$K_2 \times 10^{-1}$
40°C	1.36	2.01	2.17	0.02
60°C	0.91	0.14	2.01	0.21
80°C	1.50	0.08	2.01	1.14

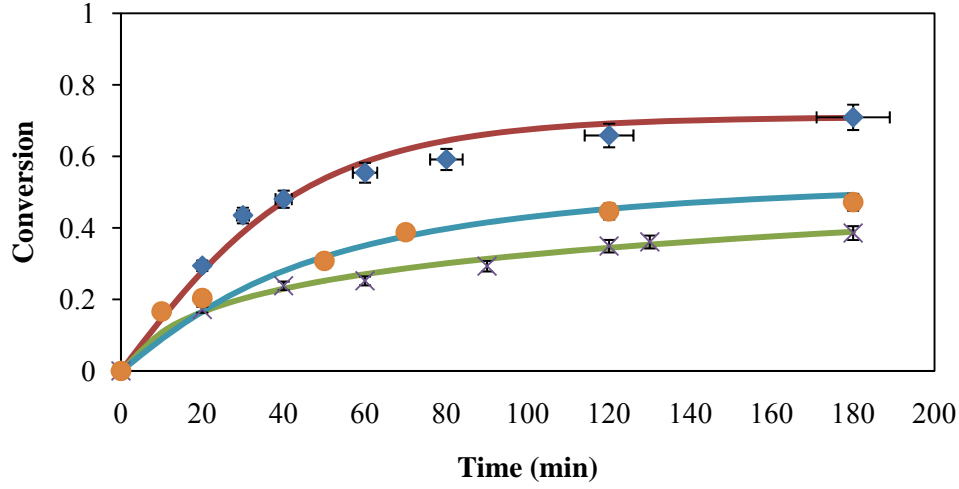


Figure 25: Conversion of palmitic acid over  $\text{AcAl}_2\text{O}_3$ . Experimental ( $\times$ ,  $\bullet$ ,  $\diamond$ ) and model ( $-$ ,  $-$ ,  $-$ ) at 40°C, 60°C and 80°C.

Based on the elementary reactions used in this model, the following reaction mechanism was proposed for palmitic acid esterification on  $\text{Al}_2\text{O}_3$  (Figure 26).

From the Arrhenius plot in Figure 27, the activation energy and the pre-exponential factor were determined to be 93.12 kJ/mol and  $7.27 \times 10^{14}$  respectively.

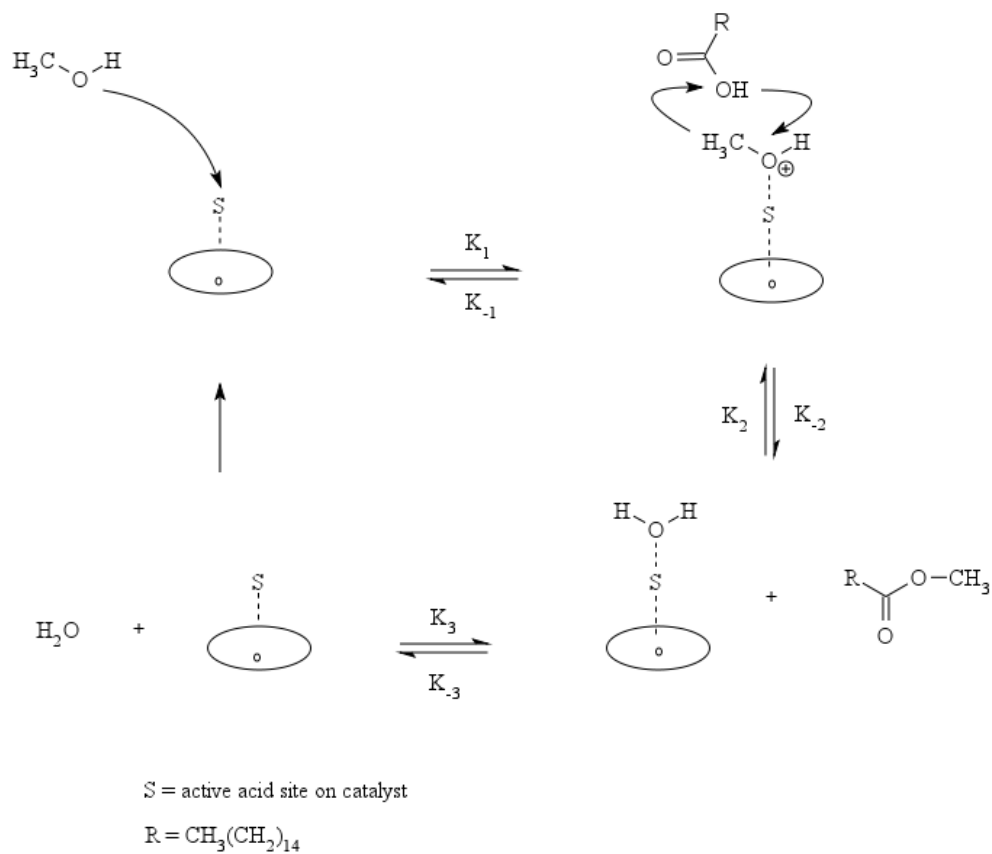


Figure 26: Illustration of palmitic acid esterification over  $\text{Al}_2\text{O}_3$

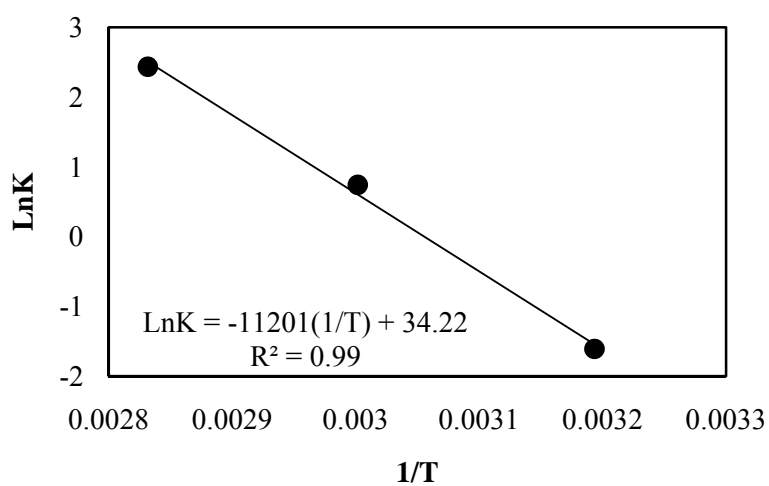


Figure 27: Arrhenius activation energy plot for  $\text{Al}_2\text{O}_3$

### 3.3.6 Transesterification of soybean oil

Heterogeneous acid catalysts have recently been used in the conversion of vegetable oil to biodiesel. The interest in this group of catalyst is mainly due to their ability to catalyze both the esterification of free fatty acids and the transesterification of triglycerides.

Sulfated zirconium oxide was tested on the transesterification of soybean oil at 98°C. The catalysts exhibited low fatty acid methyl ester yields (Table 10) compared to the high conversions observed for free fatty acid.

Table 10: Effect of treatment on transesterification activity

	$SO_4/ZrO_2$	$SO_4/ZrO_2-550^\circ C$	$SO_4/ZrO_2-650^\circ C$
Yield of fatty acid methyl ester	$31.39 \pm 0.18$	$25.82 \pm 1.31$	$25.04 \pm 1.66$

These lower fatty acid yields were probably due to the lower reaction temperature. Indeed, it has been shown that sulfated metal oxide catalysts can achieve high yields at high temperatures around 200°C (Di Serio et al., 2007; Furuta et al., 2004; Kiss et al., 2006; Kulkarni et al., 2006). In our case however, high temperature experiments were not possible due to the inability of our reactor to handle high temperatures.

Since sulfated metal oxides are very strong acids, it is unlikely that the protonation of the carbonyl group limited the overall reaction. In base catalyzed transesterification, an alkoxide (methoxide) is the nucleophile whereas in acid catalyzed transesterification, an alcohol (methanol) is the nucleophile. Given that an alcohol (ROH) is the conjugate acid of its corresponding alkoxide (RO<sup>-</sup>) and since for a given element, the negatively charged species are more nucleophilic than the equivalent neutral ones, a methoxide is a better nucleophile than an alcohol. Therefore, it is very likely that the low yields observed with

heterogeneous acid catalysts are due to the slow nucleophilic attack on the carbonyl group.

## Conclusion

In our study, sulfation and calcination was successful in increasing the activity of zirconium oxide support. Statistical analysis revealed that the effect of calcination was significant and explained well the total variation in wt % sulfur and in acidity. While  $\text{SO}_4/\text{ZrO}_2$ -550°C was efficient in the esterification palmitic acid at lower temperature, it appeared that higher temperatures were required for the transesterification of soybean oil.  $\text{SO}_4/\text{ZrO}_2$ -550°C was active in eight consecutive runs in the esterification of palmitic acid. The catalyst deactivation appeared to be due irreversible catalyst poisoning though further investigation is required to first confirm that the deactivation mechanism is catalyst poisoning and to elucidate the sources as well as the mechanism of deactivation. The kinetic study showed that the Eley-Rideal mechanism can be used to explain the esterification of palmitic acid on both  $\text{SO}_4/\text{ZrO}_2$ -550°C and  $\text{Al}_2\text{O}_3$ . The reaction of adsorbed palmitic acid with methanol in bulk fluid was the rate determining step for  $\text{SO}_4/\text{ZrO}_2$ -550°C. On the other hand, the adsorption of methanol on an active site on the catalyst was the rate determining step in  $\text{Al}_2\text{O}_3$ . This difference in adsorbed species was attributed the nature of the acid sites:  $\text{SO}_4/\text{ZrO}_2$ -550°C has mostly Brønsted acid sites whereas  $\text{Al}_2\text{O}_3$  has Lewis acid sites. The activation energy of  $\text{SO}_4/\text{ZrO}_2$ -550°C was 70.90 kJ/mol while that of  $\text{Al}_2\text{O}_3$  was 93.12 kJ/mol indicating that  $\text{SO}_4/\text{ZrO}_2$ -550°C is better in the esterification for free fatty acids.

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## Chapter four

### Production of biodiesel from sodium hydroxide zirconium oxide

N. Abdoulmoumine, F.A. Agblevor and L.E. Achenie

#### Abstract

Zirconium oxide properties as a catalyst support are well established. Sulfated zirconium oxide gained notoriety first for its zeolite-like superacidic nature but have since been used to catalyze reactions like the transesterification and the esterification of fatty acids to biodiesel. Biodiesel is a promising renewable alternative to petroleum derived diesel. While, acidic catalyst can be used for biodiesel production, their slower reaction rate usually discourages their use unless dictated by the feedstock. In this chapter, sodium hydroxide supported on zirconium oxide as heterogeneous base catalysts for biodiesel production are reported for the first time.

Sodium hydroxide solutions with concentrations of 0.5M, 1.0M and 1.5M and activation temperatures of 400°C, 500°C and 600°C were used to investigate the effect of sodium hydroxide concentrations and activation temperatures on the catalyst activity.  $\text{ZrO}_2$  impregnated with 1.0M and 1.5M NaOH and activated at 500°C and 600°C produced fatty acid methyl ester yield with the highest ester content of 90.2% achieved at 1.5M NaOH and 600°C. The fatty acid methyl ester content increased with increasing amount of catalyst and methanol molar ratio. The catalyst was able to catalyze the reaction in four consecutive runs before losing its activity permanently. Furthermore, a mixture of 30% sulfated zirconium oxide with this catalyst was able to effectively convert soybean oil containing 5% oleic acid.

