

2011

Development Of A Multifunctional Catalyst For Combined Esterification And Transesterification Of Used Vegetable Oil

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DEVELOPMENT OF A MULTIFUNCTIONAL CATALYST FOR
COMBINED ESTERIFICATION AND TRANSESTERIFICATION
OF USED VEGETABLE OIL

by

Talal Kamal Ahmed

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Department: Chemical and Bioengineering
Major: Chemical Engineering
Major Professor: Dr. Abolghasem Shahbazi

North Carolina A&T State University
Greensboro, North Carolina
2011

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DEDICATION

I would like to dedicate this thesis work to my father, Mr. Kamal Abdelhalim Ahmed Ali. For the valuable advises on how to keep the right track to my career and for his always concerns about my life, he provided me with the good family environment through all of my academic levels to ensure the good probabilities of my success.

BIOGRAPHICAL SKETCH

Talal Kamal Ahmed was born on April 19, 1977, in Khartoum, Sudan. He received the Bachelor of Science degree in Chemistry from Ein Shams University in Cairo, Egypt in 2007. He received a Six Sigma Green Belt from Department of Industrial Engineering at North Carolina Agricultural and Technical State University, Greensboro, North Carolina 2011. Mr. Ahmed has been involved in the green energy and biofuels research and development of new catalyst in the production of biodiesel from waste cooking oil and has presented the title of “A study of Heterogeneous Catalysis in Biodiesel Production” at the First International Green Energy Conference of North Carolina Agricultural and Technical State University. He is a candidate for the Master of Science degree in Chemical Engineering.

ACKNOWLEDGEMENTS

I thank Allah for helping me with his assistance in providing me with the strength to withstand the hard times in the learning procedure. I felt like the thoughts are flowing inside me during the whole work in this research and I know that is coming from no one else but him.

I am so grateful to the Department of Chemical and bioengineering of North Carolina Agricultural and Technical State University through which I was offered the chance for higher education levels to dig deeper in the research fields of the green energy fields in order to find alternative sustainable sources of energy. I am deeply grateful to Dr. Abolghasem Shahbazi, my major advisor, for sharing me with his huge experience and knowledge about those sustainable green energy fields. I am also thankful to Dr. Lijun Wang who provided me with experimental knowledge in the lab that broadens my knowledge about how to construct the plan for a big project and research.

Also I'm thankful to Michele R. Mims (Lab Manager, Sockwell Hall, NCA&TSU) who provided me with the proper tools, chemicals that helped me to finish this research. My regards also goes to my colleagues of researchers of both graduate and undergraduate level of academics in Sockwell Hall who provided me with the good environment and sometimes advises through the road of this work.

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LIST OF NOMENCLATURE

BET	Brunauer, Emmett and Teller
PBR	Packed bed reactor
TGA	Thermal Gravimetric Analysis
GC	Gas Chromatography
FID	Flame Ionization Detector
EN 14103	Standard European Method
NaOH	Sodium Hydroxide
FAME	Fatty Acid Methyl Ester
KOH	Potassium Hydroxide
H ₂ SO ₄	Sulfuric Acid
CaO	Calcium Oxide
HPLC	High Performance Liquid Chromatography
GPC	GEL Permeation Chromatography
HNMR	Proton Nuclear Magnetic Resonance Chromatography
NIR	Near-infrared
FTIR	Fourier Transform Infrared Spectroscopy
WCO	Waste Cooking Oil
FFA	Free Fatty Acids
S – ZrO ₂	Sulfated Zirconia Oxide
NS	Conventional Zirconia

$\text{ZrClO}_2 \cdot 8 \text{H}_2\text{O}$	Zirconylchloride Octahydrate
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulfate
Al_2O_3	Aluminum Oxide (Alumina)
SiO_2	Silicon Oxide (Silica)
MgO	Magnesium Oxide
XPS	X-ray Photoelectron Spectroscopy
OFR	Oscillator Flow Reactor

ABSTRACT

Ahmed, Talal Kamal. DEVELOPMENT OF A MULTIFUNCTIONAL CATALYST FOR COMBINED ESTERIFICATION AND TRANSESTERIFICATION OF USED VEGETABLE OIL. (**Major Advisor: Abolghasem Shahbazi**). North Carolina Agricultural and Technical State University.

In recent few years, biodiesel has become as one of the most potential and efficient renewable energy products to replace petroleum based diesel. Biodiesel is biodegradable, renewable and non-toxic fuel which can be produced from vegetable oils and animal fats by the transesterification reaction. In this study, heterogeneous catalysts were used to catalyze the transesterification reaction. Two solid catalysts were prepared. Calcium on Zeolite Y and sulfated zirconia. Sulfated zirconia was prepared using the solvent free method in which zirconylchloride was mixed with ammonium sulfate. The two powders were grinded for 20 min and settled at room temperature for 18 hours and finally the product was calcined at 600 °C for 5 hours. The product was characterized using BET. The results showed the surface area was 100 m²/g. Calcium on zeolite Y was prepared using the wetness impregnation method and was calcinated at 600°C for 6 hours. The reaction was conducted on a batch reactor at different temperatures and ran for 1.5 h using both catalysts. Also Calcium on zeolite Y was tested in a packed bed reactor (PBR), Thermal gravimetric analysis (TGA) was carried out to study the thermal stability of the biodiesel produced from waste cooking oil in a batch operation and a continuous process. It showed that the weight loss for this biodiesel starts at 120°C. A gas chromatography (GC) with a FID detector was used to analyze the conversion efficiency and ester profile in the biodiesel using the EN14103 method with methylheptadecanoate

(C₁₇) as an internal standard. The results showed that the conversion efficiency of the transesterification reaction in a batch operation with the Calcium catalyst was 94%, while the conversion using sulfated zirconia was 89 %. The conversion of waste cooking oil in the packed bed reactor was found to be 79.8 %.

CHAPTER 1

Introduction

In recent few years, biodiesel has become one of the most potential and efficient renewable energy products to replace petroleum based diesel. Biodiesel is a biodegradable, renewable, and non-toxic fuel, which can be produced from vegetable oils and animal fats using the transesterification reaction. The need for biodiesel produced from vegetable oils has become significant over the past decade [1]. Biodiesel is produced using the transesterification reaction of vegetable oil in the presence of a catalyst and heat energy to enhance the kinetics of the reaction by increasing the rate of reaction. As introductory studies, four techniques were developed to produce biodiesel are as follows:

- (1) Thermal cracking, which is also termed pyrolysis using heat energy,
- (2) Using solvents such as ethanol, methanol and/or other alcohols in a process termed microemulsions,
- (3) Blending process with diesel fuel, and
- (4) Transesterification using short chain alcohols as methanol or ethanol in the presence of a catalyst. This method is also called alcoholysis and the most popular method is the transesterification of vegetable oils and animal fats using methanol or ethanol [2].

1.1 Biodiesel as alternative fuel

The environmental friendly manner of biodiesel as well as the critical need for new generations of energy that would overcome the current energy sources, push the researchers to start exploring new sources of energy, in addition to that, there was always a deep thinking of how to get green by producing, developing, designing new techniques for power generation. That is why several researches have started developing alternative bio- renewable sources of energy in the recent years. Ethanol as an alternative source for gasoline was one of those alternative green energy sources; in fact many countries are already using biofuels such as bioethanol and biodiesel. Those countries are Germany, Brazil, Australia, Italy, Austria and United States [3]. The biodiesel fuel has similar fuel properties such as that of diesel produced from crude oil and it can be directly combusted in the existing diesel engines or can be modified by forming a mixture with crude oil diesel [3]. Added to the biodegradability of biodiesel it produces less harmful gas emissions such as sulfur dioxide, which is widely classified as a hazardous chemical from an environmental point of view, and still, reports show that the feedstock costs as well as the process cost is a challenging for biodiesel use as an alternative source for the petroleum based fuels [3].

1.2 Catalysis in biodiesel production

One of the proposed engineering solutions for solving the high costs associated with biodiesel production is to develop a continuous process for biodiesel production in commercial scale. It has been reported that this continuous technique will reduce the

production cost and therefore, reduce the overall cost of biodiesel, which will result in competitive biodiesel price with respect to fossil fuels [3]. Also some of those researchers started thinking of how to alternate the petroleum based fuels by biodiesel. Early studies started the first step by applying high, and strong alkaline sodium hydroxide (NaOH). They knew the chemical formula of obtaining the biodiesel was through the transesterification reaction of the triglycerides in the oil into the salt of those fatty acids (FAME). However, what they were missing is the chemical fact that the same transesterification reaction they used for biodiesel production is the same reaction used in producing soap in the soap industry either hand washing soap or body soap depending on whether the catalyst was sodium hydroxide or potassium hydroxide, respectively.

From physical chemistry point of view, if the reactants in a chemical process are in the same physical properties (gas, liquid and solid) then that reaction is known to be as a homogeneous reaction, but if any of the reactants is in different physical phase, and maintains that physical property throughout the reaction (does not leach into the reaction medium) then it is known as heterogeneous reaction. The kind of work that has been done in using sodium hydroxide as well as potassium hydroxide has faced several difficulties. That is why those researchers paved the way by admitting the chemical fact that those type of catalysts (sodium hydroxide and potassium hydroxide) are efficient catalysts in providing good conversion results in the transesterification reaction as well as the biodiesel yield, but, a new heterogeneous techniques must be developed in order to solve the problems related to the homogeneous techniques (NaOH and KOH). Production of biodiesel using heterogeneous catalyst is one of the new techniques that have been

introduced [4]. This technique would overcome the high costs that would arise from using expensive and time consuming purification process in separating the catalyst from product. It also remedies the problem of corrosion when using homogeneous acid catalyst as H_2SO_4 , which will damage the reactor as well as the used pipelines [5].

In literature studies, several solid catalysts have been introduced to the biodiesel reaction such as sulfated Zirconia. Also some catalyst supporting materials such as Alumina oxide and Silica oxides due to their high surface area as well as high acidic nature. Also some of these studies used Magnesium and Calcium as the basic active metals loaded to Alumina oxides and Silica oxides. Calcium oxide (CaO) has been used in several studies as a solid base catalyst, which has several advantages over other basic catalysts as being highly active, mild reaction conditions, stronger basic sites, long catalyst lifetimes and low catalyst costs when compared to other basic metals [6].

The fast growth of biodiesel as renewable transportation fuel will also increase the need for convenient and accurate analytical methods to control the biodiesel production. Recently several standard methods have been developed for analyzing the biodiesel components in mixtures. They included high performance liquid chromatography (HPLC), gas chromatography (GC), gel permeation chromatography (GPC), proton nuclear magnetic resonance spectroscopy (HNMR), near-infrared (NIR), and Fourier transform infrared spectroscopy (FTIR). Also, a recently used technique is the thermogravimetric analysis (TGA) to analyze the thermal stability of the biodiesel by detecting the changes in its physicochemical properties shown in the weight loss as a function of increasing temperature [1].

1.3 Waste cooking oil and biodiesel

Recently, the high cost of biodiesel is the main obstacle; it costs over US\$0.5/1, compared to US\$0.35/1 for petroleum based diesel [7]. The reason for the high costs of biodiesel is suggested mainly to be because of, the cost of virgin vegetable oil [7], and as a matter of fact, moving from petroleum based diesel to biodiesel for environmental issues would create a problem in food area due to using edible raw materials, that's why the needing for non-edible raw materials as waste cooking oils (WCO) recently increased. The use of WCO over virgin oil to produce biodiesel is a promising way to reduce the raw material cost because it is estimated to be about half the price of virgin oil, also using WCO would also assist in solving the problem of waste oil disposal [7]. The production of waste cooking oil in most of countries is considered to be huge, and that may lead to environmental contamination if a suitable disposal method is not used [5]. In 2007, United States produced about 450 million gallons of biodiesel while in 2004 the production was only 25 million gallons [5].

As a current status of biodiesel production, the fossil fuel prices are near the all-time high. Biodiesel is growing at the highest rate in industries world-wide. The global studies showed that, United States as well as some members of the European Union is strongly supporting the biodiesel production from the agricultural area. Taking 2006 as a sample of study, 6.5 billion liters of biodiesel was produced globally. The most significant fact is that 75 % of the total biodiesel production is coming from European countries, and is explained by the sustained support of European government consumption incentives [5].

The goal of this work is to develop a solid catalyst that would accomplish the following objectives:

1. To produce higher conversion rate as well as higher biodiesel yield with waste cooking oil as the feedstock, in batch as well as in continuous packed bed reactor.
2. To be insensitive to the high free fatty acid content in waste cooking oil in order to overcome the high cost associated with pretreatment of waste cooking oil.

CHAPTER 2

Literature Review

Biodiesel is produced by the transesterification reaction of vegetable oils or the esterification process of free fatty acids using lower alcohols [8]. This transesterification reaction could be done in either a homogenous or a heterogeneous phase; both of the two types of reaction could be in acidic or basic media.

2.1 Homogeneous phase of the reaction

The homogeneous phase can be either a base-catalyzed reaction or acid-catalyzed reaction.

2.1.1 *Base-catalyzed homogeneous reaction*

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are commonly known as active catalysts because of the high yield percentage $> 98\%$ in a 30 minutes reaction of short chain alcohol and oil; even if both are added at low molar concentrations of 0.5 mol% [9]. Alkaline metal hydroxides (KOH, NaOH) are cheaper than those metal alkoxides but less active [9]. However, they are still a good second choice since they are able to give the same high percentage for conversion if the catalyst concentration has been increased to 1 or 2 mol% [5]. It was studied that 100g of vegetable oil is transesterified using methanol (200 ml) in presence of fresh sodium (0.8g). For the purpose of sodium methoxide-catalyzed transesterification, the reaction between the vegetable oil and sodium methoxide in methanol had high reaction rate and was clearly

shown that only 2-5 min at room temperature (293-298 K) was sufficient enough for the triglycerides to be completely transesterified, while the same transesterification reaction required high temperatures of 303-338 K, and a reaction time of 60-360 if the acid- and alkali-catalyzed processes are introduced [9]. Glycerin formed during the transesterification process needs to be immediately removed after finishing the reaction; this is because it will be converted to formaldehyde or acetaldehyde when burned, and both would pose a health hazard [9]. The two widely used base catalysts in this phase are sodium hydroxide (NaOH) and potassium hydroxide (KOH), and used comprehensively in industries for several reasons, three are:

- (a) The reaction would require low temperature as well as atmospheric pressure.
- (b) In short reaction time, high conversion can be accomplished.
- (c) Low economical costs and availability [9].

The studies showed that the base-catalyzed reaction is 4000 times faster than the acid-catalyzed reaction; however, this catalyst is limited only for refined vegetable oil with a content of less than 0.5 wt% FFA, and the only accepted range for the FFA in the feedstock is also from less than 0.5% to less than 2% for the base-catalyzed reaction. This means that waste cooking oil (WCO) with more than 6% of FFA would not be suitable for this reaction [9]. The chemical explanation is due to high probability of saponification to occur when using base catalyst with high FFA of WCO. Also applying these homogeneous catalysts in a continuous biodiesel production of biodiesel has been studied by detecting the molar ratio of methanol to oil and the corresponding yield [3].