The kinetics of 1.5 M NaOH/ $\text{ZrO}_2$ -600°C catalyzed methanolysis of soybean oil was investigated at 60°C, 88°C and 98°C. The reaction was first order with respect to triglyceride and second order with respect to methanol. The activation energy was 49.35 kJ/mol. Eleven models based on Langmuir-Hinshelwood and Eley-Rideal kinetics were investigated and the mechanism obeyed Langmuir-Hinshelwood kinetics with the adsorption of triglycerides as the rate determining step.

Keywords: Sodium hydroxide zirconium oxide, Biodiesel, Transesterification

## 4.1 Introduction

Energy is a fundamental commodity that is required by any industrialized nation. It is now known that the global fossil fuel reserves are shrinking and forecasted to be depleted in the near future while the world energy demand increases every year. Concurrently, the staggering evidence of global warming is mandating the reduction of green house gases emission into the atmosphere. These two facts combined have provided a strong motivation for the search and development of environmentally friendly alternative fuels that can guarantee continued energy supply. Since its birth, vegetable oil was always considered as a suitable fuel for the diesel engine (Knothe et al., 2005). When vegetable oil is transesterified, one of the products, commonly referred to as biodiesel, is known to produce diesel fuel with superior properties relative to petroleum diesel. Biodiesel is biodegradable and reduces the net emission of CO<sub>2</sub> if produced sustainably (Kulkarni and Dalai, 2006). Its physical and chemical properties as well as emission profile are in general better than petroleum diesel except for high NO<sub>x</sub> content observed for biodiesel (Demirbas, 2009).

Biodiesel is produced through the alcoholysis of triacylglycerols from plant or animal source with an alcohol, usually a short-chain alcohol like methanol or ethanol in the presence of an acid or base catalyst according the reaction depicted in Figure 28. The products of the reaction in Figure 28 are glycerol and fatty acid alkyl ester, namely biodiesel.

Homogeneous base catalysis is the most common catalytic method used for biodiesel production because of the fast reaction rate and mild reaction temperatures. However,

when homogeneous base catalysis is used, extensive washing is required to remove the dissolved catalyst and to achieve fuel grade quality.

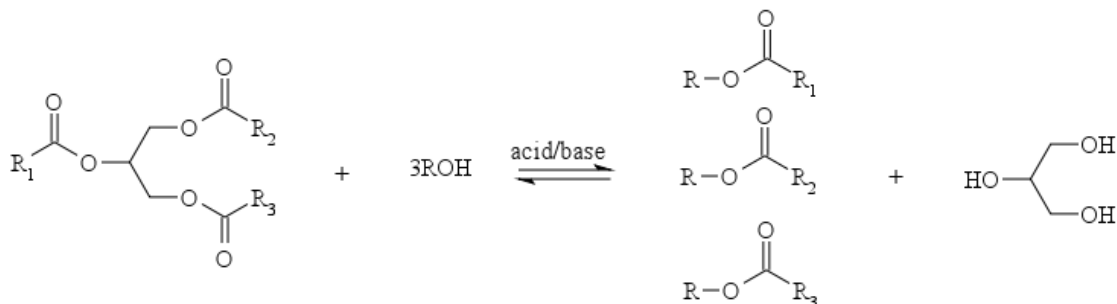


Figure 28: Transesterification of triacylglycerol with an alcohol via acid or base catalysis

In addition, homogeneous base catalysis does not promote catalyst reusability and requires acid neutralization in between steps increasing the overall chemical consumption. These drawbacks can be overcome by heterogeneous catalysis. In recent years, many publications in the area of heterogeneous catalysis for the transesterification of vegetable oil have been published. Of these publications, only a handful investigated the kinetics of transesterification and even fewer investigated the reaction mechanism of model compounds over heterogeneous base catalysts. However, little is known about the kinetics and the reaction mechanism of soybean oil transesterification over base catalysts. In this chapter, base catalysts of sodium hydroxide supported on zirconium oxide were synthesized for the first time to the best of our knowledge. First, the effects of the concentration the sodium hydroxide solution as well as the calcination temperature on the catalyst activity and physical properties were investigated. Second, the effect of the

methanol to oil molar and catalyst to oil ratios were established. Finally, the kinetics of soybean oil transesterification was studied on the best catalyst.

## **4.2 Materials and Methods**

Zirconium dioxide ( $\text{ZrO}_2$ ) was obtained from Alfa Aesar (Alfa Aesar, Ward Hill, MA). Oleic acid was purchased from Sigma Aldrich (Sigma Aldrich, St. Louis, MO). Methyl ester of palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid were obtained from Restek (Restek, Bellefonte, PA) and used as standards. Sodium hydroxide, methanol, n-hexane and acetonitrile were all purchased from Fischer Scientific (Fischer Scientific, Fair Lawn, NJ). All solvents used in this work were analytical grade and were used as received. Kroger brand soybean oil was purchased from the local Kroger grocery store (South Main Street, Kroger Store, Blacksburg, VA).

### **4.2.1 Catalyst preparation**

Before treatment,  $\text{ZrO}_2$  was ground to pass through a 20 mesh sieve before usage. Three solutions of sodium hydroxide with 0.5 M, 1.0 M and 1.5 M concentrations were used for the impregnation in order to determine the effect of solvent concentration on catalyst properties. The catalyst support,  $\text{ZrO}_2$ , and the appropriate solution of sodium hydroxide were mixed at the ratio of 1g of catalyst for 15ml of sodium hydroxide solution. The mixture was stirred overnight then the solution was filtered to obtain the residual catalyst. The resulting catalyst was dried at  $100^\circ\text{C}$  overnight and ground again to pass through a 20 mesh sieve. The dried but uncalcined catalysts are referred to as 0.5 M NaOH/ $\text{ZrO}_2$ , 1.0 M NaOH/ $\text{ZrO}_2$  and 1.5 M NaOH/ $\text{ZrO}_2$  for 0.5 M, 1.0 M and 1.5 M sodium hydroxide

respectively. Samples of these dried catalysts were further calcined at 400°C, 500°C and 600°C for 6h to investigate the effect of temperature treatment. These calcined catalysts are referred to as 0.5 M NaOH/ZrO<sub>2</sub>-400°C, 0.5 M NaOH/ZrO<sub>2</sub>-500°C and 0.5 M NaOH/ZrO<sub>2</sub>-600°C when derived from 0.5M NaOH/ZrO<sub>2</sub>, 1.0 M NaOH/ZrO<sub>2</sub>-400°C, 1.0 M NaOH/ZrO<sub>2</sub>-500°C and 1.0 M NaOH/ZrO<sub>2</sub>-600°C when derived from 1.0M NaOH/ZrO<sub>2</sub> and finally 1.5 M NaOH/ZrO<sub>2</sub>-400°C, 1.5 M NaOH/ZrO<sub>2</sub>-500°C and 1.5 M NaOH/ZrO<sub>2</sub>-600°C when derived from 1.5M NaOH/ZrO<sub>2</sub>.

#### **4.2.2 Catalyst characterization**

The effect of impregnation on the catalyst physical properties was characterized by scanning electron microscopy (FEI Quanta 600 FEG, Physical Electronics, Chanhassen, MN) with energy dispersive x-ray spectroscopy to determine the bulk elemental composition. The SEM-EDS was operated at 20keV for the elemental analysis. For surface imaging, the electron beam energy was reduced to 5keV and a spot size of 5nm was used. The catalyst BET surface area analysis was performed by a surface area and porosity analyzer (ASAP 2000, Micromeritics Norcross, GA) under nitrogen at 77K. The basicity of the catalysts was measured by colorimetric titration. For each titration, 1g of the catalyst was soaked in 10ml of deionized water and stirred for one hour. The slurry was then titrated with 0.01M HCl with phenolphthalein as indicator. The basicity is reported as mmol HCl per g catalyst. The effects of NaOH concentration (0.5M, 1.0M and 1.5M) and calcination temperature (400°C, 500°C and 600°C) on mean % wt NaOH adsorbed and mean basicity (mmol HCl/g catalyst) were investigated by a two factor analysis of variance of balanced, complete factorial design with 3 observations per

treatment for NaOH absorbed and 2 observations per treatment for basicity. The statistical analysis software, JMP, was used to perform the analysis (JMP, 2008). If necessary, Tukey-Kramer HSD was used for multiple comparisons (Sall et al., 2001).

### 4.2.3 Vegetable oil characterization

The Kroger brand soybean oil was first analyzed for acid number by ASTM D664. The moisture content was determined by Karl Fischer titration using a Metrohm 701KF Titrino titrator and 703 titration stand (Brinkmann Instruments Inc., New York, NY). The fatty acid composition of the soybean oil was determined by gas chromatography on Shimadzu GC-14A previously described.

### 4.2.4 Transesterification of soybean oil

The transesterification of soybean oil was carried out in a shaker bath maintained at 170 rpm (Precision Scientific, Model 25, Chicago, Illinois). The reaction mixture was placed in a crimp top glass bottle fitted with a rubber stopper and an aluminum seal. The European standard, EN14103, was used with palmitic acid instead methyl heptadecanoate as internal standard. The methyl ester peaks were confirmed by running a mixture of five fatty acid methyl ester standard obtained from Restek (Restek, Bellefonte, PA) and comparing the retention times. The biodiesel content, expressed as a mass fraction in percent, is given by the equation below:

$$C = \frac{(\sum A)}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$

Where

*C is mass fraction of fatty acid ester, in %, in sample*

$\sum A$  is the total peak area from the methyl esters

$A_{EI}$  is the peak area of the palmitic acid

$C_{EI}$  is the concentration, in milligrams per milliliter, of palmitic acid

$V_{EI}$  is the volume, in milliliter, of palmitic acid solution

m is the mass, in milligrams, of sample

The reaction mixture was analyzed on a Shimadzu GC14A (Shimadzu, Columbia, MD) equipped with a flame ionization detector or FID and a FAME column (Rtx-225, 30m, 0.25mm, 0.25um, Restek, Bellefonte, PA). The GC inlet and detector temperature were maintained at 220°C and 300°C respectively.