2.1.2 Acid-catalyzed homogeneous reaction

The most used acid-catalyzed homogeneous reaction is sulfuric acid (H_2SO_4). It has been used as a method of batch-wise esterification of fatty acids to synthesize the fatty acid esters [10]. This method can be used to produce large range of fatty acid esters that can be introduced in the fields of pharmaceuticals, food industry and cosmetics [10]. Unlike many feed stocks containing different types of triglycerides, using fatty acids would help in producing fatty acids alkyl esters with specific content as $\text{C}_{12} - \text{C}_{16}$ or $\text{C}_{18} - \text{C}_{22}$ esters [10]. However, problems that would show up in using batch operation modes will be a small scale of biodiesel production, the high separation costs, and purification processes, since the phase used here is homogeneous.

The advantage of using acid catalysts over base catalysts is their susceptibility to the presence of FFA in the used raw material [9]. However, the acid-catalyzed transesterification is known by its sensitivity to water concentration. The literature studies show those acid-catalyzed reactions that as less as only 0.1 wt% water in the reaction mixture is sufficient to affect the ester yields in transesterification of vegetable oil with methanol, and the reaction would completely be inhibited if the water concentration reaches 5 wt% [9].

2.2 Heterogeneous phase of the reaction

Heterogeneous reaction can involve either acid or base-catalyzed reactions. Also named as solid catalysts, those catalysts have been reported as efficient catalysts in producing higher yield and conversion of the raw material to biodiesel; however, the

main drawbacks for the solid catalysts are their preparation procedures, and the reaction conditions, which will increase the production cost, and their leaching aspect [11]. The catalyst can be truly heterogeneous if it does not leach into the reaction medium; then, it is able for re-use, has high selectivity for the desired product over the undesired product, and it is able to produce high yield and conversion to biodiesel [11].

The reaction mechanism for these heterogeneous catalysts is similar to homogeneous catalysts in potassium hydroxide as well as sodium hydroxide, and methoxide (homogenous phase), an alkoxide group is produced due to the chemical interaction with alcohol (methanol or ethanol), which will then attack the carbonyl group in the triglyceride molecule [11]. In heterogeneous basic, Bronsted and Lewis catalysts, the mechanism follows the same path by forming the alkoxide group but this time a homogeneous one, the main event here is the adsorption of alcohol and ester as the reactant on the catalyst surface, this mechanism is known as the Eley-Rideal mechanism. It has been reported that Bronsted acid is suitable for esterification reaction, while Lewis acid gets affected deeply in a manner of deactivating its catalyst efficiency by esterification. That is why it is more suitable for the transesterification reaction [11].

2.2.1 Acid catalyzed heterogeneous reaction

The main benefit of using solid acid catalysts in biodiesel production is that no polluting by-products are formed, and the catalysts do not mix with the produced biodiesel. Therefore, it does not require removal of the catalysts, which would lower the separation costs that may arise, and maintenance costs, since these kinds of catalysts are not corrosive [10]. Unlike liquid acid catalysts that have specified acid properties, solid

acids contain several acidic sites that are grouped usually according to their Lewis or Bronsted acidity, the acidity strength, number of acidic sites, and textural support properties [10].

The base catalyzed transesterification for vegetable oils has a faster rate than acid-catalyzed reaction, and basic catalysts are known to be less corrosive than the acidic compounds. In addition, these basic catalysts have run under atmospheric pressure, and needed low kinetic temperatures, normally between 25°C and 70°C. However, these alkaline catalysts still suffer from small amounts of water and/or free fatty acids in the reaction system, which will lead directly to a saponification issue, further reducing the ester yields, and harden the recovery of the glycerol; thus, the formation of emulsions [12].

To overcome the sensitivity of these alkaline catalysts to water as well the free fatty acids content of used raw materials, researchers started testing the acidic heterogeneous catalysts in the transesterification reaction of the triglycerides into biodiesel. Several acidic catalysts have been introduced in this area to take advantage of higher yields, strong Bronsted and Lewis acidic sites, and the ability to withstand these water, and free fatty acids issues. Traditionally, solving the high free fatty acids matter in some feed stock using a waste cooking oil, H₂SO₄ technique has been applied in order to participate in the esterification stage, which would minimize the acid number in these raw materials, and send the product to the transesterification stage through methanol, and the product of the transesterification is the biodiesel. However, later on these acidic catalysts showed a high corrosion issue would immerge with the usage of these acidic catalysts.

One of these difficulties is the corrosion of the pipeline used in the transportation of the biodiesel that has been produced using acidic catalysis. This matter associated with using H_2SO_4 has not stop some researchers from exploring this chemical agent, and its contribution to the biodiesel work, which is why some literature works has focused on and paid more attention on maximizing sulfuric acid.

Some researchers studied the activities of a series of layered aluminosilicates loaded with H_2SO_4 for the transesterification process of rapeseed oil, an initial molar ratio of 1:30 of oil/methanol was used and 5 wt% catalyst. The most active catalysts were those that had been treated with sulfuric acid impregnation [12]. Sulfuric acid has been used to activate montmorillonite KSF, which later showed a 100% conversion after 4 h of reaction that ran at 220°C and 52 bars. However, leaching of the sulfate ionic group made reusability of this catalyst hard to achieve. Thus, to keep the catalyst activity at a constant level, sulfuric acid re-impregnation had to be carried out after each run. Moreover, because of the leaching of sulfuric acid, it was likely that some level of homogeneous catalysis degree was taking place [12].

2.2.1.1 Sulfated zirconia acidic heterogeneous catalyst in biodiesel production

Sulfated zirconia used as an acidic catalyst has been applied as one of these heterogeneous acid catalysts in the transesterification reaction. Different catalyst preparation methods have been tested in understanding this catalyst behavior, and activity in producing biodiesel. It is more favored over other acidic heterogeneous catalysts that have a corrosive manner, high activation required for these catalysts to finish, and complete their reactions. However, several studies have been conducted in testing

zirconia in the transesterification reaction. In one study, the production of diesel fuel using solid superacid catalysts under atmospheric pressure in a fixed bed reactor was employed; these solid superacid catalysts were basically sulfated tin and zirconium oxides [12]. The catalytic efficiency of these solid catalysts in the transesterification reaction of soybean oil with methanol was evaluated under 200-300°C of heat energy, and their efficiency in esterifying n-octanoic acid with methanol [12]. The results showed that tungsted zirconia-alumina had good performance in the transesterification of soybean oil, and also played a major role in the esterification of n-octanoic acid, with conversion of over 90% for the two reactions [12]. Sulfated zirconia is already of interest in many industrial processes, such as the chemical isomerization of hydrocarbon, alkylation, esterification reactions, and recommended a good candidate for biodiesel catalytic production. However, most of authors of these published works in sulfated zirconia activity as a heterogeneous catalyst did not comment or describe the crystallinity of sulfated zirconia [12].

Table 1 shows the highest conversion obtained was 99.5% at 120°C, and the catalyst load was 5% (wt %). However, a change in the color of the biodiesel was noticed, which is why the best biodiesel yield was around 98.6%, and the optimum conditions were 5% of S-ZrO₂ catalyst. With respect to soybean oil, the temperature was 120°C, and the reaction time was 1h, which gave a colorless (no change of biodiesel color) biodiesel product. When the conventional zirconia (NS) was tested in the same transesterification conditions, no activity was found.

Table 1. Different molar ratio and corresponding conversions for SZ

Catalyst(wt%)	Time (h)	Temperature (°C)	Yield (%)
S-ZrO ₂ (5)	2	85	14.9 ± 3.1
S-ZrO ₂ (5)	2	100	68.1 ± 2.6
S-ZrO ₂ (5)	2	120	99.5 ± 1.8
S-ZrO ₂ (5)	2	150	99.8 ± 2.2
S-ZrO ₂ (1)	2	150	86.7 ± 1.8
S-ZrO ₂ (2,5)	2	150	87.6 ± 1.6
S-ZrO ₂ (5)	2	150	99.8 ± 1.5
S-ZrO ₂ (10)	2	150	99.8 ± 1.9
S-ZrO ₂ (5)	0.5	150	97.2 ± 1.1
S-ZrO ₂ (5)	1	150	99.1 ± 1.7
S-ZrO ₂ (5)	0.5	120	86.2 ± 1.2
S-ZrO ₂ (5)	1	120	98.6 ± 1.6
S-ZrO ₂ (5)	2	120	99.5 ± 1.1
SZ (5)	1	120	8.5 ± 3.8
NS (5)	1	120	No conversion

Adapted from [12]

Noteworthy, is the method used for preparing sulfated zirconia was the precipitation method. One of the catalysis methods that has been used in the preparation was the solvent free method (solventless), this method is more favored due to its friendly behavior with the environment, and it still maintains the strong acidic bronsted acidic sites. This method has been used to produce nanosized sulfated zirconia, zirconylchloride octahydrate (ZrOCl₂.8H₂O) was mixed with ammonium sulfate (NH₄)₂SO₄ with a molar ratio of 1:6, the two powders were grounded for 20 min, settled for 18 h at room temperature, and finally calcinated for 5 h at 600°C [13]. The results showed a high surface area for this prepared catalyst of 165m²/g, and a large pore volume of 0.34cm³/g. Also, it was reported that when the mixing molar ratio was increased to 1:10, the prepared catalyst exhibited a higher surface area of 193 m²/g, and more uniform pore distribution [13]. The activity of a solid catalyst depends mainly on the calcination's both

temperature and duration of time. More active metal attached to the support, was noticed when a higher calcinations temperature was used and for moderately longer periods.

2.2.2 Base catalyzed heterogeneous reaction

This area attracted the interest of big industrial plants due to the efficiency of the basic catalysts in the transesterification reaction of the triglycerides, because the problem of separation, which affected the process cost that evolved while using these catalysts in the homogeneous phase. The problem was solved by developing these catalysts in the solid phase. Many active metals have been introduced in this area as magnesium, sodium and calcium, which has been supported and by several studied such as zeolite Y, alumina (Al_2O_3) and silica (SiO_2).

2.2.2.1 Oxides of magnesium and calcium

The initial research of using magnesium oxide (MgO) in the transesterification reaction did not show good results if it is compared with sodium hydroxide (NaOH), which showed a conversion of 100% in 8 h reaction time and the used temperature was 60°C while the same reaction conditions were achieved using MgO and the conversion was only 11% [11]. The reason for this is the low surface area of this catalyst. That is why researchers started exploring some supports as zeolite Y, silica, and alumina to take advantage of the high surface area of these supports as well as adding a more basic property to the final catalyst form.

Later research using MgO as heterogeneous catalyst in the transesterification reaction was reported that MgO has a high catalytic activity of 92% yield of biodiesel when 12:1 molar ratio of methanol to oil was used, 5.0 wt% of the catalyst, and 1 h

reaction time, also it was shown that MgO achieved a good conversion producing 500 tons of biodiesel in a batch reactor running at ambient temperature [11]. The kinetic studies proved that the reaction using MgO will be faster than using the conventional base catalyzed transesterification without the formation of a byproduct. Moreover, the reaction rate under supercritical conditions of 300°C was used, high molar ratio of methanol to oil of 39.6:1, and MgO as the catalyst was so fast and got to completion in only 10 min yielding 91% of FAME [11]. Knowing the chemistry of the active metals can help predict the efficiency of the final catalyst. Using this metal as the active component in the catalyst, researchers started studying the position of magnesium in the periodic table, by laying in the second group, and third period of the periodic table made it as a second level in the basicity strength after sodium and potassium hydroxides.

To take advantage of good basic property of magnesium, MgO was loaded onto three different mesoporous silicas (MCM-41, SBA-15 and KIT-6), a high conversion was obtained proving that MgO is quite effective in which two catalysis methods were tested in coating and impregnation methods [11]. The x-ray photoelectron spectroscopy (XPS) showed a low attachment of MgO to the surface area of SBA-15 catalyst when using the situ method compared to the impregnation method. The results showed a high surface area and pore volume of the catalyst was obtained in the situ coating rather than the impregnation method. Since the mechanism of heterogeneous catalysis is adsorption, it was found that the surface Mg concentration was quite dominant over other physical elements such as surface area, pore volume, pore size, and pores distribution [11].

Like MgO, calcium oxide (CaO) has attracted the attention of many researchers

globally to the transesterification reaction of triglycerides into biodiesel. This is due to its availability, low cost, and ease of preparation. Calcium lies in the second group and fourth period of the periodic table. Again this group and period are mainly known by its good basicity strength that is sufficient to complete the transesterification reaction with a high yield of biodiesel. CaO has strong basic sites about $H_{\text{L}} = 26.5$, research has shown that using CaO as heterogeneous catalyst has several advantages such as mild reaction conditions, long catalyst lifetimes, and higher activity in the biodiesel reaction [6].

One of the major blocking factors in the efficiency of CaO in the transesterification reaction is the calcination step, which will modify CaO; also, the existence of free water, and the influence of free fatty acid (FFA) should be considered for a CaO application [11]. One study tested CaO as a solid catalyst for the transesterification of jatropha curcas oil into biodiesel. In this experiment, CaO had been treated with ammonium carbonate, and further calcinations, which led to an increase in the basicity strength of CaO to 26.5, the calcination at 900 °C resulted in a 93% conversion of jatropha oil in the biodiesel. The reaction conditions were optimized at 70°C, 1.5% catalyst amount, reaction time of 2.5 h, and the molar ratio of methanol to jatropha oil was 9:1 [11]. In addition to researchers exploring the CaO catalytic activity, nanocrystalline Calcium Oxides were used at room temperature. The reaction rate kinetically was slow requiring 6-24 h to produce a high conversion of biodiesel, and it was detected that the catalyst was deactivated after eight cycles when soybean oil was used as feedstock, and after three cycles with poultry fat [6]. Another study showed the catalytic activity of CaO can be improved by adding a little water in methanol during the

transesterification reaction of biodiesel. This led to a significant catalytic assumption that water could act as a stronger catalyst than methanol alone, and the presence of a specified amount of water could encourage the methylester formation in the transesterification reaction with supercritical methanol [6].

2.3 WCO in Biodiesel

Recently, the high cost of biodiesel is the main obstacle to its marketing and commercialization. Usually, it costs over US\$0.5/l, compared to US\$0.35/l for petroleum based diesel [7]. The suggested reason for the high costs is mainly the cost of virgin vegetable oil [7], in fact, moving from petroleum based diesel to biodiesel for environmental issues would create a problem in the food area due to using edible raw materials. However, using waste cooking oil (WCO) as feed stock in biodiesel reaction would overcome the “food versus fuel” issue which, have been fought over by some non-governmental organizations for transforming food into fuel while hunger attacks millions of people as well as malnutrition [14]. That is why the need for non-edible raw materials as WCO increased recently. The use of WCO over virgin oil to produce biodiesel is a promising way to reduce the raw material cost because it is estimated to be about half the price of virgin oil. Also using WCO would also assist in solving the problem of waste oil disposal [7]. Moreover, the high and increasing numbers of restaurants globally enhances the problem of WCO disposal, encourage researchers to start testing other new applications for WCO, and using it as a feedstock for biodiesel production would make WCO for biodiesel production as one growing research areas. Also, the disposal of WCO

would create huge problems in the areas of water treatment because these wastes are frequently drained; thus, causing other problems [8]. China only, can produce about 0.8 – 1.0 million tons of WCOs per year, and it was reported that Guangzhou, the third largest city in China, could produce more than 20,000 tons per year [15]. Also, it was stated that United States can produce above 10 million liters per year [14], which can be collected for industrial motivations [16]. These large amounts of WCO from restaurants, dining rooms, and catering establishments assisted the soap industry from frying oils; however, these applications showed poor quality, which resulted in more disposal of these wasted frying oils, which created ecological as well as economical problems [17], which was a major reason for this researcher to explore other usages for frying oils.