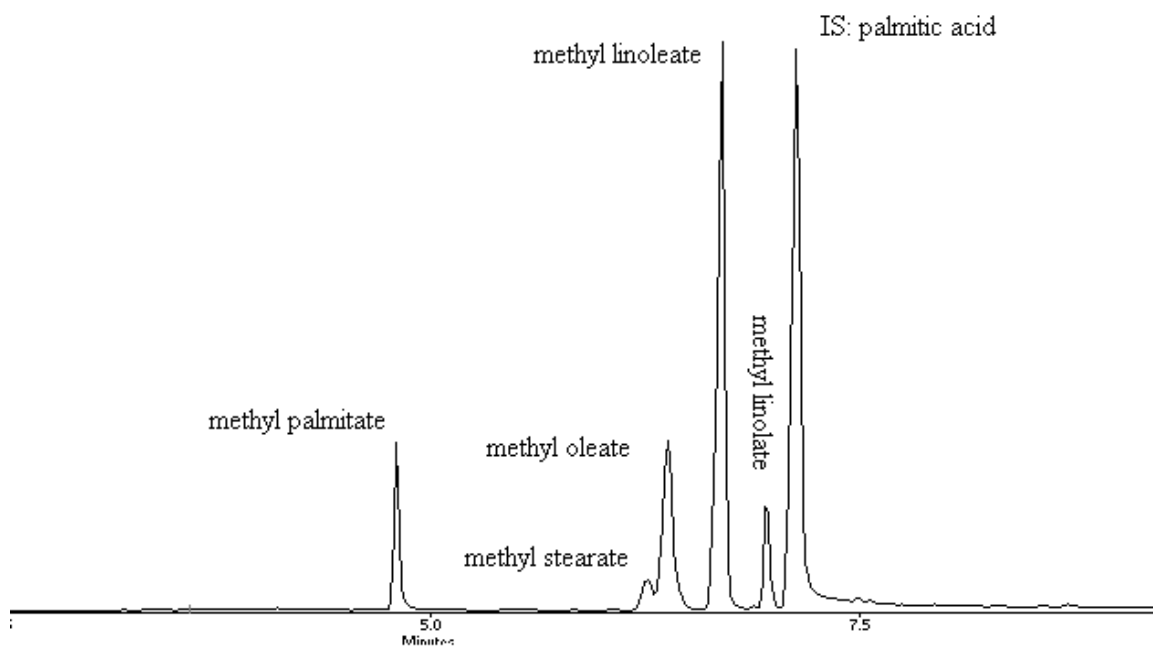


Figure 29: Typical biodiesel chromatograph depicting five fatty acid methyl ester and the internal standard

#### **4.2.5 Esterification of free fatty acids in soybean oil**

Oleic acid was mixed with soybean oil at 20% and 5 % (w/w) to mimic the composition of used vegetable oil.  $\text{SO}_4/\text{ZrO}_2$ -550°C and 1.5 M NaOH/ $\text{ZrO}_2$ -600°C were used conjointly as acid and base catalysts to attempt to selectively convert the free fatty acids by esterification and the triglycerides by transesterification. The acid-base solid catalysts ratios were studied: 0:100, 10:90, 20:80 and 30:70. The reaction mixture was analyzed by HPLC and GC to determine the conversion of oleic acid and overall biodiesel yield respectively. The HAISIL C18 column used in these experiments only detected free fatty acids under our analysis conditions but not the methyl ester or the triglycerides. Therefore, we selectively monitored the conversion of oleic acid via high liquid chromatography and the total fatty acid methyl ester by gas chromatography. The GC analysis was previously described in detail in 4.2.4 Transesterification of soybean oil. The HPLC analysis was performed on a Shimadzu HPLC 10 AVP (Shimadzu Scientific, Columbia, MD) equipped with an evaporative light scattering detector (ELSD-LT) and a HAISIL 300 C18 5 $\mu\text{m}$  column (Higgins Analytical, Mtn View, CA). The analysis was carried out in the isocratic mode and the mobile phase consisted of 100% acetonitrile (mobile phase A) and 99.9% water/0.1% acetic acid (mobile phase B). The total flow rate was 1.0ml/min with 85% phase A and 15% phase B.

#### **4.2.6 Catalyst evaluation**

The twelve catalysts prepared by impregnation with three different concentrations of sodium hydroxide and by calcination at three different temperatures were evaluated on their activity toward transesterification. The activity toward transesterification was



accessed for catalysts at the same reaction conditions, 98°C, 3 hours and 170 rpm using the same procedure described in section 4.2.4. The effects of sodium hydroxide concentration (0.5M, 1.0M and 1.5M) and calcination temperature (400°C, 500°C and 600°C) on ester content were investigated by a two factor analysis of variance of balanced, complete factorial design with three observations per treatment. The statistical analysis software, JMP, was used to perform the analysis (JMP, 2008). If necessary, Tukey-Kramer HSD was used for multiple comparisons (Sall et al., 2001).

#### **4.2.7 Catalyst life**

The catalyst life was investigated by following the change in ester content when 1.5 M NaOH/ZrO<sub>2</sub>-600°C was reused consecutively without temperature regeneration in between runs. After each cycle, the catalyst was washed and reused until the ester content was near zero. The wash step consisted of rinsing the recovered catalyst with 10 ml of hexane followed by a drying step at 80°C in a vacuum oven for one hour to evaporate the residual hexane. The catalyst was then weighed and the masses of soybean oil and methanol were adjusted to ensure that catalyst mass was 10 wt % of the soybean oil for all experiments. The reaction conditions (98°C, 1:6 oil to methanol molar ratio, 10 wt % catalyst, 3 hours reaction time and 170 rpm) were maintained constant throughout the experiment. When no activity was detected, the catalyst was washed again and calcined at 500°C in furnace for 3 hours before reuse. If the activity was restored, the experiment was repeated until the catalyst was permanently deactivated after temperature regeneration.

## 4.2.8 Kinetics of soybean oil transesterification

The kinetics of soybean oil transesterification on 1.5 M NaOH/ZrO<sub>2</sub>-600°C was investigated at 60°C, 88°C and 98°C. The reaction order, mechanism and activation energy were determined as described below.

### 4.2.8.1 Investigation of the reaction order

The approach in investigating the reaction order was previously reported by Singh et al (2007). It is well established that the transesterification reaction is reversible as shown in Figure 28. Consequently the general rate equation could be written as:

$$\frac{-dC_T}{dt} = kC_T^\alpha C_M^\beta$$

Where  $C_T$  represents the concentration of triglycerides and  $C_M$  the concentration of methanol and  $\alpha$  and  $\beta$  represent the reaction order with respect to triglycerides and methanol. We can express the general rate equation in terms of conversion.

$$C_T = C_{T_0}(1 - X)$$

$$C_M = C_{T_0} \left( \frac{C_{M_0}}{C_{T_0}} - 3X \right)$$

$$\frac{dX}{dt} = kC_{T_0}^{(\alpha+\beta-1)}(1 - X)^\alpha \left( \frac{C_{M_0}}{C_{T_0}} - 3X \right)^\beta$$

Where  $C_{T_0}$  is the initial concentration of triglycerides and  $C_{M_0}$  is the initial concentration of methanol. Since most kinetic investigation of vegetable oil transesterification reported either zero, first or second, it was first assumed that the reaction order of triglyceride and methanol could be zero, first or second order and that the overall reaction order must be

equal to or less than three ( $\alpha + \beta \leq 3$ ). The reaction order was determined by non-linear least square analysis using Polymath.

#### 4.2.8.2 Investigation of the reaction mechanism

The Langmuir-Hinshelwood approach was used in deriving the rate laws for modeling purposes (Fogler, 2006). Briefly, this approach consists of choosing a rate determining step (RDS) from a sequence of elementary reactions and assuming that all remaining elementary steps are quasi equilibrated. The rate determining step is far from its equilibrium therefore its rate controls the overall catalytic reaction rate. The quasi-equilibrated steps are then used to eliminate intermediate species that could not be measured. The rate laws obtained by this approach are then used to deduce the most probable rate law by nonlinear least squares regression analysis.

The nonlinear least squares regression analysis was performed on the Polymath software (Polymath, 2010) and the kinetic parameters were estimated by minimizing the objective function  $S$  using the Levenberg-Marquardt algorithm.

$$S = \sum_{n=1}^N (n_{SBO,n} - \hat{n}_{SBO,n})^2 \rightarrow \delta_{min}$$

Where is  $n_{SBO,n}$  the  $n$ th experimental number of moles of soybean oil and  $\hat{n}_{SBO,n}$  the corresponding estimate,  $N$  is the total number of experimental values and  $\delta$  is the parameter column vector.

Discrimination between models was conducted in several parts. First, the physical meaning and correctness of the estimates were first considered. In the case of the rate constants for example, all models yielding negative values within the confidence interval are automatically eliminated. Second the distribution of residuals was analyzed. If the

nonlinear regression model represented the experimental kinetic data correctly, the residuals will be randomly distributed around the line that represent  $\mu = 0$ . When an inappropriate model is used, the residual plot will show a clear trend like a linear trend. Models displaying this behavior were eliminated on statistical ground. Third, the confidence interval was considered as a large interval can not only produce negative parameters but are usually indication of an unstable model. An unstable model may yield very inaccurate values and absurd results for even a small range of extrapolation. In such cases, the parameters with the large confidence interval are often unnecessary in the model and could be removed to see if they are indeed significant. Once the regression results have been processed according to the procedures described above and if the models converge, model selection is done based on the coefficient of determination and residual sum of squares. If two coefficients of determinations are similar, the residual sum of squares is used to choose the best model.

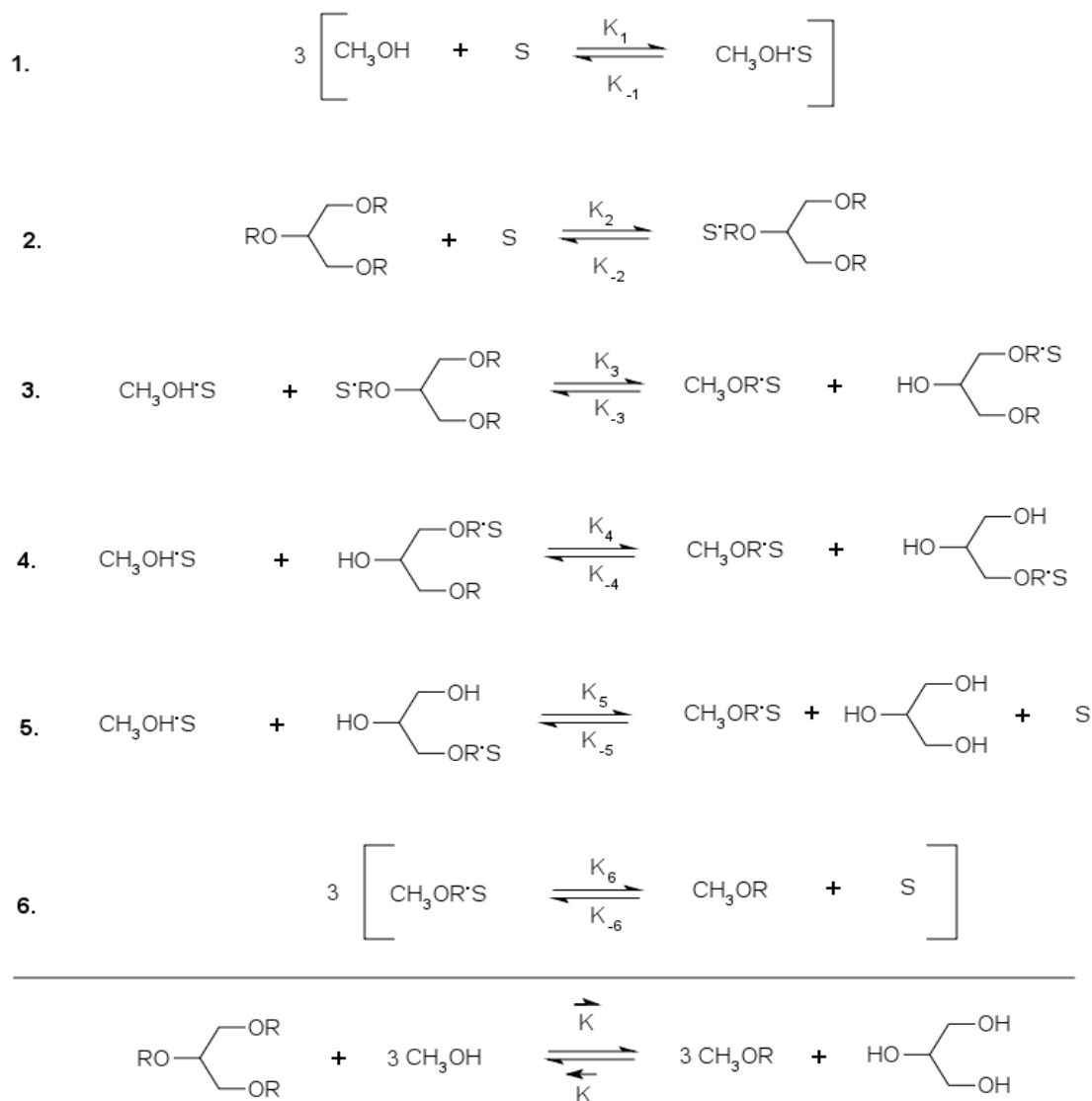
#### **4.2.8.2.1 Mechanism based on Langmuir-Hinshelwood kinetics**

Since Langmuir-Hinshelwood mechanism has been successfully used to model the reaction kinetics of numerous heterogeneous system, our first mechanism was based on this well-tested mechanism. Previously, Langmuir-Hinshelwood mechanism was used to model the transesterification of ethyl acetate (Dossin et al., 2006). Our proposed mechanism of triacylglycerol transesterification is composed of 6 elementary reactions. The following assumptions were made in deriving the rate laws used in the kinetic modeling of the mechanism of transesterification on 1.5 M NaOH/ZrO<sub>2</sub> catalyst:

1. There was no internal and external mass transfer limitation in the system

2. Diacylglycerol and monoacylglycerol intermediates were adsorbed on an vacant active site.
3. Several authors monitored the concentrations of diacylglycerol and monoacylglycerol and showed that these intermediate rapidly disappear as evidence by concentrations much lower than that of the triacylglycerol (Freedman et al., 1986; Karmee, 2006; Nouredini, 1997; Veljkovic et al., 2009). Based on these observations, it was appropriate to use include simplification of most and least abundant reactive intermediates in the active site balance.
  - a. Adsorbed methanol and methyl ester were assumed to be the most abundant reactive intermediates (MARI).
  - b. Diacylglycerol and monoacylglycerol intermediates were assumed to be the least abundant reactive intermediates and were therefore eliminated from the active site balance.
4. Glycerol was not adsorbed on vacant active sites.

Based on the elementary reactions depicted in Figure 30 and the assumptions above, the rate laws in Table 11 were derived and in the investigation of the reaction mechanism by computational modeling.



S = a vacant active site

R = fatty acid

Figure 30: Six steps reaction mechanism based on the Langmuir-Hinshelwood model for the transesterification of soybean oil over NaOH/ZrO<sub>2</sub>

Table 11: Transesterification kinetic models based on Langmuir-Hinshelwood kinetics

Model #1	Rate determining step	Rate law
1	Methanol adsorption	$\frac{Lk_1 \left( N_A - \frac{N_F^{1/3} N_C}{K^{1/3} K_1^{2/3} K_6^{2/3} N_B^{1/3}} \right)}{1 + \frac{K_1^{1/3} N_F^{1/3} N_C}{K^{1/3} K_6^{2/3} N_B^{1/3}} + K_2 N_B + \frac{N_C}{K_6}}$
2	Triglyceride adsorption	$\frac{Lk_2 \left( N_B - \frac{N_C^3 N_F}{K K_1^2 K_6^2 N_A^3} \right)}{1 + K_1 N_A + \frac{K_2 N_C^3 N_F}{K K_1^2 K_6^2 N_A^3} + \frac{N_C}{K_6}}$
3	Adsorbed methanol and adsorbed triglyceride	$\frac{Lk_3 K_1 K_2 \left( N_A N_B - \frac{N_C^3 N_F}{K K_1^2 K_6^2 N_A^2} \right)}{\left( 1 + K_1 N_A + K_2 N_B + \frac{N_C}{K_6} \right)^2}$
4	Adsorbed methanol and adsorbed diglyceride	$\frac{Lk_{-4} \left( \frac{K K_1 N_A^2 N_B}{N_C} - \frac{N_C^2 N_F}{K_1 K_6^2 N_A} \right)}{K_5 \left( 1 + K_1 N_A + K_2 N_B + \frac{N_C}{K_6} \right)^2}$
5	Adsorbed methanol and monoglyceride	$\frac{Lk_{-5} \left( \frac{K K_1^2 K_6 N_A^3 N_B}{N_C^2} - \frac{N_C N_F}{K_6} \right)}{\left( 1 + K_1 N_A + K_2 N_B + \frac{N_C}{K_6} \right)^2}$
6	Methyl ester desorption	$\frac{Lk_{-6} \left( \frac{K^{1/3} K_1^{2/3} K_6^{2/3} N_A N_B^{1/3}}{N_F^{1/3}} - N_C \right)}{1 + K_1 N_A + K_2 N_B + \frac{K^{1/3} K_1^{2/3} N_A N_B^{1/3}}{K_6^{1/3} N_F^{1/3}}}$

#### 4.2.8.2.2 Mechanism based on Eley-Rideal kinetics

The reaction mechanism of transesterification of ethyl acetate over solid base catalysts was previously shown to obey Eley-Rideal kinetics (Dossin et al., 2006; Hattori et al.,

2000). Consequently, a mechanism composed of five elementary reactions was proposed in the present work and is illustrated in Figure 31.

The following assumptions were considered in the deriving the rate laws:

1. There was no internal and external mass transfer limitation in the system
2. Only methanol is adsorbed on the surface

Based on this mechanism, five governing rate laws were derived and shown in Table 12.

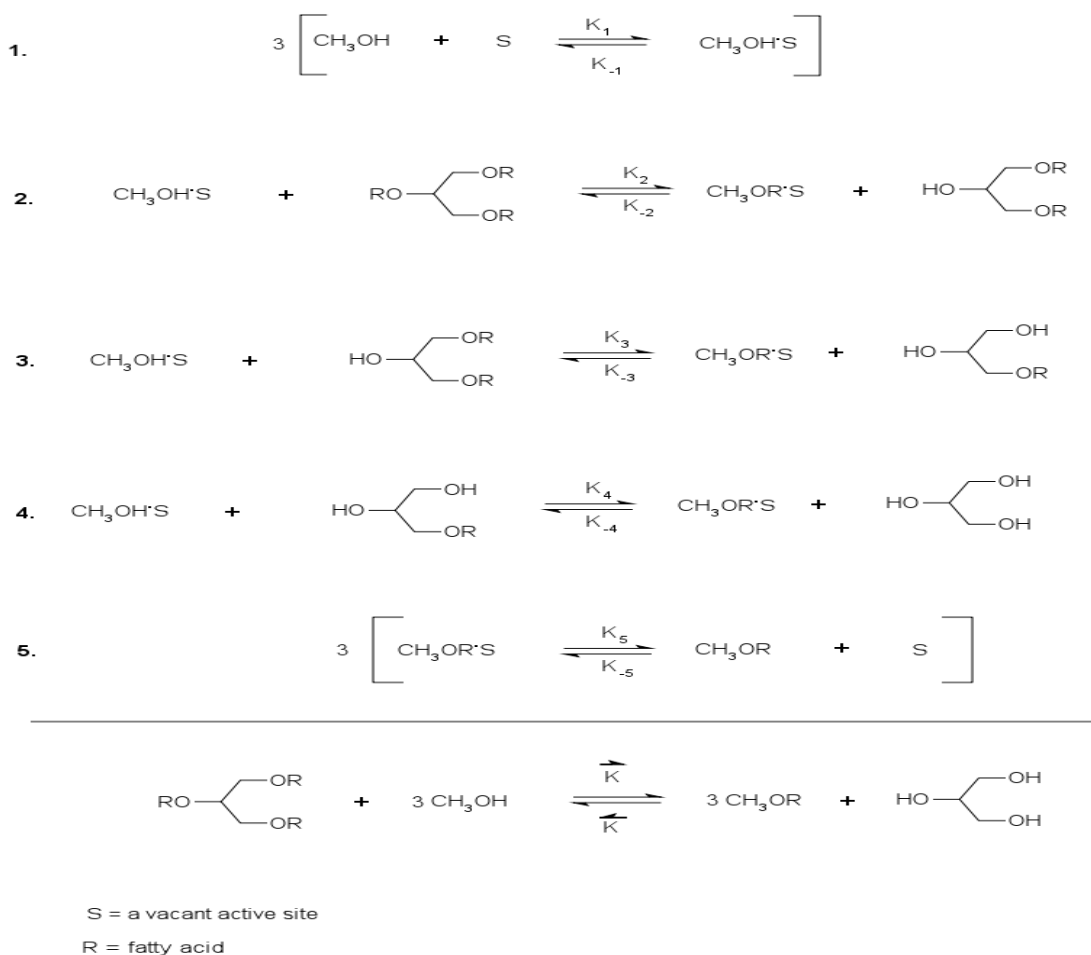


Figure 31: Five steps reaction mechanism based on the Eley Rideal model for the transesterification of soybean oil over NaOH/ZrO<sub>2</sub>



Table 12: Transesterification models based on Eley Rideal kinetics

Model #	Rate determining step	Rate law
7	Methanol adsorption	$\frac{Lk_1 \left( N_A - \frac{N_C N_F^{1/3}}{K^{1/3} K_1^{2/3} K_5^{2/3} N_B^{1/3}} \right)}{1 + \frac{K_1^{1/3} N_C N_F^{1/3}}{K^{1/3} K_5^{2/3} N_B^{1/3}} + \frac{N_C}{K_5}}$
8	Triglyceride and adsorbed methanol	$\frac{Lk_2 K_1 \left( N_A N_B - \frac{N_C^3 N_F}{K K_1^2 K_5^2 N_A^2} \right)}{1 + K_1 N_A + \frac{N_C}{K_5}}$
9	Diglyceride and adsorbed methanol	$\frac{Lk_3 K_2 \left( \frac{K_1^2 K_5 N_A^2 N_B}{N_C} - \frac{N_C^2 N_F}{K K_5 N_A} \right)}{1 + K_1 N_A + \frac{N_C}{K_5}}$
10	Monoglyceride and adsorbed methanol	$\frac{Lk_{-4} \left( \frac{K K_1^2 K_5 N_A^3 N_B}{N_C^2} - \frac{N_C N_F}{K_5} \right)}{1 + K_1 N_A + \frac{N_C}{K_5}}$
11	Methyl ester desorption	$\frac{Lk_{-5} \left( \frac{K^{1/3} K_1^{2/3} K_5^{2/3} N_A N_B^{1/3}}{N_F^{1/3}} - N_C \right)}{1 + K_1 N_A + \frac{K^{1/3} K_1^{2/3} N_A N_B^{1/3}}{K_5^{1/3} N_F^{1/3}}}$

### 4.3 Results and discussion

Impregnation is a simple and effective method that consists of soaking a catalyst support in solution of a desired catalytic agent. Using this method and sulfuric acid as a catalytic agent, zirconium oxide has been previously used to successfully generate a very acidic heterogeneous catalyst, namely sulfated zirconium oxide for the esterification and/or the

transesterification of vegetable oil to biodiesel. Consequently, this approach was adopted to impregnate sodium hydroxide on zirconium oxide thus producing a basic heterogeneous catalyst that can be utilized for the transesterification of soybean oil. We investigated the effect of the concentration of sodium hydroxide and the calcination temperature on the properties of the catalysts.