The usage of low costs feed stock as WCOs is not fully accepted because of the high processing costs that would emerge, which would be required due pretreatments, this would further push the total costs upward. That is why the usage of WCOs as a feedstock for biodiesel production is accompanied with the existence of a catalyst [14]; thus, the reaction rate between the chosen alcohol with this feedstock under moderate conditions would be kinetically slow, and would be reflected in small amounts of produced biodiesel.

2.4 Critical and advanced techniques of biodiesel production

Several biodiesel production techniques have been introduced. Here, we have explained the techniques that have been applied in homogeneous as well as heterogeneous catalysis. The following are the other methods and techniques used and

introduced so far.

2.4.1 Enzyme-catalyzed transesterification

The enzymatic methanolysis using lipases for the transesterifications of oil into biodiesel is also increasingly researched in order to overcome the issue involving the recovery as well as the treatment of the bi-product that requires complex processing equipment [9]. In order to the high costs of using lipase catalyzed transesterification, enzyme immobilization is introduced for ease of recovery and reused, however, still the industrial application of this technology` has been quiet less due to the high costs of biodiesel production as well as some technical challenges [9]. The enzymatic catalysis still caught researcher's attention in the last ten years, due to easy recovery of product, mild reaction conditions, insensitive to high free fatty acids and the ability of the catalyst to maintain its activity to be reused [5].

One issue that accompanied this technique is the deactivation of enzyme, which leads to low biodiesel yields percentage, and is explained by the low solubility of methanol at moderate concentrations, however, this problem can still be overcome by stepwise addition of methanol [9]. The literature also supports the solubility of alkyl esters is higher than that in oil. Previous literature studied the solubility of methanol in alkyl esters, and reports it was higher than in oil. This procedure will also limit the deactivation enzymes. Low solubility of glycerol in biodiesel poses a challenge in enzymatic transesterification of oil because it reduces the enzymes activity that can be, resolved by adding 1, 4-dioxane as a co-solvent to solubilize methanol. However, the high percentage of this solvent was necessary to obtain a reasonable conversion [9].

2.4.2 Production of biodiesel using ultrasound irradiation technique

Sonochemistry applications have attracted many researchers in the areas of developing chemical technologies for the past two decades [18]. Since transesterification reaction of vegetable oil into biodiesel is an equilibrium reaction, it was found that the ultrasound energy is efficient to make the emulsions from immiscible liquids in which this transesterification reaction can easily reach equilibrium in a short reaction time and higher yields of FAME [18]. Also using sonochemical reactors can enhance the mass transfer and interphase mixing between the phases as well as minimizing the extreme required conditions concerning temperature and pressure [17]. Some earlier methods used in cavitation reactors for intensification of biodiesel production. Mainly, this method is based on using pure vegetable oils as a feedstock, which will result in higher process costs as well as some ethical issues related to the usage of pure oils, which is the reason most recent ultrasonic techniques in biodiesel production started using waste cooking oil as the raw material in order to overcome the cost issue [17].

In this technique, a continuous ultrasonic reactor was used for the transesterification reaction of feedstock. Methanol was carried out using a circulation process at room temperature, which resulted in a high yield of biodiesel in a short reaction time with the molar ratio of methanol to oil 5:1, and the used catalyst was potassium hydroxide (KOH), at 0.7 wt% [18]. In addition to that, some studies used WCO as the feedstock for the transesterification reaction with methanol, using KOH as a catalyst in which a continuous ultrasonic reactor is used by a two-step process [18]. In this technique, the fact of the transesterification reaction as an equilibrium reaction

system, took most of the attention. This is why they focused on shifting the equilibrium to the right that is known as the forward reaction (formation of FAME). Therefore, a multi-step transesterification processes was introduced to minimize the effect of glycerin, which thought to be a forward reaction inhibitor and the method suggested a continuous removal of glycerin from the reaction mixture after each step and finally, the overall reaction's equilibrium would be shifted towards the formation of methyl esters (forward reaction) [18].

2.4.3 Transesterification reaction using microwave

In recent years, electromagnetic energy had gained much attention by many researchers [5]. Irradiation is a good example showing the benefits that can be obtained when introducing this technique in the transesterification reaction. It showed several advantages, such as higher yields of cleaner product, lowered energy consumption, and environmental benign compared to the conventional heating in different chemical reactions [5].

A conventional heating process is highly proportional to the thermal conductivity of material, specific heat and density, which caused a significant drawback due to its limitation, also conventional heating suffers from the poor distribution of heat across the reaction vessel resulting in more energy (than the theoretical value), and a slow reaction rate [5]. In addition, direct contact between the heated vessel and the reaction components (reactants) may lead to product decomposition, when heated for long time, when using microwaves techniques. The energy is transferred through the microwaves in the form of electromagnetic fields, and not thermal heat reflux, in which the molecules or

ions become continuously oscillated with polar ends by the oscillating microwave field, leading to more collisions, and frictions between the moving molecules, and would create heat energy, which will increase the temperature of the reacting media resulting in higher yield of products in short reaction time. However, the main drawbacks of using microwave irradiation for biodiesel production are the scaling-up from the lab scale to large industrial scale as well as the safety of this process [5].

2.4.4 Transesterification reaction using oscillator flow reactor (OFR)

OFR is a novel type continuous flow reactor, the parts of this reactor are tubes accompanied by equally spaced orifice plate baffles [5]. An oscillator motion is created upon the net flow of the process fluid, resulting in flow patterns that are conducive for efficient heat, and mass transfer; moreover, each baffle acts as a separate stirred tank reactor forming ideal mixing, and suspension by forming vortices between orifice, and the oscillating fluid making this reactor suitable enough for biodiesel production. Especially, when the biodiesel reaction phase is heterogeneous which, is due to the existence of three immiscible phases in one reaction (oil-alcohol-catalyst) [5]. Also, a comparative study between the conventional heating traditional method and the microwave continuous flow in the energy consumption is shown in Table 2 [5].

Table 2. Conventional heating versus micro-reactor

Entry	Reaction conditions	Energy Consumption (Kj/L)
1	Conventional heating	94.3
2	Microwave continuous flow (7.2 L/min feedstock flow)	26
3	Microwave continuous flow (2 L/min feedstock flow)	60.3 (92.3)
4	Microwave heating (4.6 L batch reaction)	90.1

2.4.5 Production of biodiesel by supercritical transesterification

In transesterification using alkali-catalyzed, acid-catalyzed or enzyme-catalyzed reactions, an excess of methanol is used to push the reaction in the forward direction in order to achieve high yield of biodiesel [19]. Many of the biodiesel industries use the alkali catalyzed process, while one of the problems of using this type of catalysis is its sensitivity to both water and free fatty acids, which they are able to react with the alkali catalyst resulting in the production of soaps and water [19]. That's why it is required to use refined vegetable oils with free fatty acids content of less than 0.5% (acid value less than 1) and this would maximize the methyl esters production [19].

The effects of water presence are the ester saponification, can consume the catalyst and minimize the catalyst efficiency, it was studies that the negative effect of water presence is greater than that of free fatty acids, that's why the water content should always be maintained below 0.06% [19]. Most industries use a middle stage in which the free fatty acid, and water contents are minimized in the feed stream, the free fatty acid is reduced by taken to the path of esterification reaction with methanol in the presence of sulfuric acid, and this middle step will affect the overall production process efficiency as well as increasing capital cost [19], this is why the factors that hinders the efficient use of waste cooking oil, animal fats, and crude oils as raw materials for the biodiesel production is because of their high free fatty acid, and water contents [19].

That's why the production of biodiesel using supercritical transesterification has merged to overcome that high production's cost. It is mainly named as the supercritical

alcohol transesterification, if the used alcohol is methanol then the name will be the supercritical methanol method. The advantages of supercritical methanol are:

1. No catalyst is required;
2. No sensitivity to both water and free fatty acid;
3. Simultaneous esterification of the free fatty acid in the oil.

Using this method would overcome the middle step in soap and catalyst removal which would decrease the high capital cost, however, the extreme conditions of pressure (100-200 bars) and temperature (200-300°C) for the methanol to reach the critical conditions would increase the production's cost due to the energy issue.

2.5 Novel reactors in continuous biodiesel production

Several types of reactors have been introduced in the field of transesterification reaction for producing biodiesel. The goal was to scale up the biodiesel product. This is one of the disadvantages of batch operations in which biodiesel are produced in only laboratory scales.

2.5.1 Static mixers

The main parts of this type of reactor is motionless geometric elements that is especially designed, and is enclosed within a pipe or column and create special radial mixing of the two immiscible liquids as they pass through the mixer. These static mixers have been used recently for continuous biodiesel production in combination with other equipment [20]. Some modifications have been applied to this design in order to achieve more production percentage. One was a stand-alone closed-loop static mixer system, the

system consists of two stainless steel static reactors (4.9 mm ID x 300 mm long) accompanied by 34 fixed right-and left-hand helical mixing elements [20].

High quality biodiesel was produced using this type of reactor while the used catalyst was sodium hydroxide, the qualification analysis of the produced biodiesel showed it met the ASTM D6584 specification, the optimum conditions for the successful completeness of the reaction was at 60°C, the used concentration of sodium hydroxide was 1.5%, molar ratio of methanol to oil 6:1, and a reaction time of 30 min, while the total glyceride content of the produced biodiesel was lower than 0.24 wt% [20]. Also some other modifications has been done as a reactor/separator design involving a static mixer of continuous behavior for biodiesel synthesis and product separation at the same time, the used feedstock was the waste canola oil, which has been pretreated, and the solution of potassium hydroxide in methanol flow into a static mixer, which was then applied to the reaction medium through injection with no moving parts [20]. The emulsified reactants were introduced into the reaction chamber from the mixer with lowering bulk viscosity; then, separated into two layers under laminar flow conditions in the main body of the reactor; the phase with less density (biodiesel) was separated as an upper layer, while the phase with higher density (glycerol) settled as the lower phase [20].

2.5.2 Micro-channel reactors

Those types of reactors have shown good performance in terms of the reaction rates by improving the efficiency of heat and mass transfer and utilizing considerable high surface area/volume ratio and short diffusion distance, the useful characteristics of

those type of reactors have been approved by the higher yields of 90% at mild reaction conditions [20]. Potassium hydroxide- transesterification reaction has been studied using the unrefined rapeseed oil as well as cottonseed oil with the presence of methanol in capillary micro-reactors with inner diameter of 0.25 mm; the surprising fact was that at only 5.89 min residence time the yield was 99.4% which is the methyl ester content of this biodiesel [20]. The catalyst concentration was 1%, the molar ratio of methanol to oil was 6:1, and the temperature was 60°C more modifications has been done by designing the zigzag-micro-channel reactors for continuous alkali-catalyzed biodiesel production, the configuration of these type continuous reactors is accompanied with a narrower channel size and more turns, the main goal of this type continuous biodiesel production is to intensify the biodiesel production rate by obtaining smaller droplets compared to those micro-channel reactors with T or Y-flow structures [20]. The yield of such reactor was as fast in terms of the reaction kinetics, only 28 s residence time, molar of 9:1 of methanol to oil, and a catalyst concentration of 1.2 wt% of sodium hydroxide were sufficient enough to produce a yield of 99.5% of methyl ester [20].

The advantages of use of micro-channel reactor (small size) will offer minimization in the footprint requirements, construction, and operation costs. Also, it is easy to scale-up, which may be readily achieved by connecting more reactors of the same proven dimensions in parallel [20]. This approach can minimize the risk associated the scaling up in conventional reactors. One significant advantages of using the micro-channel reactors is that less energy is also consumed for the same amount of biodiesel, if it is compared with the conventional stirred reactor. The reason for this is the high heat

transfer rates achieved in these micro-channel reactors [20].

2.5.3 Plug-flow and fixed-bed reactors

A plug-flow reactor has not been applied in biodiesel on a usual basis, which is why many questions need to be answered by investigating the reactor in biodiesel applications, such as the flow velocity determination of this reactor [21]. Fast velocity will result in a shorter residence time, which then will lead to an incomplete reaction, because the residence time plays a major role in the conversion process, also the slow flow velocity will form a laminated flow inside the reactor, while the turbulent flow will not be formed; therefore, a uniform mixture of the reaction medium will not be produced [21]. These two conditions will lead to less biodiesel produced due to low biodiesel conversion rate; therefore, more studies needs to be done exploring the effect of the residence time in a plug-flow reactor in order to achieve a high conversion rate and high biodiesel yield [21].

Several studies has been conducted exploring the fixed-bed reactor in the transesterification reaction for biodiesel production, because fixed-bed reactor would offer a chance in using solid catalyst(heterogeneous reaction) instead of those homogeneous catalysts which will support the idea that mentioned earlier in lowering the separation cost and the overall production costs. One of these studies tested the fixed-bed reactor under the conditions of 65°C as reaction temperature, methanol to oil ratio of 8:1, a fixed catalyst load to the reactor and the feedstock in this work was the Chinese wood oil, which has been pretreated [21]. Different residence time was obtained by varying the flow rate of the feedstock to oil, which resulted in variation of the acid value and

corresponding esterification conversion. When the residence time was as high as 45 min, the acid value of the feedstock was reduced from 7.02 mg KOH/g to 1.28 mg KOH/g [21].

However, increasing the residence time over 45 min up to 90, would slightly decrease the acid value of the product. This can be explained by, the reversed esterification reaction between methanol, and the free fatty acid. When the reaction time is long, a hydrolysis reaction of the free fatty acid ester will take place, which supports producing more fatty acid ester as well as water. Finally the acid value will drop to a lower value. [21].

2.5.4 Oscillatory flow reactors

These reactors are tubular reactors in which the orifice plate baffles are equally spaced, and the oscillatory flow is produced using a piston drive, when a bulk fluid is applied in the reactor, the oscillatory motion interacts with this bulk fluid for the purpose of intensifying the radial mixing, some enhancements in mass and heat transfer are detected while keeping the plug flow [20]. This type of reactor can also accomplish long resident times because the intensity of mixing degree is not directly dependent upon the Reynolds number (from fluid mechanics point of view) so the bulk flow through it. Basically, it is associated with the formed oscillatory conditions; therefore, this reactor can be designed with a short length-to-diameter ratio, and this will decrease the design costs, which further improves the economy of biodiesel production because of the smaller (foot print), lower capital, pumping cost, and easier control [20].

The oscillatory flow reactor (OFR) has been studied and tested in several

commercial plants due to their impact in two critical factors of biodiesel production, which are the capital cost as well as the energy consumption factor [20]. Most literature studies reported that the transesterification reaction of oils into biodiesel can be done using this reactor at moderate low temperatures, which will overcome the energy consumption issue. Also mentioned earlier, the residential time associated with using this type reactor in a continuous process is long enough to provide the proper conversion percentage, which will have a greater influence on the design cost because the designed reactor has a short length-to-diameter issue, which further decreases the overall cost of the biodiesel production. When this type of reactor technique is employed, the disadvantages of using this technique, from the researcher's view, are difficulty in producing the uniform oscillator reaction medium under operating conditions. In addition, most work using this technique has used potassium hydroxide, sodium hydroxide in producing biodiesel, which means this system, favored the homogeneous phase of reaction, and the system will face a separation cost factors. As mentioned earlier in the disadvantages of using the homogeneous phase of reaction in the transesterification reaction of oils into fatty acid methyl esters.

In addition to all those literature studies concerning biodiesel quality control, some studies were concerned with the biodiesel tolerance to low temperature. Biodiesel has always been compared to petroleum based diesel [22]. A major challenge using biodiesel as a sustainable alternative fuel for diesel engines is improving its low temperature flow characteristic [22]. Also, was reported that biodiesel from waste tallow as a feedstock in the transesterification reaction gave higher yield of biodiesel up to 93%

and 99% [23]. The conditions were optimized to be 5 grams of used tallow, oil to methanol ratio was 1:30, temperature was 50°C to 60°C, some H₂SO₄ has been used and the reaction ran for 24h [23]. Some global continents showed great interest in biodiesel as an alternative fuel source [24]. Europe, as an example, the most important biofuel is biodiesel, represents about 82% of the biofuel production; moreover, biodiesel production in 2003 in the United Europeans was 1,504,000 tons [24]. The motivation of researchers to explore biodiesel as an alternative source of energy is due to recent increase in petroleum prices, and the uncertainty of petroleum availability [25].

Additionally, sulfuric acid in the transesterification reaction has been strongly effective [26]. Conversion using jatropha oil with only sodium hydroxide showed a conversion of only 47.2%, while the addition of sulfuric acid pushed the conversion up to 92.8% , with a reaction time of 4h [26]. Also jatropha oil has been used as a raw material in the transesterification reaction while the catalyst was nanosized and mixed Mg/Al oxides, the conversion was 95.2% [27]. Jatropha oil, non-edible vegetable oil, has also been tested under microwave irradiation technique which enhances the kinetics of the reaction (reaction rate) from 150 min to only 2 min [28]. Moreover, the catalytic activity in the transesterification reaction has been studied [29]. Homogeneous liquids and heterogeneous solids in both batch, and continuous processes have been discussed [29].

One of the biggest known challenges for heterogeneous catalyst is its economic competitiveness due to the high energy consumption factor [30]. However, the homogeneous catalyst is still faced with the saponification problem as well as its sensitivity to high free fatty acid raw materials [31]. Also some other used oil as hazelnut

waste, and sunflower oil as a raw material has been studied as well as the continuous production of biodiesel to overcome the high production cost problem [32] and [33]. Other techniques strongly recommended running the transesterification reaction at supercritical alcohol conditions; however, it was mentioned earlier that this technique still has a high energy consumptive technique [34]. Heterogeneous catalysts (acid or base) are still a promising field for biodiesel production [35] thru [37]. Moreover, some techniques used Bronsted ionic liquids, in which the strong ionic property of these liquids has been used as a catalyst in the transesterification reaction [38]. The effect of alcohol, waste cooking raw material, usage of virgin raw material, the efficiency of acid, and alkali catalysts in the process of biodiesel production has been reported in earlier studies [39 thru 42].

Some studies varied the transesterification reaction between the batch operations and the continuous production of biodiesel, which showed the economical analysis between the two operations [43] and [44]. In addition, some techniques used the ion exchange resins for biodiesel production [45]. Lewis acids in both homogeneous and heterogeneous phase have shown good influence on the process of biodiesel production [46], [47], and [48]. Also, more studies focused on the supported zirconia catalysts and their catalytic activity in several chemical reactions as well as the transesterification reaction [49] and [50].

CHAPTER 3

Materials and Method

3.1 CA-Y catalyst preparation

Calcium on zeolite Y is prepared using the wetness impregnation method, this method showed effective results in terms of the active metal (Calcium) attachment to the support (Zeolite Y), and since heterogeneous catalysis is based on the strong attachment to the active metal to the chosen support, that is why this method has been selected in this work to obtain the most effective catalyst active sites as much as we can. It has been mentioned before, that both the calcinations temperature and the duration of calcination time play a major role in the catalyst activity. This can be explained by the uniform pores distribution as well as the perfect pore volume that can be obtained by manipulating these two parameters. Ca-Y is shown in Figure 1.

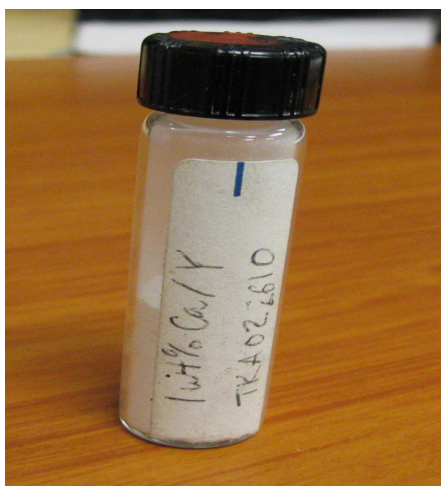


Figure 1. Ca-Y

The higher calcination temperature as well as the higher calcinations period will result in higher and well exposed active sites of the generated catalyst. However, a calcination temperature higher than the tolerant range for the proposed catalyst as well as a longer calcination period exceeding the optimum calcination time of the catalyst will result in destroying the active sites and the catalytic activity of the catalyst (the terminology used in such cases is the poisoning of the catalyst). That is why it is recommended that before running the procedure of developing homogeneous or heterogeneous catalyst is to know the physical, chemical and thermal properties of the active component as well as the catalyst support. In this work, the chemical property of calcium according to the periodic table of chemical elements has been studied, thermal as well as physical properties of calcium has been reviewed and finally the decision of the optimum calcination temperature as well as the isothermal calcination period of time for calcium has been specified. Also a wide range of Zeolite Y was studied as a group to explore and detect the optimum calcinations temperature and the preferred calcination cycle time. Also it is significant to choose the proper solvent for the impregnation method under the considerations of environment point of view. In this work, calcium Nitrate as a powder is from Fischer, zeolite Y is from Aldrich.

3.2 Catalyst preparation

The method used for preparation of Calcium on Zeolite Y is named as the wetness impregnation method. Fifty grams of Zeolite Y is calcinated at 400 °C for 4 hours and allowed it to cool at room temperature for 6 hours. Also 5 cc solution of Calcium Nitrate

is prepared. Using a pipette this solution is loaded onto Zeolite Y with a continuous grinding, the Calcium is loaded to Zeolite Y in 20 minutes. The Calcium load on Zeolite Y was calculated to be 2% loading, these calculations considered the percentage of calcium in calcium nitrate tetrahydrate. The resulting product (refer to Figure 2) is dried using a vacuum at 100 °C for 4 hours and finally this product is calcinated at 600 °C for 6 hours.

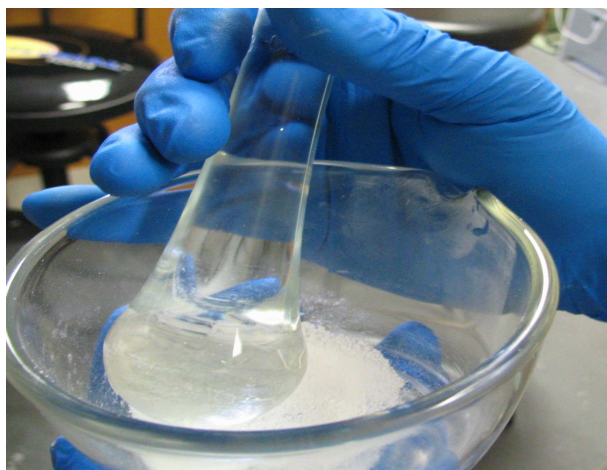


Figure 2. Grinding stage of Ca-Y

The prepared catalyst is allowed to cool down at room temperature for 18 hours. Sulfated zirconia was prepared using the solvent free method. Zirconylchloride octahydrate was mixed with ammonium sulfate and the molar ratio was 1:6. The two chemicals (powder form) were allowed to settle at room temperature for 18h and the final product was calcined at 600 °C for 5h. Also the grinding of both calcium nitrate and zeolite Y was done in a ceramic crucible to ensure the adsorption of the alkaline metal

(calcium) to the support surface area (zeolite Y). Proper adsorption will further contribute to the catalytic efficiency in the transesterification reaction. 0.2 g of the prepared catalysts is taken to be tested under BET for catalyst's characterization purpose.

3.3 BET Analysis

Brunauer, Emmett and Teller, the BET, was bought from NOVA 2200e for surface area and pore size analysis for the prepared catalyst's characterization. The process was started by placing the catalyst inside the cell to do degas out for 3 hours. Then the sample was removed and placed inside a liquid nitrogen cell to study the adsorption of Nitrogen on the catalyst. BET would scan for surface area, pore size, and pore volume of the catalyst. The results show that the surface area of this catalyst is 534 m²/g. the surface area of sulfated zirconia was found to be 100 m²/g.

3.4 Batch Reaction procedure

1. Mix 500 ml Methanol and 2.5 g of prepared Ca – Y in tube for 20 minutes, methoxide is then prepared.
2. Place stir bar gently into the beaker, pour 100 ml of soybean oil into beaker, place the oil onto stir/hot plate.
3. Set hot plate to 55 degree Celsius, and stir to 400 rpm, allow oil to reach reaction temperature, the hot plate will bring the temperature to 55; (this is below the evaporation temperature of methanol which is 64 degree

Celsius). We want to run the reaction at a temperature below the evaporation temperature of methanol.

4. Add the methoxide to oil when the temperature has stabilized at 55 degree Celsius and keep stir at 400 rpm.
5. Run the reaction for 1.5 hrs.

A high amount of methanol is used because a portion of methanol will start evaporating at 60⁰C and only 20% will stay in the system to complete the transesterification process. In addition to that the used batch reactor with magnetic mixing is to confirm both uniform and constant concentrations during the reaction process. Also, the oil has polar and non polar groups while the alcohol is polar; it requires a continuous mixing for the two liquids to enhance the reaction.

3.5 Separation procedures

The product mixture is placed in separator funnel and, allowed to separate at room temperature for 10 hours. Two layers are formed. The top layer is biodiesel and the bottom layer is glycerol. The top layer of biodiesel is removed and is mixed with 0.3 ml of Acetic acid to ensure that all of the undesired salts are removed.

The product is centrifuged for 20 minutes at 1400 rpm and allowed to settle down. Then, it is filtered with 0.2 μ m filter paper to remove all of the suspended residuals. The reason for adding acetic acid to biodiesel is to remove the calcium salts. Those salts are formed during the reaction of calcium on zeolite Y with the triglycerdies (feedstock). This step is used for further purification of the biodiesel.

3.6 GC analysis

Gas Chromatography (GC) is an analytical instrument mostly used in identifying and analyzing different known chemical compounds on the basis of separation and comparison to a set of standards. This equipment is accompanied by a separator column, the different unknown components of a mixture is identified according to the varying molecular weight of those components. Those known components will run through the column and be separated according to the difference in molecular weight, since we are applying several hydrocarbons that are known as biodiesel components (methyl esters, glycerol, monoglyceride, diglyceride and triglyceride) we would expect the separation between them will be based on the difference in molecular weight, generally known as lighter and heavier keys (light and heavy unknown components, respectively). GC generally consists of an inlet, separator column and a detector, the detector could be thermal conductivity detector (TCD) or flame ionization detector (FID). Other types of detectors have been introduced to GC but those two are the most commonly used detectors. The GC that we used here was from Agilent Technologies the version of this

This GC consists of an inlet with a carrier gas, capillary column and FID detector. The used gases are hydrogen, air for igniting the flame ionization detector and helium which is an inert carrier gas.

Hydrogen and air goal is to activate FID by generating flame; while helium is used as a carrier gas. Helium is an inert gas and is not going to interact with the sample of known or unknown components Chemostation is 7890 A. Agilent 7890A is shown in Figure 3.



Figure 3. Agilent 7890A GC

Two methods were introduced here for biodiesel both quantitative and qualitative analysis, EN 14103 which is the European standard method for testing biodiesel and ASTM D6584, which stands for the American Standard testing Materials method also used for biodiesel testing.

3.6.1 EN 14103

This method is used to study and determine the Methyl esters content in the produced biodiesel that is intended for use as pure biofuel or as a blending agent for heating and diesel fuels. Also this method will determine the linolenic acid methyl ester content. According to the European standard method, the limitation on the biodiesel is that the ester content of FAME must be higher than 90% (m/m) and the linolenic acid content must be between 1% (m/m) and 15% (m/m). In addition to that, this method is designed for FAME which contain methyl esters between C₁₄ (methyl myristate) and C₂₄ (methyl lignocericate) the reference number that is commonly used by the European

standard for those two types of biodiesel calculations is EN ISO 5508[ICS 67.200.10].

This method requires an internal standard which is C₁₇ (methyl heptadecanoate) for internal calibration calculations.

3.6.1.1 Tools

1. Glassware
2. 10 ml capacity screw-cap vials accompanied with PTFE septa.
3. 10 ml capacity volumetric flask.
4. Milliliter capacity pipette.

3.6.1.2 Reagents

All of the used reagents are of recognized analytical grade.

1. Heptane
2. The internal standard Methyl heptadecanoate (C₁₇) of known purity (99%)

3.6.1.3 Preparation of Methyl heptadecanoate

In EN 14103, Methyl heptadecanoate is considered as the internal standard for the quantification analysis, by which its area, height and width are being used to compare them with the methyl esters profile in the biodiesel to be able to calculate both of the total methyl esters content as well as the total content of linolenic acid methyl ester content.

10 mg/ml solution of methyl heptadecanoate was prepared by accurately weighing 100 mg of methyl heptadecanoate in a 10 ml volumetric flask and making it up to the volumetric flask mark with heptane.

3.6.1.4 Preparation of the biodiesel sample

Accurately weighed 25 mg of the biodiesel sample in a 10 ml vial, and then add

0.5 ml (500 μ l) of methyl heptadecanoate solution using a pipette.