### 4.3.1 Catalyst characterization

In the general, SEM-EDS analysis showed the NaOH adsorbed on  $\text{ZrO}_2$  was lower at 400°C and 600°C and higher at 500°C for all catalysts with the highest NaOH adsorption observed for 1.5M NaOH/ $\text{ZrO}_2$ -500°C. The NaOH adsorbed for uncalcined catalysts was similar to that measured for catalysts calcined at 400°C for 1.0M and 1.5M NaOH. However, catalysts calcined at 500°C and 600°C yielded similar or higher NaOH adsorbed for all levels of NaOH concentration.

Table 13: SEM-EDS Elemental Composition of 0.5M NaOH/ $\text{ZrO}_2$  catalysts

	$\text{ZrO}_2$	$\text{NaOH-ZrO}_2^{\text{ab}}$	$\text{NaOH-ZrO}_2$ 400°C <sup>a</sup>	$\text{NaOH-ZrO}_2$ 500°C <sup>b</sup>	$\text{NaOH-ZrO}_2$ 600°C <sup>b</sup>
<b>Zr</b>	72.82±3.21	69.22 ± 7.78	78.25 ± 2.62	71.87 ± 4.03	70.88 ± 2.56
<b>O</b>	22.44±4.63	24.62 ± 3.26	19.56 ± 2.40	23.97 ± 3.05	24.43 ± 1.40
<b>C</b>	4.73±1.37	4.61 ± 4.09	1.91 ± 0.29	2.44 ± 0.26	3.07 ± 1.15
<b>Na</b>	NA	1.37 ± 0.31	0.48 ± 0.24	1.72 ± 0.80	1.63 ± 0.54

The basicity of uncalcined catalysts was lower than that of calcined catalysts for all treatment levels as illustrated in Table 16, Table 17 and Table 18. Calcination at 400°C, 500°C and 600°C produced a trend similar to that observed for wt % NaOH adsorbed

indicating that the basicity was generated by the adsorbed NaOH as a result of the impregnation and calcination treatment. The basicity was lower at 400°C and 600°C and higher at 500°C. The lower basicity of NaOH/ZrO<sub>2</sub> could indicate that basicity is not solely generated by impregnation but rather the interaction between impregnation and calcination.

Table 14: SEM-EDS Elemental Composition of 1.0M NaOH/ZrO<sub>2</sub> catalysts

	<b>ZrO<sub>2</sub></b>	<b>NaOH-rO<sub>2</sub><sup>ab</sup></b>	<b>NaOH-ZrO<sub>2</sub> 400°C<sup>a</sup></b>	<b>NaOH-ZrO<sub>2</sub> 500°C<sup>b</sup></b>	<b>NaOH-ZrO<sub>2</sub> 600°C<sup>b</sup></b>
<b>Zr</b>	72.82±3.21	73.27 ± 5.43	72.55 ± 1.08	70.91 ± 4.04	72.54 ± 5.68
<b>O</b>	22.44±4.63	22.42 ± 4.65	22.95 ± 0.59	24.47 ± 3.09	23.10 ± 4.70
<b>C</b>	4.73±1.37	2.57 ± 0.24	2.80 ± 0.56	2.63 ± 0.32	2.80 ± 0.20
<b>Na</b>	NA	1.76 ± 0.79	1.70 ± 0.11	1.99 ± 0.71	1.57 ± 0.96

Table 15: SEM-EDS Elemental Composition of 1.5M NaOH/ZrO<sub>2</sub> catalysts

	<b>ZrO<sub>2</sub></b>	<b>NaOH-ZrO<sub>2</sub><sup>a</sup></b>	<b>NaOH-ZrO<sub>2</sub> 400°C<sup>a</sup></b>	<b>NaOH-ZrO<sub>2</sub> 500°C<sup>a</sup></b>	<b>NaOH-ZrO<sub>2</sub> 600°C<sup>a</sup></b>
<b>Zr</b>	72.82±3.21	75.44 ± 2.17	74.81 ± 1.53	70.44 ± 4.61	71.68 ± 1.33
<b>O</b>	22.44±4.63	20.80 ± 1.59	21.40 ± 1.15	24.00 ± 2.81	23.72 ± 0.99
<b>C</b>	4.73±1.37	2.35 ± 0.15	2.29 ± 0.15	2.55 ± 0.25	2.43 ± 0.12
<b>Na</b>	NA	1.41 ± 0.49	1.51 ± 0.23	3.01 ± 1.72	2.18 ± 0.35

Table 16: Basicity of 0.5M NaOH/ZrO<sub>2</sub> catalysts

	<i>ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub>-400°C</i>	<i>NaOH/ZrO<sub>2</sub>-500°C</i>	<i>NaOH/ZrO<sub>2</sub>-600°C</i>
Basicity (mmol HCl/g catalyst)	0	0.293	0.400	0.433	0.365
Standard deviation	0	0.0035	0.0042	0.0042	0.0071

Table 17: Basicity of 1.0M NaOH/ZrO<sub>2</sub> catalysts

	<i>ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub>-400°C</i>	<i>NaOH/ZrO<sub>2</sub>-500°C</i>	<i>NaOH/ZrO<sub>2</sub>-600°C</i>
Basicity (mmol HCl/g catalyst)	0	0.288	0.424	0.415	0.388
Standard deviation	0	0.0014	0.0071	0.0148	0.0113

Table 18: Basicity of 1.5 M NaOH/ZrO<sub>2</sub>

	<i>ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub></i>	<i>NaOH/ZrO<sub>2</sub>-400°C</i>	<i>NaOH/ZrO<sub>2</sub>-500°C</i>	<i>NaOH/ZrO<sub>2</sub>-600°C</i>
Basicity (mmol HCl/g catalyst)	0	0.296	0.537	0.531	0.457
Standard deviation	0	0.0007	0.0035	0.004	0.032

The surface area analysis of the treated catalyst showed that the BET surface area decreased gradually as the calcination temperature increased as illustrated in Figure 32 . It has been reported that zirconium oxide crystallizes at or near 450°C (Srinivasan et al., 1992). Therefore, the calcination at 100°C and 400°C would yield amorphous catalysts whereas calcination at 500°C and 600°C would produce crystalline catalysts. Since amorphous catalysts usually have higher surface area than their crystalline counterpart, the crystallization of the catalyst at higher calcination temperature resulted in the decrease in surface area. Before the crystallization, more amorphous catalysts were produced explaining similarity between the surface areas of the uncalcined catalyst (NaOH/ZrO<sub>2</sub>) and the catalyst calcined at 400°C (NaOH/ZrO<sub>2</sub>-400°C) when compared to the untreated ZrO<sub>2</sub>. At higher calcination temperature however, more crystalline catalysts were produced accounting for the significant decrease in surface area at 500°C and 600°C. It appeared that NaOH impregnation did not shift the crystallization temperature

of zirconium oxide upward as has been reported previously for sulfated zirconium oxide (Arata, 1996; Arata and Hino, 1990; Corma, 1995). Furthermore, the surface area appeared to be affected only by the calcination temperature.

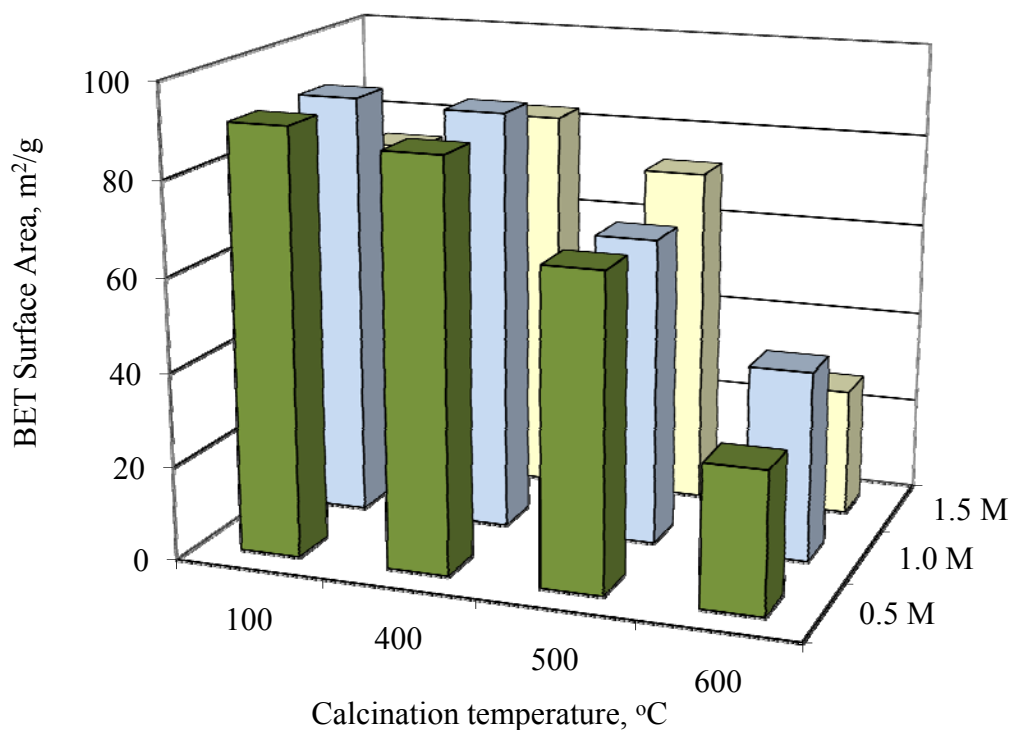


Figure 32: BET surface area of NaOH/ZrO<sub>2</sub> catalysts

#### 4.3.1.1 Effect of sodium hydroxide concentration and calcination temperature on NaOH adsorbed on NaOH/ZrO<sub>2</sub>

The interaction effects between the levels of NaOH concentrations (0.5M, 1.0M and 1.5M) and the levels of calcination temperature (400°C, 500°C and 600°C) was observed and analyzed by a two factor analysis of variance. This analysis revealed that the effects of NaOH concentration were significant ( $F(2, 35) = 4.42$ ,  $MS = 1.85$ ,  $P < 0.05$ ), as were the effects of calcination temperature ( $F(2, 35) = 9.52$ ,  $MS = 4.00$ ,  $P < 0.05$ ).

<0.05). However, their interaction effects were not statistically significant  $F(4, 35) = 2.05$ ,  $MS = 0.86$ ,  $P > 0.05$ . Moreover, 14% of the total variation in NaOH adsorbed was explained by the concentration of NaOH, 30% by the calcination temperature and 13% by their interaction and 43% is unexplained (Table 19).

Table 19: Two factor analysis of variance of the mean NaOH adsorbed

Source of Variation	SS	df	MS	F	P-value	R <sup>2</sup>
NaOH concentration, M	3.71	2	1.85	4.42	0.022	0.14
Calcination temperature, °C	8.00	2	4.00	9.53	0.001	0.30
Interaction	3.43	4	0.86	2.05	0.116	0.13
Error	11.33	27	0.42			0.43
Total	26.47	35				1.00

Therefore, it could be concluded that the effects of NaOH concentration and calcination temperature were in fact independent of one another and that calcination temperature determined the property of the final properties of the catalyst more than NaOH concentration. Since both NaOH concentration and calcination temperature were statistically significant, Tukey-Kramer HSD multiple comparison procedure was used to compare the mean NaOH adsorbed for the different levels of NaOH concentration and calcination temperature independently.