3.6.1.5 *Chromatographic analysis*

EN ISO has specified the analysis conditions in order to analyze the biodiesel sample, also this method is a significant tool in allowing one to verify that the biodiesel sample matches the standard biodiesel qualifications and limitations that represented in the total ester content must be higher than 90% and the linolenic acid content must be between 1% and 15% (m/m). The chromatographic conditions such as the injected quantity, oven temperature programming, carrier gas pressure and the split mode flow rate were adjusted in a manner that the full methyl ester peaks and profile of the lignoceric (C₂₄) and nervonic (C_{24:1}) could accurately be visualized. In addition to that, the integration events are carried out only for the region from methyl myristate (C₁₄) peak up to that of the methyl ester in nervonic acid (C_{24:1}) taking all the peaks between those two methyl esters under consideration. It has been noted that in this method the presence of unknown peaks other than saturated and mono-unsaturated FAME in the area between the linolenic acid (C_{18:3}) and the nervonic acid (C_{24:1}), that will be an indicator of some fish oil contaminated with the sample. This method would give several qualifications as well quantification facts about the produced biodiesel, and can specify in some manner the purity of the analyzed biodiesel sample.

3.6.1.6 *Calculations method*

A formula was developed to calculate the total percentage of the ester content (C), which is expressed as a mass fraction in percent:

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

Where:

$\sum A$ is the total peak area from the methyl ester in C_{14} up to that in $C_{24:1}$;

A_{EI} is the peak area corresponding to methyl heptadecanoate or named as C_{17} (internal standard);

C_{EI} is the concentration, expressed in milligrams per milliliter, of the methyl heptadecanoate solution that being used;

V_{EI} is the volume, in milliliters, that taken from the methyl heptadecanoate solution;

m is the mass, in milligrams, of the sample.

When using this type of calculations, one should note that if the used raw material is vegetable oils, the result of the calculation based on relative areas is considered to represent a percentage by mass. Also, if the mean of two calculations of total ester content is higher than 100.8%; then, those results should be discarded and one should verify the experimental conditions as well as the purity of the used internal standard (methyl heptadecanoate) by using this method to determine the total ester content of commercial or an experimentally prepared mixture and finally always the result should be expressed to one decimal place [ICS 6.200.10].

3.6.1.7 Determination of linolenic acid methyl ester

The European standard method for biodiesel limitation has specified that the total percentage of linolenic acid methyl ester content (L) in the biodiesel sample must be between 1% and 15%, using EN14103 analysis method will allow us to verify that if the obtained biodiesel will pass this requirement or not, this is another qualification property

can be added to this method as one of the advantages of using it. Again the result here in such calculation is expressed to one decimal place; the calculation of the total percentage of linolenic acid methyl ester content is done using the following formula:

$$L = A_L \times 1 / [(\sum A) - A_{EI}] \times 100 \%$$

Where:

$\sum A$ is the total peak area ranging from the methyl ester in C₁₄ up to that in C_{24:1};

A_{EI} is the peak area corresponding to the internal standard (methyl heptadecanoate):

A_L is the peak area corresponding to linolenic acid methyl ester.

Also the calculations of the biodiesel yield are done through the following equation:

$$\text{Yield} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \times 100 \% \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\% \approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100 \% \approx$$

$$\frac{C_{\text{esters}} \times n}{P_{\text{oil}}} \times 100 \%$$

P_{oil}

Where:

Both m_{actual} as well as $m_{\text{theoretical}}$ are the mass of obtained fatty acids methyl ester.

Also, m_{oil} (g) is the mass of soybean oil, C_{esters} (g/ml) is the mass concentration of fatty acid methyl esters that has been acquired by the GC, n is the diluted multiple of fatty acid methyl esters, ρ_{oil} (g/ml) is the density of soybean oil, V_{esters} (ml), and V_{oil} (ml) are volumes of fatty acid methyl esters layer, and the layer of soybean oil, respectively.

3.6.1.8 EN 14103 chromatographic conditions

The Agilent 7890 A has built-in macros in the software. This software was configured to run and analyze the biodiesel calculations in terms of total methyl ester content as well as the total linolenic acid content, and later, we present an analysis of monoglyceride, diglyceride, triglyceride, and glycerol contents in the produced biodiesel and that method is named as ASTM D6584. This GC was configured to analyze and study the biodiesel samples. The main analyzing component is the dedicated capillary design accompanied with a capillary split and split less ratio (S/SL) inlet as well as a ‘capillary only’ flame ionization detector or FID. A typical plumbing diagram is shown below (adapted from Agilent – specials and solutions group – reference: 7890-0300). Different GC parts are shown in Figure 4.

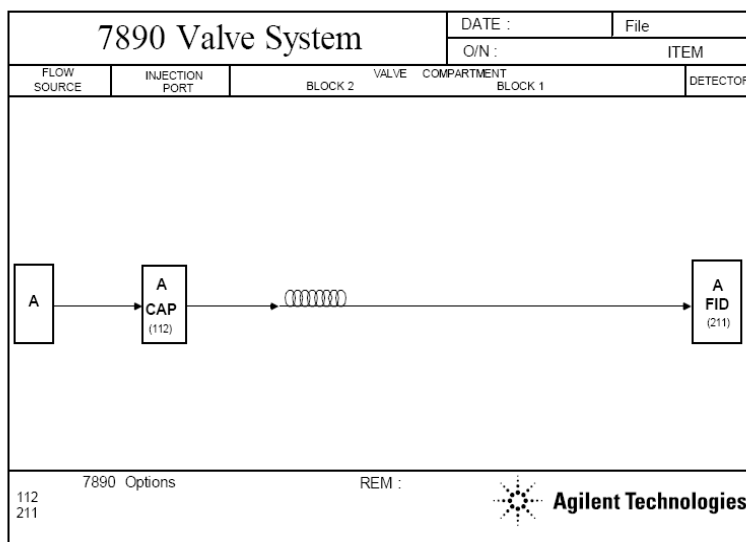


Figure 4. The different GC parts

Conditions as well as parameters during running this method according to EN14103 conditions were as follows:

1. The oven equilibration time is 0.5 min and the oven temperature program was 150 °C for 1 min then 15 °C/min to 200 °C for 0 min and finally 2 °C/min to 250 °C for 5 min, while the run time is 34.333 min.
2. The mode used here was split mode and the inlet conditions are 250 °C for the heater, pressure is 10.881 psi, total flow 79.5 ml/min, septum purge flow 3 ml/min, split ratio is 50:1 and split flow of 75 ml/min.
3. The type of detector used here is flame ionization detector (FID), which was adjusted with H₂ flow of 40 ml/min, Airflow of 400 ml/min, make up flow of 45 ml/min and the heater of detector is adjusted to be running at 250°C.

3.6.2 ASTM D 6584 method

The American Standard Testing Materials, This method is used to detect the content of monoglycerides, diglycerides, triglycerides and glycerol (bonded and free glycerol). It is considered to be as a quantitative tool in analyzing the biodiesel sample to evaluate the free and total glycerin in B-100 methyl esters by gas chromatography. The range of detection of free glycerin is specified to be from 0.005 to 0.05 mass% while the total glycerin ranges from 0.05 to 0.5 mass%. The limitation on using ASTM D6584 in analyzing biodiesel sample is that it cannot be applied to methyl esters of vegetable oil that obtained from lauric oils as coconut oil and palm kernel oil. SI units are the units used in expressing the data in this method. No other units of measurement are included in this standard.

3.6.2.1 Terminology

Here, we define some of the terms used throughout this method.

3.6.2.2 Biodiesel (B-100)

The fuel is comprised of mono-alkyl esters of long chain fatty acids from vegetable oils or animal fats

3.6.2.3 Bonded glycerin

The bonded glycerin is known as the portion of glycerin bonded to monoglyceride, diglyceride and triglyceride molecules.

3.6.2.4 Total glycerin

The total glycerin is defined as the total of free and bonded glycerin added to each other.

3.6.2.5 Test method

The sample is analyzed using gas chromatography, after silyating with N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA). The calibration is done using two internal standards and four reference materials. Monoglyceride, diglyceride and triglyceride are calculated by comparing them to monoolein, diolein and triolein standards, respectively. The bonded glycerin content of the biodiesel sample is calculated by applying average conversion factors to the mono-, di- and triglycerides. The values of free and bonded glycerin is very significant to be known, because, high content of free glycerin may lead to critical problems during the storage or may be in the fuel system, due to separation of the glycerin. In addition, high total glycerin may cause injector fouling as well as contribute to the formation of deposits at injection nozzles, pistons and valves. The

conditions of this method are as follows:

1. Open tubular column accompanied with a 5% phenylpolydimethylsiloxane bonded and cross linked phase internal coating, Column 1 is DB – 5 HT 15 m x 0.32 mm x 0.10 μ m Capillary column Combined with a 1 m x 0.53 mm deactivated fused silica pre-column. The maximum tolerance temperature of this column is 400°C.
2. Oven initial temperature is 50°C, the oven program is done through a temperature ramp or rates:
 - a) Rate 1: 15°C/min to 180°C and hold it at that value for 1 min.
 - b) Rate 2: 7°C/min to 230°C and the hold time is for 0 min.
 - c) Rate 3: 30°C/min to 380°C and hold it at that temperature for 10 min.
3. Back inlet heater is 50°C, pressure of 7.5 psi and septum purge flow of 15 ml/min.
4. The injection type is cool on column injection and the biodiesel sample size for injection is 1 μ L.

3.6.2.6 *ASTM D6584 reagents and materials*

The purity of all reagents should be of reagent grade chemicals; also those reagents conform to the specifications and limitations of the Committee on analytical reagents of the American Chemical Society where those types of specifications are available. Those reagents must be of a sufficient purity to verify ensuring the accuracy of the analysis as well as the determination.

3.6.2.6.1 n-Heptane

Reagent grade, brought from ACROS, n-Heptane, it is of spectro grade.

3.6.2.6.2 MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide)

Also used in reagent grade, is from Agilent technologies.

3.6.2.6.3 Carrier gas

The carrier gas used in this work is helium, which is known as inert gas. The grade of helium is scientific, in which suitable agents has been added to ensure the removal of water, oxygen and hydrocarbons and the pressure is adjusted to be at 80 psi which is sufficient enough to verify a constant carrier gas flow rate.

3.6.2.6.4 Microlitre syringes

Microliter syringes of 100 μ L and 250 μ L capacities have been used in injecting the samples.

3.6.2.6.5 Screw Cap Vials

Those vials are 10 ml capacity and accompanied with polytetrafluoroethylene (PTFE) faced septa. ASTM D 6584 requires five standard solutions for the purpose of generating the calibration curve and two internal standards, those five standard solutions are prepared in 5 vials and the amount added is listed in the Table 3.

Table 3. The five standard solutions and their amounts

Standard Solution Number	1	2	3	4	5
μ L of glycerin stock solution	10	30	50	70	100
μ L of monoolein stock solution	20	50	100	150	200
μ L of diolein stock solution	10	20	40	70	100
μ L of triolein stock solution	10	20	40	70	100
μ L of butanetriol stock solution	100	100	100	100	100
μ L of tricaprinn stock solution	100	100	100	100	100

The five standard solutions, 1, 2, 4-butanetriol or butanetriol (first internal standard) and 1, 2, 3-tridecanolyglycerol or tricaprin (second internal standard) were all brought from Agilent technologies. Some biodiesel methods such as EN 14103, requires only one internal standard (C₁₇ methyl heptadecanoate) that can explained as, the calculations made in EN 14103 requires only one level of standard and according to the area, height and width of the internal standard peak, the methyl ester profile of peaks are compared to that of the internal standard. But, two internal standards are utilized in ASTM D6584 which means the mono-, di-, triglycerides and glycerol peak profile this means we need the peak height and width of the two internal standards in order to determine the peak profile of mono-, di-, triglycerides and glycerol. To complete the analysis we need to compare the peaks of monoolein (for monoglycerides detection), diolein (for diglycerides content) and triolein (for triglycerides detection) and compare these peaks with that of the two internal standards. Another reason of using two internal standards in ASTM D6584 method, while only one used in EN 14103, is that, in ASTM D6584, the profile of monoolein, diolein and triolein shows up in wider ranges than that of EN 14103. Also the retention times are so closed in value that is why the need of two internal standards for full separation between peaks and accurate as well as precise calculations is essential in this method.

3.6.2.7 Calibration and standardization

Agilent Technologies prepared the five standard solutions using fresh compounds, the standard components were weighed into volumetric flasks and the nearest mass to 0.1 mg was recorded, then the volumetric flasks was diluted to the mark with pyridine. The

prepared standard solutions (calibration solutions) were stored in a refrigerator when not in use [D6584-07].

3.6.2.7.1 Standard solutions

In this work, the five standard solutions were prepared by adding the components in the above table according to the specified amounts in the table by means of microliter syringes to the 10 ml septa vials. 100 μ L of MSTFA is added to each of the five standard solutions. Vials were closed and shaken. Allow these vials to stand from 15 to 20 min at room temperature conditions. Finally, add 8 ml of n-heptane to the five vials and shake.

3.6.2.7.2 Standardization

The five standard solutions are injected one at a time, the calibration standards were analyzed under the same operating conditions as the sample solutions in order to ensure high accuracy of the prepared calibration table and therefore, precise calculations of mono-, di-, triglycerides and total glycerol (bond and free glycerol). 1 μ L of the reaction mixture is injected into the cool on-column injection port and the analysis is then started. For each reference substance, a chromatogram and peak report is obtained. The data (peak height, area and width) for those five standards after integration is saved to be the standard biodiesel template. All of the calculations of the biodiesel samples in detecting mono-, di-, triglycerides and glycerol (ASTM D6584) will be based on those saved standard solutions.

3.6.2.8 Sample preparation procedure

1. The instrument operating variables are set to the values mentioned earlier as analysis conditions for ASTM D6584.

2. An approximate of 100 mg of the biodiesel mixture is weighed directly into a 10 ml septa vial.
3. 100 μ L of each internal standard (first and second internal standard) is added using microliter syringes.
4. 100 μ L of MSTFA is added to the sample mixture.
5. The vials are shaken to ensure the complete derivitization of the biodiesel sample with MSTFA solution.
6. The mixture is allowed to stand and set for 15 to 20 min at room temperature conditions.
7. An approximate of 8 ml of n-heptane is added to the vial and shaken.

3.6.2.8.1 Injection and identification of peak methods

1 μ L of the biodiesel reaction mixture after it has been treated with MSTFA, first internal standard(butanetriol), tricaprin (second internal standard) is injected into the cool on-column injection port and the analysis is monitored to watch the obtained chromatogram as it is running inside the column, the chromatogram and peaks profile (for the whole glycerin content) as well as the integration report is finally obtained according to the data that has been built –in the calibration table that has been developed earlier and saved. The peaks are identified by comparing the retention times to those of the standard solutions.

The additional peaks are identified using the relative retention times and reference chromatograms that has been provided by ASTM D6584 method. The mono-, di-, and triglycerides are separated with respect to the carbon number (CN). Monoglycerides are

mainly consist of four overlapping peaks associated with relative retention times (RRT) of 0.76 and 0.83 to 0.86 according to the second internal standard (tricaprin). A pair of peaks methyl esters bearing a carbon number of 24 might appear with relative retention time of 0.80 to 0.82 and must not be included in the calculation of monoglycerides.

Also the carbon number is a prime factor in separation of diglycerides, but due to varying double bonds in the molecules, this creates a problem expressed as that, the baseline of resolution of the peaks does not occur, grouping of 3 to 4 peaks with relative retention time of 1.05 to 1.09 (CN 34, 36, and 38) must be contributed to diglycerides, also triglycerides are separated with carbon number shown as, the peaks with relative retention time of 1.16 to 1.31 (CN 52, 54, 56, and 58) must be included in the calculation.

When all of the peaks are identified, the areas of those peaks representing glycerin, mono-, di-, and triglycerides are measured. The slope and y-intercept of the calibration functions have been used to calculate the mass of each component.

3.6.2.9 Continuous Tubular Reactor

In this work, the transesterification reaction of soybean oil using calcium on zeolite Y (solid catalyst) is tested in a Continuous Tubular Reactor, most known as packed bed reactor (PBR). This reactor was bought from Autoclave Engineers and the reactor model we used is called BTRS-Jr. This unit is designed with four feed lines (input). It could be four liquids or four gases or a combination of both. The maximum flow rate is 12,000 SCCM, the lowest pressure is 20 psi and the system can go to higher pressure up to 1450 psi. Also, it is equipped with temperature controllers to adjust the reactor oven temperature, reactor wall and the temperature inside the reactor which can

go up to 650 °C. The reactor volume is 10 ml and since it is a PBR so the only parameters we need to pay attention to is the volume of this reactor as well as the weight of the loaded catalyst to the bed reactor. The furnace covering the reactor can increase the temperature of the wall as inside to 650°C. BTRs, Jr is shown in Figure 5.



Figure 5. BTRs, Jr unit

There is also a 6 inlets valve to switch on the product automatically to the GC for online analysis of the produced biodiesel. This transfer line is heat traced. There is an insulated tube that connects between the outputs of the sample valve to the injection port at the gas chromatography; the reason of heating this line is to maintain this line in hot conditions so that there are no cold spots would be between instruments which will provide optimum reproducibility. However, in this work, samples of the biodiesel are collected and injected manually, from the condenser line to the GC. This Tubular reactor has a purge line and we use nitrogen to purge the system, and it has air inlets to control the heaters valves. The BTRS-Jr system is also accompanied with a reactor status valve

which sends the reactants on line to the reactor or off line bypassing the reactor, which will enable the operator to collect the reaction samples. An HPLC pump series III pump (10 ml/40 ml Heads) is hooked up directly to the top of the reactor. It is accompanied by ASI check valves which enable pumping highly viscous fluids such as oils in which the viscosity can go up to 60 centipoises. The oil and methanol are mixed together in the inlet at room temperature. We are using, three different molar ratios of oil to methanol in this research 1:3, 1:5 and 1:12. The catalyst (Ca – Y) is preloaded to the reactor. A layer of glass wool keeps the catalyst in the reactor and prevents it from going through the output line to the pump. A recycle line is used to collect samples of product for analysis at specific time intervals and temperatures. This will give a clear study of the reaction kinetics for this catalyst. This would also show the catalyst activity as well as the catalyst lifetimes which is the number of runs the catalyst will maintain the same activity.

The conditions of this reactor was adjusted at 5 ml/min, the feed condition was at room temperature, oil is mixed with methanol before sending them the reactor, basic condensed was attached to the feed inlet where a recycle line is installed, too, 1/16 inch type of pipe system is installed at both of the inlet as well as the outlet of the reactor, where the product is collected in time intervals of 15 min. when the reaction was run at moderately elevated temperatures, some pressure adjustments inside the reactor was done, because of the generation of methanol vapor pressure at those high temperatures.

3.6.2.10 TGA ANALYSIS

Thermal gravimetric analysis, TGA, is a technique for characterizing thermal stability of material (compound or mixture) by measuring changes in its physiochemical

properties expressed as weight change as a function of increasing temperature. Therefore the decrease in mass is related to the increasing temperature and this decrease in mass corresponds to the thermal stability of that material and it reflects the thermal degradation to the gaseous phases.



Figure 6. TGA

TGA does not require any solvent or reagent to be used. These analyses can be used to monitor the biodiesel production in industry. It can determine the optimum time to complete the conversion of the reaction. It can also give a strong comment on the efficiency of biodiesel production process. However, TGA cannot predict the biodiesel quality as the percentage of the methyl esters content in the biodiesel as well as linolenic acid methyl esters. Those calculations are produced by using the GC.

The analysis of soybean-based biodiesel and oil were finished with 50 μ L samples corresponding to 54.38 mg by weight. Also the samples were ramped at 50 degree Celsius per minute in atmosphere of nitrogen at a constant purge rate of 50 mL/min at the pan. Although other heating rates were tested as 100 ml/min, 50mL/min as a purge rate

proved to be logical with the results obtained. The temperature range examined was from 50 – 600 degree Celsius.

3.6.2.11 WCO preparation

Also in this work, WCO was tested as a feedstock in a continuous transesterification process using packed bed reactor. Some pretreatments have been applied to WCO before installing it as the feedstock for the transesterification reaction. WCO was filtered to remove all of the cooking residuals from the oil, heated to 40°C, finally added sodium sulfate (Na_2SO_4) to reduce the free fatty acid number before running WCO in the transesterification reaction otherwise severe saponification issue will be faced. Figure 7, shows waste cooking oil.



Figure 7. Waste cooking oil

CHAPTER 4

Results and Discussion

4.1 BET results

The BET instrument for scanning a surface area, pore volume, and pores distribution for the developed calcium on zeolite Y (Table 4, and Figure 8.); sulfated zirconia catalysts (Table 5, and Figure 9) showed a high surface area of 534 m²/g and a moderate surface area of 110 m²/g for calcium on zeolite Y and sulfated zirconia, respectively. The surface area of the two catalysts was done by embedding a code in the BET software, while the pore volume, pore size and pore distribution was calculated using Excel, plotting the pore width (Å) versus the desorption of nitrogen on the catalyst surface. Table 4 gives the results for the case of calcium on zeolite Y. Sulfated zirconia showed a smaller surface area of 110 m²/g, which still conforms with literature studies showed before. First, this result might cause one to believe that this catalyst showed poor performance, and poor catalytic activity. However, we will show later on the performance of this catalyst in the batch operation work. Eventhough this catalyst has a small surface area compared to other efficient bronsted acidic heterogeneous catalysts, this catalyst still showed a uniform pore size, pore volume, and pore distribution. This type catalyst analysis offers an opportunity for predicting the catalyst activity.

Literature studies showed that sulfated zirconia has a smaller surface area when compared to other acidic catalysts, which can be explained by the crystal structure of this catalyst, and the preparation of the catalyst is key. We used the solvent free method

(solventless), which has been favored due to an environmental point of view. No solvent is used in this method, and it was only ion exchanged between the two powders (zirconylchloride octahydrate and ammonium sulfate), the function of the solvent in catalyst preparation as in the wetness impregnation method for catalysis is to provide more adherence to the overall prepared catalyst, which results in more surface area.

Table 4. BET data for Ca-Y

Relative pressure ratio	Pore volume (cc/g)	Desorption rate (cc/s)
0.108346	180.6901	0.53806
0.129472	181.4953	0.65566
0.140942	181.8111	0.72202
0.156506	182.2028	0.81479
0.94974	183.0801	105.85
0.216989	183.5284	120.81
0.6572	184.4312	156.99
0.289013	184.8317	175.97

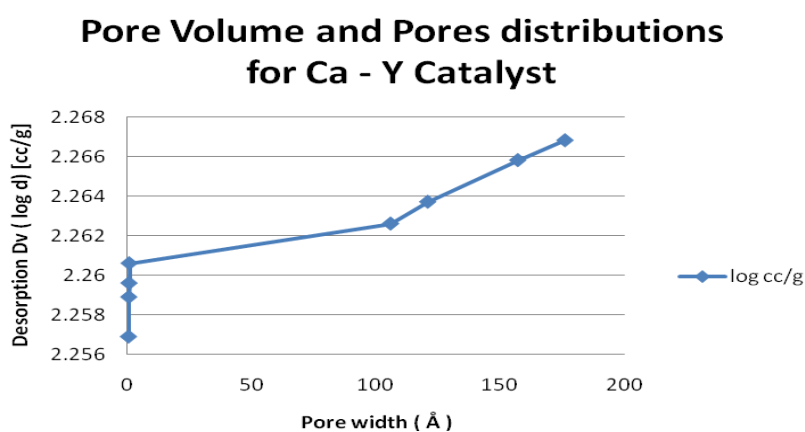
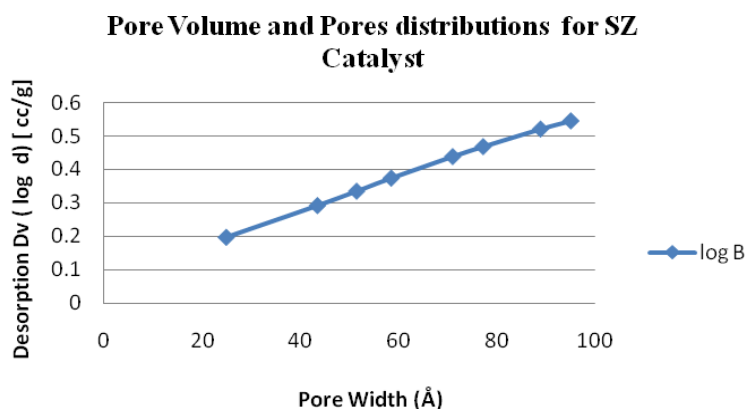


Figure 8. Pore volume and pore distribution for Ca-Y

Table 5. BET data for SZ

Relative pressure ratio	Pore volume (cc/g)	Desorption rate (cc/s)
0.046797	1.5731	24.971
0.096178	1.9563	43.522
0.12199	2.1585	51.502
0.147252	2.3603	58.536
0.195525	2.7374	71.04
0.22054	2.9311	77.236
0.268678	3.3058	88.92
0.293594	3.4978	95.071

**Figure 9. The pore volume and pore distribution of sulfated zirconia**

Since sulfated zirconia was prepared using the solventless method, the overall catalyst produced has a low surface area because of the significant surface chemistry fact, which states that the calcination stage of the catalyst was developed to remove the solvent molecules (H_2O) from the surface of the produced catalyst. Doing this will result in a spreaded surface area for this catalyst, and good adsorption for the catalyst to the support surface. Because no external solvent was added, it was predicted that the surface area for sulfated zirconia after calcination would still be moderately low. Since, this catalyst has

a high bronsted acidic factor, it was applied in the transesterification reaction of triglycerides in the biodiesel.

While running this catalyst in the batch operation system, it was clearly shown that the strong acidic active sites of have been leached and exposed to the reaction media, which is explained by the on- site view of the reaction, the key areas on this catalyst and active acidic sites has been fully exposed to the reactant (triglycerides of the oil and methanol), resulting in better conversion than a high surface area acidic heterogeneous catalyst.

4.2 Batch operation results

Both of the two catalysts (calcium on zeolite Y and sulfated zirconia) were tested in batch operation conditions as mentioned earlier, it was predicted that calcium on zeolite Y would perform better and provide high yield and conversion compared to sulfated zirconia, the reasoning is the high surface area of the produced catalyst (534 m²/g). The method used in preparing this catalyst (wetness impregnation method) will provide more adherence and adsorption of the active component (calcium) to support (zeolite Y). Additionally, the two cycles of calcination had been prepared prior to loading calcium to zeolite Y, and after the loading process is also considered a strong factor in the efficiency of calcium on zeolite Y catalyst.

4.2.1 EN 14103 results using Ca-Y as the catalyst

As mentioned earlier, this method (European Standard method), is used to evaluate the biodiesel product from qualitative and quantitative standpoints. The

purpose of this method is also to see whether the product of the transesterification reaction matches the European limitations, which specifies the methyl ester content in the final product should not be less than 90%, and the linolenic acid methyl ester content should be less and between 1% (m/m) and 15% (m/m). The calculations were done using an excel spreadsheet. The function is already loaded to do these calculations. The results for calcium on zeolite y are shown in Table 6.

Table 6. The conversion efficiency versus time with the three different molar ratios

time (min)	Conversion % (m/m)		
	1:3	1:5	1:12
0	0	0	0
15	30.7	40.1	48.1
30	42.9	58.8	54.6
45	50.6	68.3	62.8
60	75.8	85.4	86.3
75	90.3	93.5	93.7
90	93.8	93.7	93.7
105	94	93.79	93.8

There is only one parameter to consider in a batch reaction and that is time. Since this is a batch reaction, the purpose of these tests is to study the effect of reaction time on the conversion efficiency. As shown in Tables 4, 5, and 6, the analysis of the biodiesel product has been conducted under isothermal conditions (60°C) for various time intervals. Table 6 shows that reaction rate is a function of reaction time and the molar ratio between oil and methanol. For process optimizations we need to study the effect of temperature on the batch reaction. Hence, we conducted a series of tests in different temperatures. The effect of temperature on the reaction rate is shown in Table 7.

In this work, it was also necessary to study the effect of molar ratio on the transesterification reaction, which would be a way to study the catalytic behavior under different molar ration. Figure 10 shows the effect of temperature on the conversion rates for different molar ratios.

Table 7. The conversion versus temperature for the three different molar ratios

Temperature (K)	Conversion % (m/m)		
	1:3	1:5	1:12
303	42.1	54.2	68.7
313	54.6	64.8	82.4
323	63.9	86.6	88.7
333	84.6	93.3	93.8
343	93.6	93.8	93.84

An assumption was that at zero time reaction, the conversion is 0 %, the relation between the reaction time, and the conversion showed a typical rate as those shown in literature studies. In this work, the conversion as a fuction of time conformed with the kinetic energy theory. Table 7 showed that the conversion rate correponding to the molar ratios of 1:3 kept increasing up to the temperature of 343 K, while that of the molar ratio of 1:5 has reached the maximum conversion at the temperature of 333 K. That means if the used molar ratio is 1:5, then the optimum temperature should be 333 K. Further temperature would slightly increase the conversion but not a significant one. Also in case of the molar ratio of 1:12, the reaction reached the highest conversion at temperature of 333 K. The slight incese in the conversion at temperature of 343 K can be negelected. Figures 10 and 11, represents the time and temperature effects, to further evaluate and optimize this process in batch operations when calcium on zeolite Y is introduced.