Table 20: Mean NaOH adsorbed by levels of NaOH concentration

<i>Levels of NaOH concentration</i>	<i>Mean wt % NaOH adsorbed</i>	<i>SE</i>
0.5M	1.28 <sup>a</sup>	0.187
1.0M	1.28 <sup>a</sup>	0.187
1.5M	1.96 <sup>b</sup>	0.187

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)

Table 21: Mean NaOH adsorbed by levels of calcination temperature

<i>Levels of calcination temperature</i>	<i>Mean wt % NaOH adsorbed</i>	<i>SE</i>
400°C	0.87 <sup>a</sup>	0.19
500°C	1.64 <sup>b</sup>	0.19
600°C	2.00 <sup>b</sup>	0.19

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)

#### **4.3.1.2 Effect of sodium hydroxide concentration and calcination temperature on the basicity of NaOH/ZrO<sub>2</sub>**

Like NaOH adsorbed, the effects of NaOH concentration (0.5M, 1.0M and 1.5M), the effects of calcination temperature (400°C, 500°C and 600°C) and their interaction on the basicity was analyzed by a two factor analysis of variance. The effects of calcination temperature on the mean basicity were highly significant ( $F(2,17) = 33.84$ ,  $MS = 0.006$ ,  $P < 0.001$ ) but not very important as they explained only 19% of the total variation in basicity. Likewise, the effects of NaOH concentration were also significant ( $F(2,17) = 128.05$ ,  $MS=0.022$ ,  $P < 0.001$ ) however very important because they explained 74% of the total variation. Therefore, while both main effects were highly significant, the effects of NaOH concentration were more influential on the catalyst basicity than the effects of calcination temperature. The interaction effects between NaOH concentration and calcination temperature were slightly statistically significant ( $F(4,17)=3.71$ ,  $MS=0.001$ ,  $P = 0.047$ ) but not important because they only explained 4% of the total variation. Only 3% in the total variation remained unexplained indicating that NaOH concentration and calcination temperature satisfactorily explained the variation in basicity.

Table 22: Two factor analysis of variance of the mean basicity of NaOH/ZrO<sub>2</sub> catalysts

<i>Source of Variation</i>	<i>SS</i>	<i>Df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>R<sup>2</sup></i>
<b>NaOH concentration, M</b>	0.043	2	0.022	128.05	< 0.001	0.74
<b>Calcination temperature, °C</b>	0.011	2	0.006	33.84	<0.001	0.19
<b>Interaction</b>	0.003	4	0.001	3.71	0.047	0.04
<b>Error</b>	0.002	9	0.000			0.03
<b>Total</b>	0.059	17				1.00

Post hoc analysis using Tukey-Kramer HSD indicated that 1.0M NaOH/ZrO<sub>2</sub> calcined at 500°C and 600°C and 1.5M NaOH/ZrO<sub>2</sub> calcined at 400°C and 500°C were not significantly different while all remaining catalysts were significantly different at the 0.05 level.

Table 23: Basicity as a function of NaOH concentration and calcination temperature

<i>Levels of NaOH concentration</i>	<i>Levels calcination temperature</i>	<i>Mean basicity</i>	<i>SE</i>
<i>M</i>	<i>°C</i>	<i>mmol HCl/g</i>	
0.5M	400	0.40 <sup>ad</sup>	0.0092
	500	0.43 <sup>ab</sup>	0.0092
	600	0.37 <sup>d</sup>	0.0092
1.0M	400	0.42 <sup>a</sup>	0.0092
	500	0.41 <sup>ad</sup>	0.0092
	600	0.39 <sup>ad</sup>	0.0092
1.5M	400	0.54 <sup>c</sup>	0.0092
	500	0.53 <sup>c</sup>	0.0092
	600	0.46 <sup>b</sup>	0.0092

Means followed by the same letter are not significantly different at the 0.05 level using Tukey-Kramer HSD (Zar, 1999)



### 4.3.2 Soybean oil characterization

The Kroger brand soybean oil had very low free fatty acid and water as seen in Table 24.

Table 24: Properties of Kroger brand soybean oil

<i>Property</i>	<i>Mean</i>	<i>Standard deviation</i>
Acid number, mg KOH/g	0.314	0.046
Moisture content, % wt	0.147	0.0207

The gas chromatographic analysis revealed that Kroger brand soybean oil was composed of 84% unsaturated fatty acid. The results are consistent with results published by various authors (See Table 25).

Table 25: Fatty acid composition in soybean oil

<i>Fatty acids, %</i>	<i>Canacki et al, 2001</i>	<i>Brown, 2000</i>	<i>This work</i>
<b>Palmitic acid, C16:0</b>	10.6	9.8	12.1
<b>Stearic acid, C18:0</b>	6.4	2.4	4.2
<b>Oleic acid, C18:1</b>	22.5	28.9	22.9
<b>Linoleic acid, C18:2</b>	52.3	50.7	53.1
<b>Linolenic acid, C18:3</b>	8.2	8.2	7.7

### 4.3.3 Catalyst evaluation

The catalysts were evaluated on their ability to transesterify soybean oil into biodiesel.

The yield of fatty acid methyl ester increased gradually as calcination temperature and sodium hydroxide concentration were increased. Calcination at 400°C produced the least active catalysts although all catalysts achieved yields above 50% as can be seen in Figure 33. Furthermore, impregnation with 0.5M NaOH was least effective in producing active catalysts as indicated by the relatively low yield of fatty acid methyl ester across all

calcination temperatures. The differences in yield between different levels of NaOH concentration and calcination temperature could indicate the existence of an optimum treatment conditions.

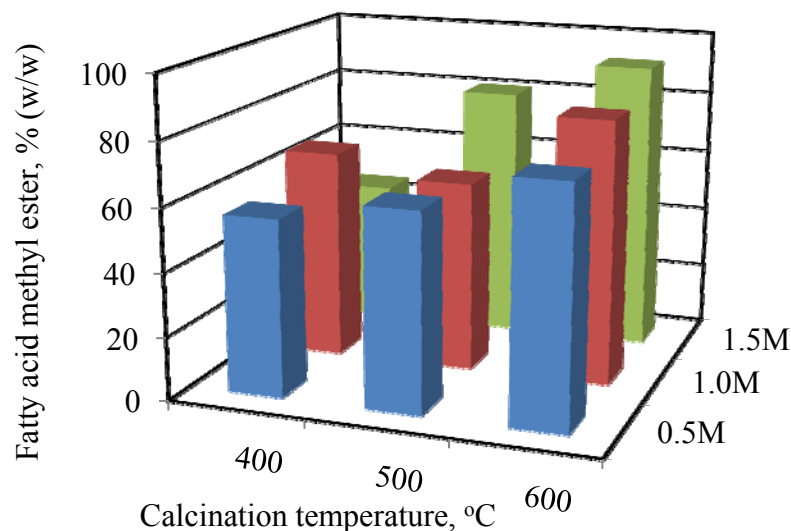


Figure 33: Effect of calcination temperature and NaOH concentration on biodiesel yield

The results of the two factor analysis of variance are consistent with our discussion. The effects of calcination temperature were slightly significant ( $F(2, 26) = 4.09$ ,  $MS = 0.0157$ ,  $P = 0.03$ ) and unimportant as they only explained 5% of the total variation in the fatty acid methyl ester yield. The effects of NaOH concentration were highly significant ( $F(2,26) = 44.70$ ,  $MS = 0.1711$ ,  $P < 0.001$ ) and very important because they explained only 57% of the total variation. It was therefore concluded that concentration of sodium hydroxide solution used for impregnation affected the fatty acid methyl ester yield more than the calcination temperature. The interaction effects between NaOH concentration and calcination temperature were also highly significant ( $F(4, 26) = 10.06$ ,  $MS = 0.0385$ ,  $P < 0.001$ ) but important as they explained 26% of the total variation. Finally, the unexplained variation only accounted for 12% of the total variation indicating that the

variation is satisfactorily explained by the two factors, sodium hydroxide concentration and calcination temperature, as well as their interaction.

Table 26: Two factor analysis of variance of mean fatty acid methyl ester yield

Source of Variation	SS	Df	MS	F	P-value	R <sup>2</sup>
<b>Calcination temperature, °C</b>	0.0313	2	0.0157	4.094	0.0342	0.05
<b>NaOH concentration, M</b>	0.3421	2	0.1711	44.701	0.0000	0.57
<b>Interaction</b>	0.1540	4	0.0385	10.063	0.0002	0.26
<b>Error</b>	0.0689	18	0.0038			0.12
<b>Total</b>	0.5964	26				1.00

#### 4.3.4 Catalyst life

1.5 M NaOH/ZrO<sub>2</sub>-600°C was able to effectively catalyze the transesterification of soybean oil in four consecutive runs at which point the catalyst lost its activity permanently. In total, the catalyst catalyzed the reaction for nine consecutive hours before deactivating. Titration of the permanently deactivated catalyst showed that the catalyst was no longer basic. The loss of basicity suggested leaching of the adsorbed sodium hydroxide. However, in a previous study, we observed a similar deactivation phenomenon on sulfated zirconium oxide. It was concluded then that irreversible catalyst poisoning was the most likely deactivation mechanism. Therefore, it is believed that sodium hydroxide leaching and irreversible poisoning contributed to the permanent deactivation of the catalyst.

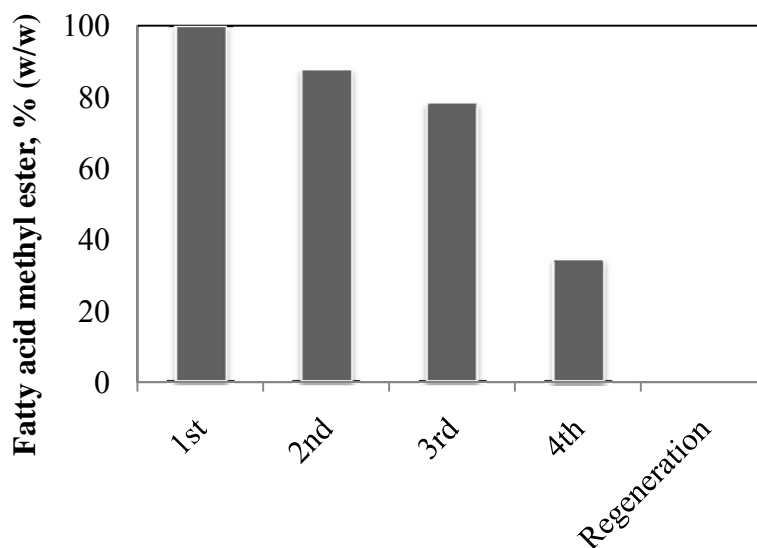


Figure 34: Deactivation of 1.5 M NaOH/ZrO<sub>2</sub>-600°C

#### 4.3.5 The effect of catalyst concentration

The rate of biodiesel production was improved by increasing the concentration of the heterogeneous catalyst and thus the concentration of active site in the reaction mixture.

Five concentrations of 1.5M NaOH/ZrO<sub>2</sub>-600°C (3, 5, 7, 10 and 15 wt %) were tested in these experiments.