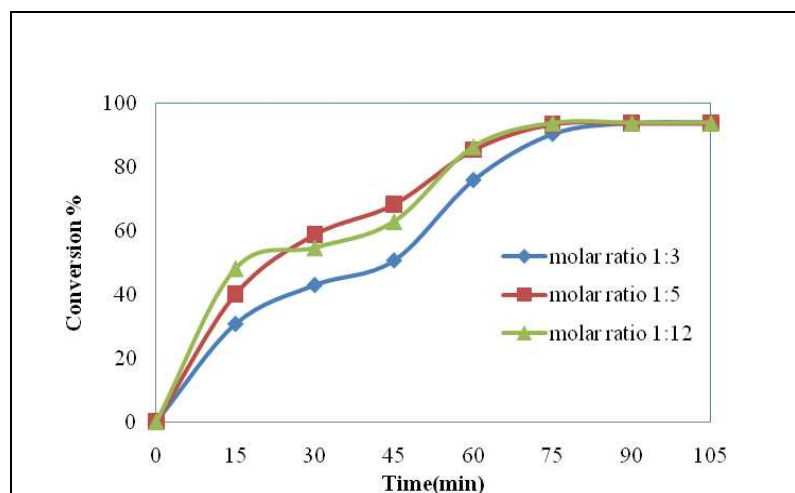


Figure 10. The time versus conversion in the different three molar ratios

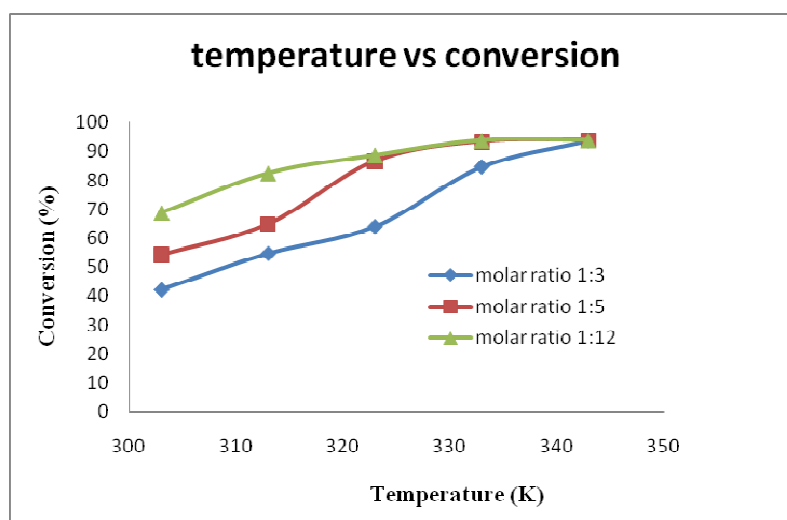


Figure 11. The temperature effect

4.2.2 Batch operations results for sulfated zirconia (SZ)

The same reaction condition was maintained between calcium on zeolite Y and sulfated zirconia, such as the the isothermal catalyst test, molar ratio variation, and the corresponding conversion percentage for each case. The results of the isothermal

reaction test using sulfated zirconia are shown in Table 8, and the conversion efficiencies are shown in Table 9.

Five levels of temperatures were studied, namely, 303, 313, 323, 333, and 343 K, the results shown in Table 9 verified the molar ratio as well as the temperature effects on the activity of calcium on zeolite Y.

Table 8. Temperature and molar ratio effect on the conversion percentage

Temperature (K)	Molar ratio	Conversion (%)
303	1 to 3	42.1
303	1 to 5	54.2
303	1 to 12	68.7
313	1 to 3	54.6
313	1 to 5	64.8
313	1 to 12	82.4
323	1 to 3	63.9
323	1 to 5	86.6
323	1 to 12	88.7
333	1 to 3	84.6
333	1 to 5	93.3
333	1 to 12	93.8
343	1 to 3	93.6
343	1 to 5	93.8
343	1 to 12	93.84

Table 9. The conversion efficiency of SZ versus time for the three molar ratios

Time (min)	Conversion (100 % m/m)		
	1:3	1:5	1:12
0	0	0	0
15	18.33	28.6	36.8
30	33.6	43.6	54.6
45	43.4	58.2	66.2
60	56.3	63.7	74.6
75	78.1	86.4	86.5
90	88.7	88.5	88.3
105	88.83	88.7	88.5

4.2.3 EN 14103 GC chromatogram

The GC was configured to do the methyl ester content, and the linolenic acid methyl ester contents. The GC parameters such as oven, inlet conditions, the capillary column, and the flame ionization detector were all set up with a fixed base line, and to obtain the peaks shape. Conditioning the column after each set of runs led to the recovery of the column sensitivity in identifying the unknown methyl esters, no overlapping between peaks of the close retention times, and obtaining good separation. The integration events was done according to method requirements, which are the integration events are carried out only for the region from methyl myristate (C₁₄) peak up to the methyl ester in nervonic acid (C_{24:1}), and taking all the peaks between these two methyl esters under consideration, the chromatogram is shown in Figure 12..

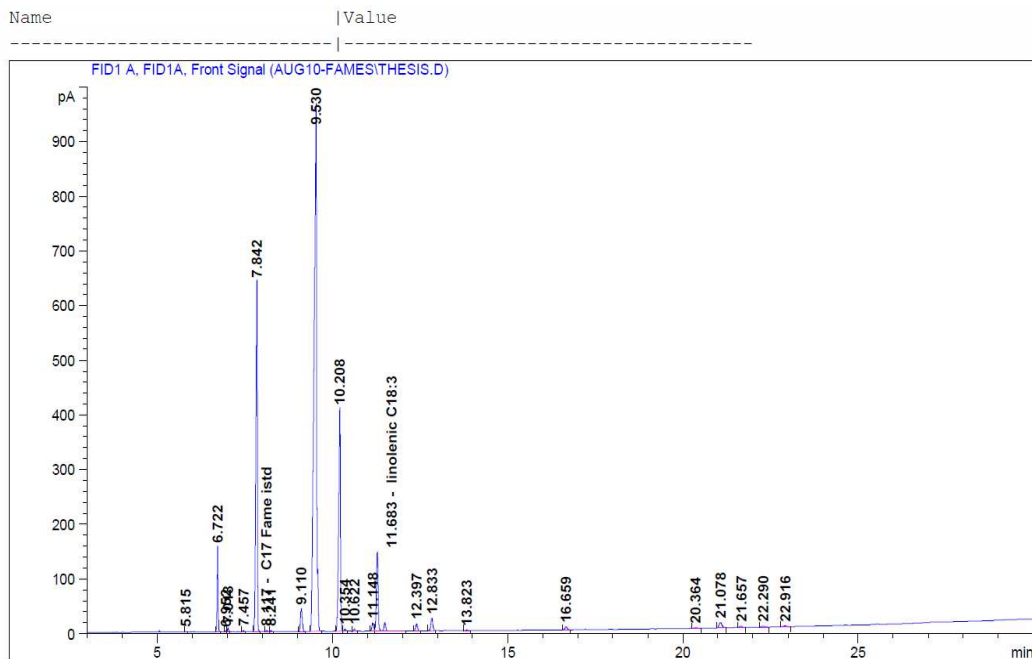


Figure 12. The chromatogram of the biodiesel produced using Ca-Y

The biodiesel production rates, using calcium on zeolite Y, were similar to those described in previous studies. Moreover, this figure shows the kinetic theory of the biodiesel reaction in batch operations which states that increasing the reaction time will result in more conversion. This catalyst behaves in the same manner as other solid alkaline catalysts in which the range of conversion was between 30.7% to 94% corresponding to the reaction time ranging between 15 min to 105 minutes, when the molar ratio for oil to methanol was 1:3. These studies were made at isothermal condition (333 K), to study the reaction kinetics behavior with time, the molar ratio of 1:5 showed that the conversion ranged from 40.1% to 93.79%, increasing the conversion rate is explained by the effect of time reaction on conversion, which verifies the batch reaction from a chemical engineering stand point.

Further more, the molar ratio of oil to methanol is elevated to 1: 12, higher conversion rates were obtained, the conversion ranged from 48.1 % to 93.8%. the three different reaction parameters that this work is concerned about as the kinetics of this catalyst in both of batch and continuous reactions. Calcium on zeolite Y results has agreed with the literature studies [6] that has been conducted in exploring the catalytic activity of calcium for example as CaO, as base heterogeneous catalayst, the mild reaction conditions of using calcium in the transesterification reaction. It has been proved in this study that the conversion efficiency started at 303 K with well mixing in batch operaion and the conversion rate kept the linear function with temperature as it is shown in the effect of temperature on the transesterification reaction.

Calcium on zeolite Y as a catalyst has a large surface aea (534 m²/g) that was

sufficient enough to complete the conversion of the triglycerides of oil into methyl esters, the batch tests showed the ease of the active sites exposure of this catalyst to reactants (oil and methanol) high yields of biodiesel were obtained with the application of this catalyst to the transesterification reaction. The GC parameters were fixed to analyze both of the two biodiesel samples (Ca-Y and SZ), the chromatogram of biodiesel based on sulfated zirconia is shown in Figure 13.

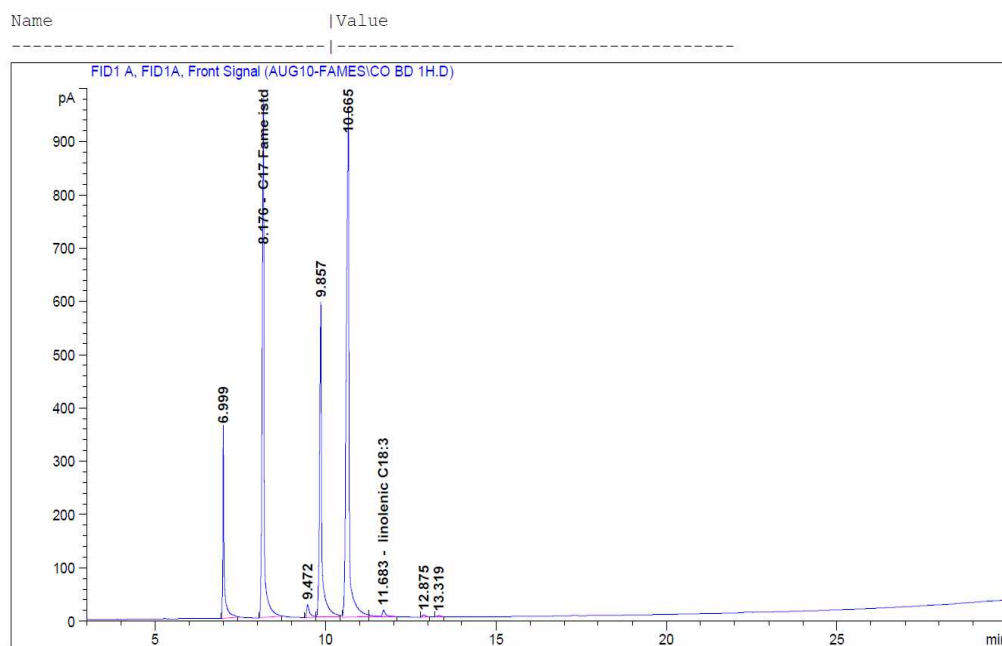


Figure 13. The chromatogram of the biodiesel produced using SZ

Attached in the EN 14103 method, an excel sheet was designed to analyze the chromatogram peaks into a language of numbers, the following excel sheet shows the calculation method for the biodiesel sample prepared using Ca-Y [adapted from Agilent technologies method documents].

4.2.3.1 Determination of methyl ester and linolenic acid content

The calculations were done using an excel sheet attached to the method, the amounts of internal standard as well as the sample is shown in Table 10.

The same kind of calculations has been conducted to obtain the total methyl ester content as well the linolenic acid total content for the biodiesel prepared using sulfated zarconia, the results for the total ester content was 88.8 %, and the total linolenic acid content in the biodiesel was 4.2%.

Table 10. Methyl esters calculation

Action	Amount
C17 weight (mg)	250
C17 purity (%)	99.5
Heptane total volume (ml)	5
Concentration (mg/ml)	10
Sample weight (mg)	25
Internal standard added volume	0.5
FAME total area (from report)	14040
C17 area (from report)	8433
Total ester content (%)	94.984
C18:3 area (from report)	3269
Total C18:3 methyl ester content (%)	9.3

4.2.4 ASTM D 6584 results

This method is used to evaluate the monoglycerides, diglycerides, triglycerides and glycerol contents in the biodiesel product. The results are shown in Tables 11 and 12.

Table 11. The total biodiesel content produced using Ca-Y according to ASTM D 6584 method

Glycerol	0.00%
Monoglycerides	0.08%
Diglycerides	0.05%
Triglycerides	0.01%
Total Glycerol (free plus bound)	0.03%

Table 12. Biodiesel analysis when sulfated zarconia is used as the catalyst

Glycerol	0.00%
Monoglycerides	0.03%
Diglycerides	0.22%
Triglycerides	0.02%
Total Glycerol (free plus bound)	0.05%

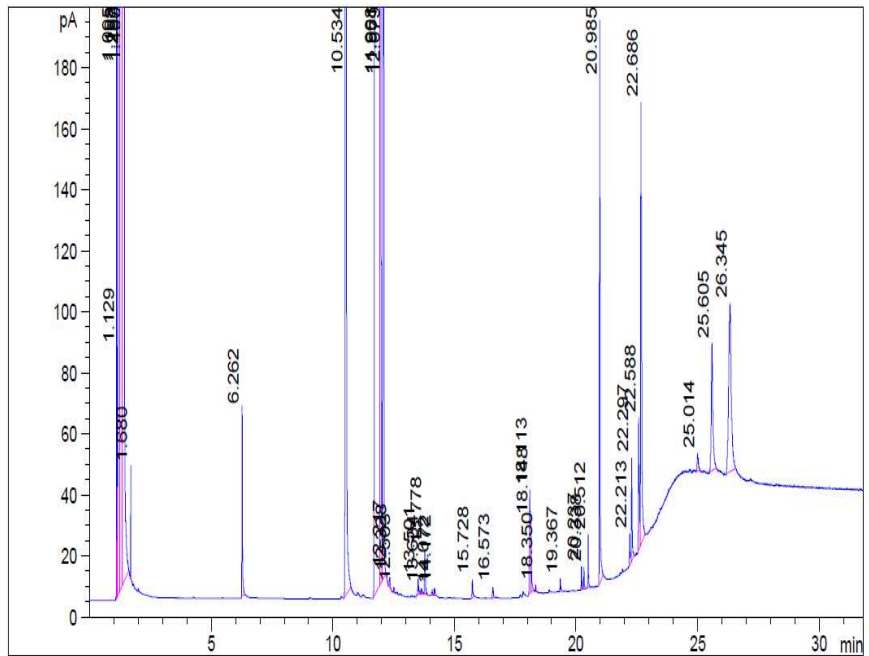
In table 11, we can see that the quantification analysis of the biodiesel produced by using calcium on zeolite Y, showed that smaller residues of glycerides are bounded to the biodiesel layer. Monoglycerides were less than 0.1%. This result is very important because The American standard testing material (ASTM D6584) requires that monoglyceride should always be less than 0.1% in the biodiesel. Also diglycerides were found to be 0.05%, this percentage is also considered low. In addition to that, the triglycerides percentage was lower than 0.01%. This result can tell us that the residual oil (unreacted) in the biodiesel is in small percentage.

Also the GC analysis for the biodiesel produced using sulfated Zarconia (table 12), showed that the percentage of monoglycerides in the biodiesel is less than 0.1% (0.03%), while diglycerides and triglycerides percentages are found to be 0.2% and 0.02%, respectively. Also those results give strong comment on the purification process that has been used in this work. The results for the biodiesel also produced using sulfated

zirconia according to ASTM D 6584 are shown in Figures 14 and 15. The chromatogram of the biodiesel produced using calcium on zeolite Y showed that monoglycerides appeared at the retention time of 14. Diglycerides showed up at at 20 while triglycerides appeared in the chromatogram at the retention time of 26.

Also the chromatogram of sulfated zirconia biodiesel sample showed that there were some shifting in the retention times of monoglycerides, diglycerides and triglycerides compared to those of calcium on zeolite Y biodiesel sample. Monoglycerides appeared at retention time of 15, diglycerides at time retention of 19.

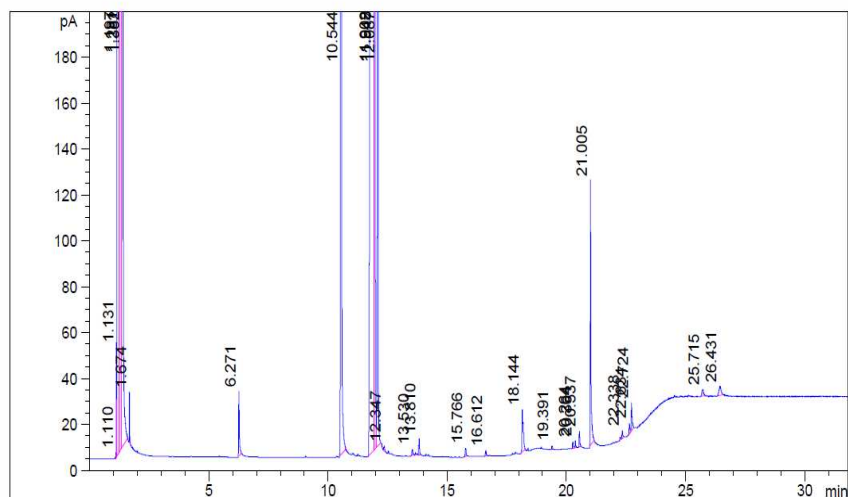
Acq. Method C:\CHEM32\1\METHODS\TA.M
 Analysis Method : C:\CHEM32\1\METHODS\TA.M



Special BioDiesel Report ASTM 6584

Figure 14. ASTM D 6584 analysis for the biodiesel sample produced using Ca-Y

Acq. Method C:\CHEM32\1\METHODS\TA.M
Analysis Method : C:\CHEM32\1\METHODS\TA.M



Special BioDiesel Report ASTM 6584

Calibration Information

Figure 15. ASTM D 6584 analysis for the biodiesel sample produced using SZ

4.2.5 TGA results

The purpose of using this technique in this work was to study the thermal stability behavior of the biodiesel product for the two catalysts (Ca-Y and SZ). The results are shown in Figure 16.

The biodiesel sample produced using SZ (sulfated zirconia) showed a similar behavior as that of Ca-Y. The TGA results showed that the weight loss detected for biodiesel at 120 degree Celsius corresponds to the weight percentage of biodiesel in the sample. Similarly, the weight loss associated with soybean oil (at 325 degree Celsius) corresponds to the weight percentage of the soybean oil present in the sample. Because the temperature difference between these detected temperatures is rather high (205 degree

Celsius), this technique can be used to differentiate between biodiesel and soybean oil.

These results are also shown in Figure 17.

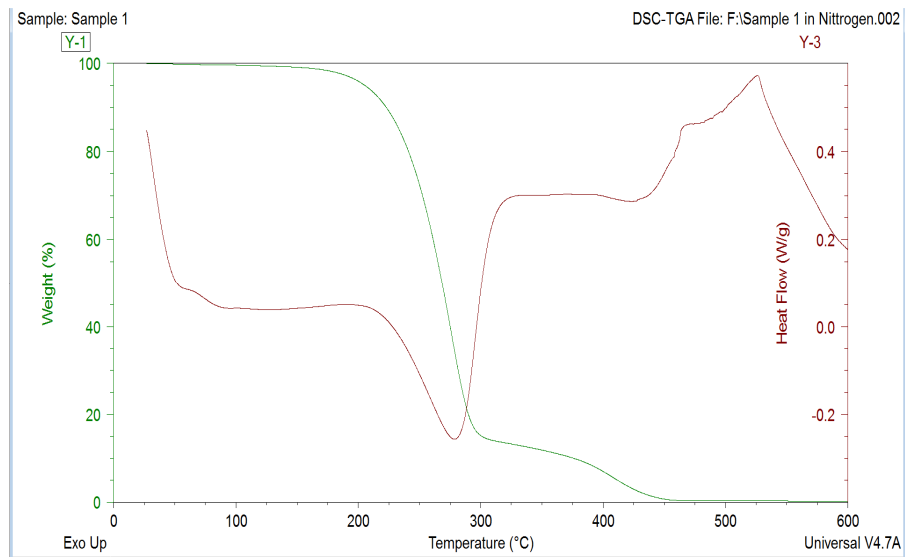


Figure 16. TGA results for the biodiesel sample produced using Ca-Y

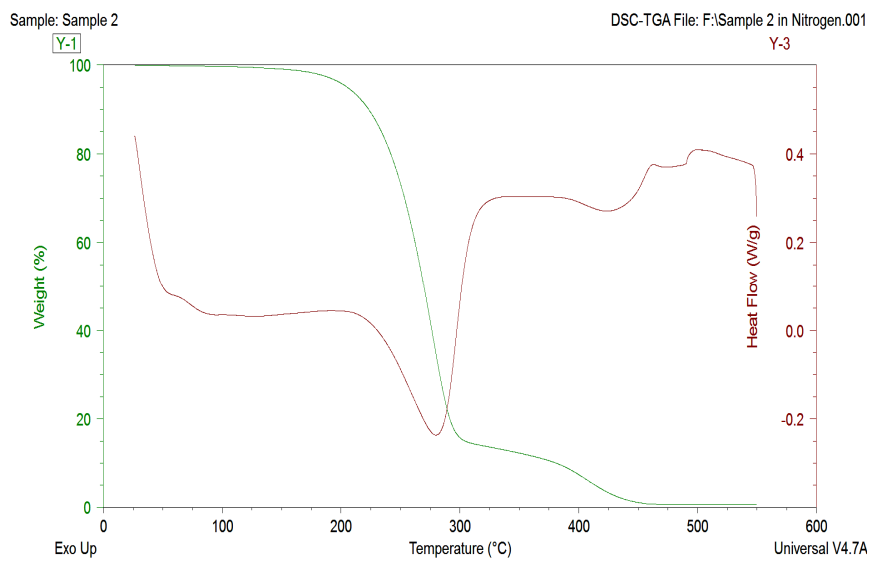


Figure 17. TGA results for SZ biodiesel

4.3 Packed bed reactor (PBR) with WCO results

As mentioned earlier, the catalyst was tested in a continuous process of transesterification using PBR calcium on zeolite Y; because this catalyst showed good performance in the batch operations as was shown by the analytical equipments used in this work (GC and TGA). Also the decision of applying this catalyst in the packed bed reactor was to study the catalytic activity in a continuous transesterification reaction of used cooking oil that was subjected to previously specified pretreatment stages, using sodium sulfate (Na_2SO_4), which is on the path of chemical interaction with the free fatty acid molecules forming esterified fatty acid molecules. The result of this chemical interaction was the reduction of free fatty acids to lower values, which will pave the way for furthering the transesterification reaction without going through the emulsification of the produced methyl esters (saponification). In this work, the results of using Ca-Y with waste cooking oil as feedstock will be shown in the same manner used in presenting the results for testing this catalyst in batch operations. In this work, calcium on zeolite Y was tested in a continuous transesterification reaction, the catalyst was preloaded to a 5 ml reactor, the conditions of the PBR was adjusted as discussed in Chapter 3. Three different molar ratio of 1:3, 1:5, and 1:12 of oil to methanol were tested to study the effect of the molar ratio on the catalytic activity of calcium on zeolite Y in the continuous transesterification reaction. The conversion percentage as a function of temperature when calcium on zeolite Y was used in the PFR system gave satisfactory results, taking the molar ratio of 1:12 as a sample for experimental studies, the temperature range for study at this molar ratio was from 303 K to 343 K, the corresponding conversion percentages

for this range of temperatures was from 42.4% to 79.9%. These kind of results will enable us to study the kinetic behavior of this catalyst, and again this study was parallel to most of the literature studies, which had stated that this catalyst can be activated using mild reaction conditions. Unlike other heterogeneous acid catalysts that require a high amount of activation energy supply as well stimulate the catalysts in the transesterification reaction field. This about calcium on zeolite Y as solid alkaline catalyst will attract more attention and interest because lower energy is consumed when such catalyst is applied in the batch as well as continuous transesterification reaction. However, in this work, it was found that when this catalyst was introduced in a continuous fixed bed reactor, the conversion rates, and the biodiesel yield increased while increasing temperature as well the molar ratio of oil to methanol until it reached an area of constant conversion percentage with a slight change in conversion.

From this research standpoint, the reason that the reaction kept a constant conversion attitude in the continuous fixed bed process at temperatures up to 343 K was because of the molar ratio effect on the activity of this catalyst in the continuous transesterification reaction. This work studied only three different moderately low molar ratios (1:3, 1:5, and 1:12). The molar ratio was not increased to higher levels because the goal of this experiment was to study the catalytic activity of calcium on zeolite Y as a catalyst in the transesterification reaction. This is a good reason to recommend that future studies explore the behavior of this catalyst in the biodiesel production area in which higher molar ratios should be employed in this reaction. . The results are shown in Table 13.

Table 13. The conversion efficiency as a function of temperature for the three molar ratios

Temperature (K)	Conversion % (m/m)		
	1:3	1:5	1:12
303	32.2	38.1	42.4
313	40.4	49.2	58.9
323	46.6	53.4	72.4
333	67.6	76.1	76.8
343	79.6	79.8	79.9

Since the major factors in this work was affecting the continuous biodiesel production using calcium on zeolite Y as the active catalyst, is the reason it was necessary to study the conversion efficiency at consecutive cycles while the temperature was kept constant (isothermal efficiency study of Ca-Y in continuous transesterification reaction). Tables 14, 15, 16 and Figure 18 show the catalyst (Ca-Y) life times with number of cycles.

Table 14. The conversion variance versus number of continuous cycles when the molar ratio is 1:3

Cycle	Temp (K)	Conversion (%)
1	333	16.3
2	333	24.8
3	333	42.1
4	333	58.3
5	333	68.6

Also in table 15, the isothermal conditions were kept while the change of conversion with the cycle number is clearly shown.

Table 15. The conversion efficiency with variant cycles at molar ratio of 1:5

Cycle	Temp (K)	Conversion (%)
1	333	22.3
2	333	32.8
3	333	51.1
4	333	64.6
5	333	72.1

Table 16. The conversion efficiency versus time when the molar ratio is 1:12

Cycle	Temp (K)	Conversion (%)
1	333	26.1
2	333	38.5
3	333	59.6
4	333	73.5
5	333	79.9

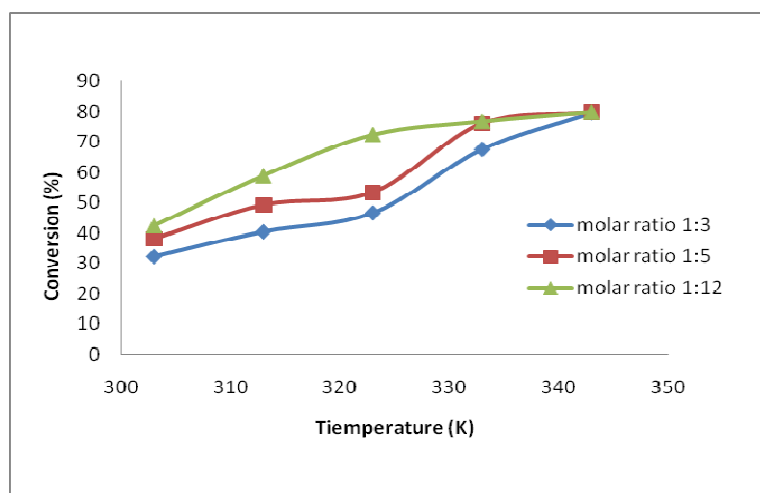


Figure 18. Temperature versus conversion at molar ratios of 1:3, 1:5, and 1:12

The results showed that by having fixed 5 cycles for the three different molar ratios while the reaction conditions were isothermal, calcium on zeolite Y showed a similar molar effect profile as the studies in the previous literature. If we studied just

cycle number 4 for the three different molar ratios, it was clearly shown that when the molar ratio was 1:3 the fourth cycle produced a conversion percentage of 58.3%; when the molar ratio was 1:5 the same cycle generated a conversion percentage of 64.6%, when the molar ratio was elevated to 1:12, the conversion efficiency increased to 79.9%.

4.4 Statistical analysis

In this work, some statistical analysis has been done on both batch operations data and BTRs, Jr data, to study the statistical significance of these data. The analysis was done using a P- value (probability value). Table 17 shows the P-value for the batch operations with the molar ratios of, 1:3, 1:5, and 1:12.

Table 17. P-values for batch operations

Molar ratio	<i>P-value</i>
1:3	2.24E-08
1:5	1.45E-08
1:12	2.87E-09

As shown in Table 17, the data for the three different molar ratios at batch operations all have a P-value less than 0.05, which means none of the data fall outside the normal curve. The same analysis was done to the BTRs, Jr. (packed bed reactor), at the three different molar ratios as shown in Table 18.

Table 18. P-values for BTRs, Jr data

Molar ratio	<i>P-value</i>
1:3	1.01E-08
1:5	7.84E-09
1:12	5.2E-09

P-values of the BTRs data for the three different molar ratios are less than 0.05, which again means these data fall inside the normal curve and the differences among those data are statistically significant.

CHAPTER 5

Conclusion

In this work, a heterogeneous catalysis was studied in the transesterification reaction in biodiesel production. An acid solid catalyst (sulfated zirconia) as well as a solid basic catalyst were tested in batch operations to study the catalyst activity, the activation energy of the catalyst, the ability of easier separation of the catalyst from the product medium, and the ease of the purification process for the final product.

The following conclusions can be drawn from this study:

1. Calcium on zeolite Y was prepared using the incipient wetness impregnation method, while sulfated zirconia was prepared using the solvent free method (solventless).
2. The BET showed that, calcium on zeolite Y has surface area of 534 m²/g, while the surface area of sulfated zirconia was 100 m²/g.
3. Calcium on zeolite Y showed higher susceptibility towards the molar ratio. The batch operations using this catalyst showed higher conversion rate of 94%, while the highest conversion rate using sulfated zirconia in batch operations was around 90%.
4. Calcium on zeolite Y used in PBR with 10 ml volume resulted in the maximum conversion of 79.8% when waste cooking oil was used as a feedstock. Minimum volume for PBR reactor should be calculated in

order to increase the conversion rate. The catalyst loading to the support, reactor volume and the reactant volumetric flow should all be adjusted for this catalyst to obtain higher biodiesel yields.

5. Calcium loading onto zeolite Y was 2%, the reaction required some increase in the temperature (activation energy) as well as an increase in the reaction time up to 105 min. It is recommended to use higher calcium loading percentage on zeolite Y to reduce the energy consumption as well as minimizing the required time to complete the reaction.
6. Calcium on zeolite Y showed higher catalyst life times of 5 cycles.

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