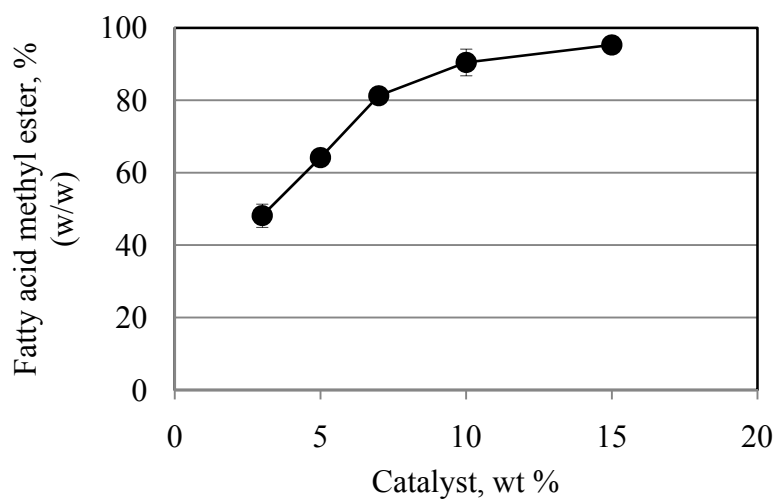


Figure 35: The effect of wt % of catalyst on fatty acid methyl ester yield

As illustrated in Figure 35, the % wt fatty acid methyl ester increased from 3% to 10% and remained relatively unchanged when the concentration was increased to 15% wt indicating that the optimum catalyst concentration under these conditions was 10 wt %.

#### **4.3.6 The effect of oil to methanol molar ratio**

Transesterification of triacylglycerol to biodiesel only requires three moles of alcohol for every mole of oil. It is however well known in homogeneous systems that an excess of alcohol increases the reaction rate by shifting the equilibrium toward ester formation (Ma and Hanna, 1999; Meher et al., 2006). Several investigators demonstrated that an analogous phenomenon existed in heterogeneous systems (Hak-Joo et al., 2004; Lingfeng et al., 2007; Liu et al., 2008a; Liu et al., 2008b; Xie and Li, 2006). Consequently, five molar ratios (1:3, 1:6, 1:9, 1:12 and 1:15) were investigated in this experiment to observe the effect of molar ratio on the fatty acid methyl ester yield.

The minimum ester yield was 79% at 1:3 molar ratio. All molar ratios produced yields very closed to 100%. The observations are in agreement with previous reports (Lingfeng et al., 2007; Liu et al., 2008a; Liu et al., 2008b). However, few studies demonstrated that increase in oil to alcohol molar ratio resulted in a decrease in biodiesel yield (Hak-Joo et al., 2004; Xie and Li, 2006).

#### **4.3.7 Esterification of free fatty acid in soybean oil**

In order to simulate a waste vegetable oil as a potential cheaper and alternative feedstock, pure soybean oil was mixed with pure oleic acid at 5% and 20% by weight of soybean oil. In preliminary investigations,  $\text{SO}_4/\text{ZrO}_2$ -550°C was successfully used to convert

100% palmitic acid and 20% oleic acid in methanol. However, this catalyst only modestly catalyzed soybean oil transesterification.

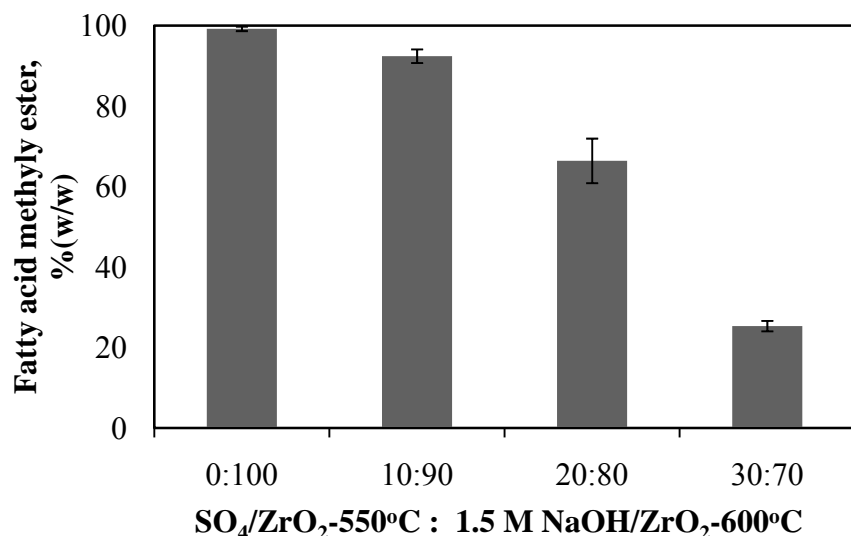


Figure 36: Soybean oil conversion to biodiesel by mixed acid base catalysts

When 1.5 M NaOH/ZrO<sub>2</sub>-600°C was used alone, the catalyst achieved 58% conversion of oleic acid. It is believed that the lewis acid sites on zirconium oxide acted as a weak acid catalyst in the esterification of oleic acid. The conversion increased to 74% with a mixture of 10% SO<sub>4</sub>/ZrO<sub>2</sub>-550°C and 90% 1.5 M NaOH/ZrO<sub>2</sub>-600°C. Subsequent increases in the content of the acid catalysts from 10% to 30% did not increase the conversion of oleic acid (see Figure 37).

Using the same approach with soybean oil containing 5% oleic acid, a similar trend was observed where the highest yield achieved by the catalysts reached a plateau. It was previously established that the adsorption of methanol was the first elementary reaction in free fatty acid esterification on sulfated zirconium oxide. Therefore, to increase probability of methanol absorption, the oil to alcohol molar ratio was increased from 1:6 to 1:20. The conversion of oleic acid reached 97% on 30/70 acid base catalyst mixture

indicating that the ratio can be used to convert waste vegetable oil with up to 5% free fatty acid.

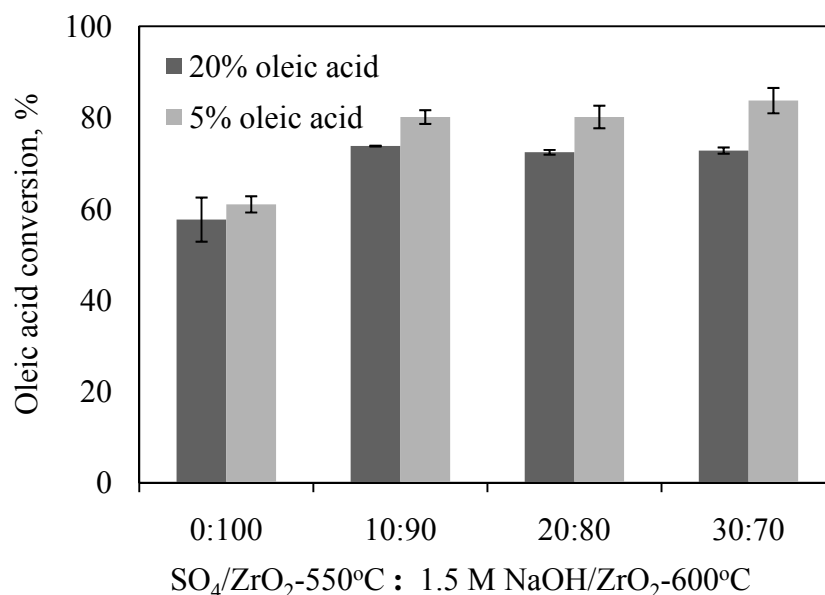


Figure 37: The conversion of soybean oil containing 20% oleic acid with various acid base catalyst ratio

#### 4.3.8 Kinetics of soybean oil transesterification

The effect of temperature and time on the fatty acid methyl ester content is shown in Figure 38. As would be expected, the ester content increased with both increasing temperature and time. At 60°C, the ester content was low and remained below 60% at 200 min. However, when the temperature was increased to 88°C and 98°C, the methyl ester yield was 84% and 99% respectively at the same time. The kinetic curves were not sigmoidal in shape as observed by others (Freedman et al., 1986; Veljkovic et al., 2009). Since the sigmoidal shape was attributed to mass transfer limitation, we concluded that the external mass transfer limitation was probably negligible in this investigation.

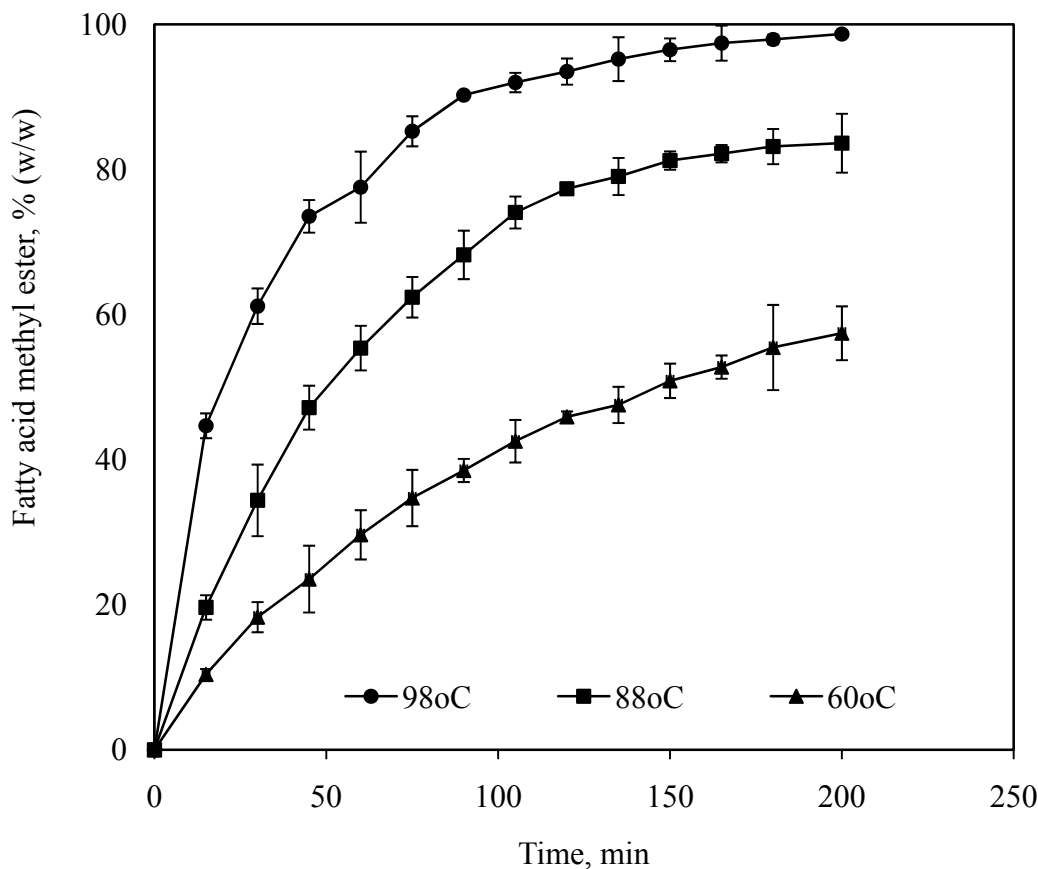


Figure 38: Effect of time and temperature on the methyl ester content

#### 4.3.8.1 Reaction order and activation energy

Eight cases were evaluated in order to determine the overall reaction order at 60°C, 88°C and 98°C. The coefficients of determination were the highest at all temperatures when a first order with respect to triglycerides and a second order with respect to methanol were assumed with  $R^2$  of 0.99, 0.98 and 0.99 for 60°C, 88°C and 98°C respectively. Therefore, a third order for the overall reaction best fitted the experimental data.

The activation energy and pre-exponential factor were both determined to 49.35 kJ/mol and  $6.43 \times 10^9 \text{ M}^{-1} \text{ min}^{-1}$ .



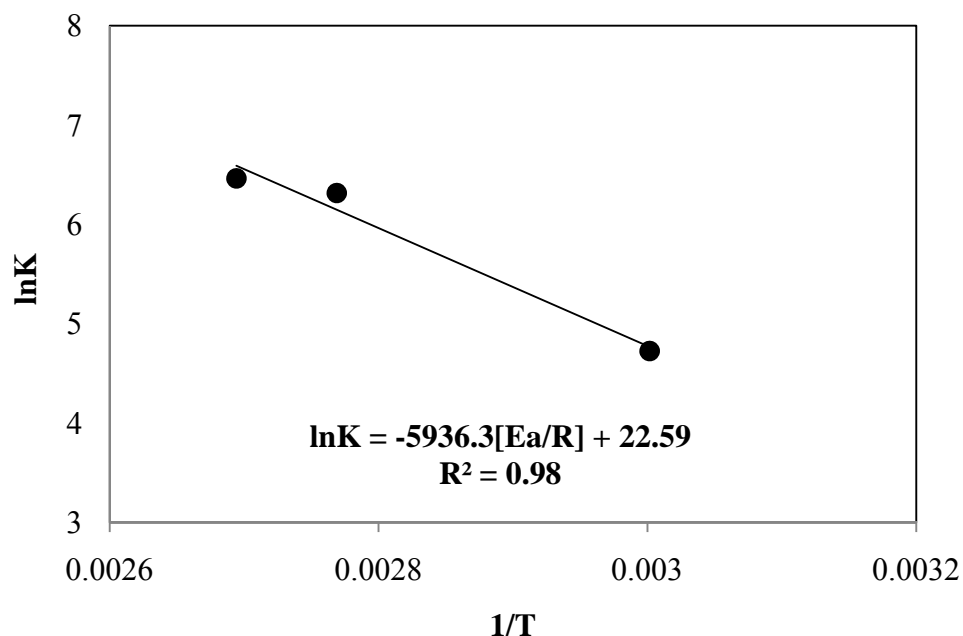


Figure 39: The Arrhenius activation energy plot

#### 4.3.8.2 Reaction mechanism

In the search for the reaction mechanism and the kinetic parameters its rate law, eleven models based on Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) kinetics were evaluated by non-linear regression analysis. Eley-Rideal and Langmuir-Hinshelwood based Rate laws that assumed methanol adsorption as rate determining step did not converge at all temperature and were eliminated. Models that assumed fatty acid methyl ester desorption as rate determining were also eliminated for similar reasons. Of the remaining models, only two models based on Eley-Rideal and Langmuir kinetics yielded physically meaningful and statistically important regression analysis.

The LH model (#2) that assumed the adsorption of triglycerides to be rate determining step fitted well the experimental results at all temperatures despite its large number of

unknown variables. The coefficients of determinations were 0.99, 0.99 and 0.98 at 60°C, 88°C and 98°C respectively. The estimated kinetic parameters are shown in Table 27.

Table 27: Estimated kinetic parameters based on LH model #2

	$\alpha \times 10^{-3}$	$K$	$K_1 \times 10^{-3}$ ( $\text{mol}^{-1}$ )	$K_6 \times 10^{-3}$ ( $\text{mol}$ )	$K_2 \times 10^{-4}$ ( $\text{mol}^{-1}$ )
60°C	12.50	112.77	142.57	11.23	31.23
88°C	27.06	553.45	117.92	14.77	9.97
98°C	65.49	641.00	60.56	18.30	7.78

Where  $\alpha$  is  $Lk_2$

In addition to the LH model described above, the ER model (#8) that assumed the surface reaction between adsorbed methanol and unadsorbed triglyceride as rate determining step produced statistically similar result to the LH model. Upon elimination of unnecessary terms in the corresponding rate laws, the coefficients of determinations were 0.98 for all temperatures. However, when this model was used, it was observed that the surface reaction was most likely irreversible. The irreversible nature of the surface reaction is a significant deviation from the homogeneously catalyzed transesterification where all reactions are reversible. Based on these results, it was concluded that the transesterification of soybean oil on 1.5 M NaOH/ZrO<sub>2</sub>-600°C most likely obeyed Langmuir-Hinshelwood kinetics. The quality of the regression analysis on the Eley-Rideal model suggested that a simpler, irreversible Eley-Rideal mechanism could satisfactorily explain the reaction mechanism. In either reaction mechanisms, it appeared that the rate determining step was the first elementary reaction that enabled the reaction between triglyceride and methanol.

## Conclusion

Zirconium oxide impregnation with sodium hydroxide was demonstrated to produce base catalysts that can catalyze the transesterification of soybean oil to biodiesel. Statistical analysis was used to better understand the effect on treatments on the catalyst properties:

1. Sodium hydroxide concentration and calcination temperature interaction effects were not statistically significant on the mean amount of sodium hydroxide adsorbed and calcination temperature was more important than sodium hydroxide concentration in explaining the total variation.
2. Sodium hydroxide concentration and calcination temperature interaction effects were slightly statistically significant on the mean basicity and sodium hydroxide concentration was far more important than calcination temperature in explaining the total variation.
3. Sodium hydroxide concentration and calcination temperature interaction effects were highly statistically significant on the fatty acid methyl ester yield and the concentration of sodium hydroxide was very important, explaining more than half of the total variation biodiesel yield.
4. BET surface area decreased with increase in sodium hydroxide concentration and in calcination temperature.
5. All levels of treatments produced basic catalysts with better performance than the sulfated zirconium oxide catalysts previously described in Chapter 3.

The most active catalyst was produced by impregnation with 1.5 M NaOH followed by calcination at 600°C. Increase in catalyst concentration resulted in an increase in

ester content reaching a maximum around 10 wt % catalyst. Increase in oil to methanol molar ratio also resulted in an increase in ester yield as well. Furthermore, a mixture of 30%  $\text{SO}_4/\text{ZrO}_2$ -550°C and 70% 1.5 M NaOH/ $\text{ZrO}_2$ -600°C achieved 97% conversion on oleic acid in synthetic waste oil containing 5% oleic acid when the oil to methanol ratio was high enough.

An investigation of the kinetic of soybean transesterification at 60°C, 88°C and 98°C revealed that the reaction order was first order with respect to triglyceride and second order with respect to methanol. The activation energy and the pre-exponential factor were 49.35 kJ/mol and  $6.43 \times 10^9 \text{ M}^{-1} \text{ min}^{-1}$  respectively. After analysis of eleven models, it was concluded that the reaction obeyed Langmuir-Hinshelwood kinetics.

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## Appendices

### Appendix A: Nomenclature used in kinetic study of palmitic acid esterification

A	Palmitic acid
C	Palmitic acid methyl ester
B	Methanol
S	Vacant catalyst active site
D	Water
L	Total catalyst active sites
A*S	Palmitic acid adsorbed on a vacant active site
C*S	Palmitic acid methyl ester adsorbed on an active site
C <sub>A</sub>	Concentration of palmitic acid, M
C <sub>B</sub>	Concentration of methanol, M
C <sub>C</sub>	Concentration of palmitic acid methyl ester, M
C <sub>D</sub>	Concentration of water, M
C <sub>A0</sub>	Initial concentration of palmitic acid, M
K <sub>1</sub>	Adsorption of palmitic acid equilibrium constant, dm <sup>3</sup> mol <sup>-1</sup>
K <sub>3</sub>	Desorption of palmitic acid equilibrium constant, mol dm <sup>-3</sup>
K <sub>2</sub>	Rate determining step reaction rate constant
k <sub>2</sub>	Rate determining step forward reaction rate constant dm <sup>3</sup> min <sup>-1</sup> g <sup>-1</sup> cat
k <sub>-2</sub>	Rate determining step reverse reaction rate constant, dm <sup>3</sup> min <sup>-1</sup> g <sup>-1</sup> cat

X Conversion of palmitic acid

## **Appendix B: Nomenclature used in kinetic study of soybean oil transesterification**

A	Methanol
B	Triglyceride
D	Diglyceride
E	Monoglyceride
F	Glycerol
C	Fatty acid methyl ester
A*S	Adsorbed methanol
B*S	Adsorbed triglyceride
D*S	Adsorbed diglyceride
E*S	Adsorbed monoglyceride
C*S	Adsorbed fatty acid methyl ester
R	Specific reaction rate, $\text{mol min}^{-1} \text{g}^{-1} \text{cat}$
L	Total active site density, mol
N <sub>A</sub>	Methanol at a given time, mol
N <sub>B</sub>	Triglyceride at a given time, mol
N <sub>C</sub>	Fatty acid methyl ester at a given time, mol
N <sub>F</sub>	Glycerol at a given time, mol



### **Kinetic parameters from mechanisms based on Langmuir-Hinshelwood kinetics**

- $K_1$  Methanol Adsorption equilibrium rate constant,  $\text{mol}^{-1}$
- $K_2$  Triglyceride adsorption equilibrium rate constant,  $\text{mol}^{-1}$
- $K_3$  Reaction between adsorbed methanol and adsorbed triglyceride equilibrium rate constant
- $K_4$  Reaction between adsorbed methanol and adsorbed diglyceride equilibrium rate constant
- $K_5$  Reaction between adsorbed methanol and adsorbed monoglyceride equilibrium rate constant,  $\text{mol}$
- $K_6$  Fatty acid methyl ester desorption equilibrium rate constant,  $\text{mol}$
- $k_1$  Forward reaction rate constant for methanol adsorption,  $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
- $k_2$  Forward reaction rate constant for triglyceride adsorption,  $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
- $k_3$  Forward reaction rate constant for surface reaction between adsorbed methanol and adsorbed triglyceride,  $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
- $k_{-4}$  Reverse reaction rate constant for the surface reaction between adsorbed methanol and adsorbed diglyceride,  $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
- $k_{-5}$  Reverse reaction rate constant for the surface reaction between adsorbed methanol and adsorbed monoglyceride,  $\text{mol}^{-2}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
- $k_{-6}$  Reverse reaction of fatty acid methyl ester desorption,  $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$

### **Kinetic parameters from mechanisms based on Eley-Rideal kinetics**

- $K_1$  Methanol adsorption equilibrium rate constant,  $\text{mol}^{-1}$
- $K_2$  Reaction between adsorbed methanol and triglyceride equilibrium rate constant

$K_3$	Reaction between adsorbed methanol and diglyceride equilibrium rate constant
$K_4$	Reaction between adsorbed methanol and monoglyceride equilibrium rate constant
$K_5$	Fatty acid methyl ester desorption equilibrium rate constant, mol
$k_1$	Forward reaction rate constant of methanol adsorption, $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
$k_2$	Forward reaction rate constant of the surface reaction between adsorbed methanol and triglyceride, $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
$k_3$	Forward reaction rate constant of the surface reaction between adsorbed methanol and diglyceride, $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
$k_4$	Reverse reaction rate constant of the surface reaction between adsorbed methanol and monoglyceride, $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$
$k_5$	Reverse reaction rate constant of fatty acid methyl ester desorption, $\text{mol}^{-1}\text{min}^{-1}\text{g}^{-1}_{\text{cat}}$