# BIOFUEL MANUFACTURING AND CHARACTERIZATION FROM WASTE COOKING OIL USING BATCH TRANSESTERIFICATION PROCESS

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## ABSTRACT

Other energy sources are now being used more. OPEC has recently struggled with rising oil prices and environmental concerns. Biofuel is gaining popularity as an alternative to petroleum diesel due to its similar fuel characteristics and lower pollution level. It can be used in conventional diesel engines as long as the biodiesel percentage is less than 100%. A heterogeneous catalyst (TiO2-supported-MgO) trans esterified waste cooking oil with methanol, resulting in biodiesel. Waste cooking oil (WCO) was used in this case because it is one of the cheapest oil sources for biodiesel production. Every day, unused cooking oil is available in every fast food and restaurant worldwide. The experiment reported here used pre-prepared waste frying oil. This was achieved by adding 5% oleic acid to a 90% soybean oil mixture. XRF, BET, and XRD were used to characterize 10% MgO/TiO2 catalyst with titanium supports produced by incipient wetness impregnation. Using a catalyst and methanol and hexane solvents, waste vegetable oil was converted to biodiesel in these tests. Transesterification was performed using an 18:1 methanol/oil ratio. The methanol to oil ratio was 18:1, and the methanol to hexane ratio was 1:1. Each variable affects waste vegetable oil conversion. The researchers used 1HNMR to better understand the FAME structure. Reaction time, temperature, and co-solvent hexane all increased oil conversion rates.

**Keywords:** Biodiesel (FAME), Waste Cooking Oil, Titanium-Supported-Magnesium Oxide Catalyst (Mgo/Tio2), Oleic-Acid, Hexane Co-Solvent, Transesterification, XRF Analysis, BET Analysis, XRD Analysis, 1HNMR Analysis.

## I.    INTRODUCTION

In response to regulatory pressure and global pollution concerns, governments and lawmakers are demanding alternative energy sources. Biodiesel has earned a reputation as a reliable energy source. Biodiesel and biodiesel blends are used primarily for their fuel security and environmental benefits. South Africa used biodiesel to power heavy-duty vehicles prior to WWII. South Africa started commercial biodiesel production in 1979 by Trans esterifying and refining sunflower oil to a quality comparable to petroleum diesel fuel (Sani et al., 2013). Biodiesel became unattractive after the discovery of fossil fuels — affordable, safe, and efficient energy sources. The use of biodiesel has resumed its upward trend, but new local, environmental, and economic pressures have stymied this. Biodiesel is a type of engine fuel derived from animal, plant, and microalgal fats. Oilseeds are used to make biodiesel fuel. Biodiesel can be used as a direct replacement for petroleum diesel or as part of a blend that can be used in a conventional diesel engine. Though diesel engines were originally powered by straight vegetable oil (SVO), petroleum diesel fuel became a popular choice for diesel engines during the twentieth century due to its accessibility and affordability. According to engineering literature, SVO has serious issues that reduce engine life significantly (Dahiya, 2014). Fuel pumps are prematurely worn out by SVO with an excessive amount of viscosity injectors. It also changes the design of the injector spray, increasing the number of droplets and their size. Spray penetration is improved while the spray angle is reduced (Anjaneya, 2014).

Transesterification is a chemical reaction that produces fatty esters (a type of biodiesel) and glycerin when methanol or ethanol reacts with vegetable oils. Biodiesel is a term that refers to a 100 percent pure fuel (B100) that meets ASTM's biodiesel fuel requirements and is governed by ASTM standard D 6751. (National biodiesel board, 1996). Several common cooking oils, such as olive, palm, soybean, canola, and sunflower, can be used as biodiesel substitutes. The majority of these oils are being pursued by the food industry for use in foods intended for human consumption. As a result, the development of biodiesel from edible oils has been hampered significantly. Waste cooking oil can be used to make non-edible oils and is a cheaper alternative to edible

vegetable oil. Because of its affordability, using waste cooking oil that would otherwise be discarded to make biodiesel is one of the most environmentally friendly options available to consumers. According to a new report from the United States, the US produces 100 million gallons of waste cooking oil per day, while the UK produces nearly twice that amount. Due to the volatile nature of the biofuels industry, farmers in the agricultural sector now feel compelled to invest in "On-farm energy." Farmers appear to be recognizing that producing biodiesel on their own farms has the potential to provide a reliable and secure fuel supply while also benefiting the environment and extending the life of their equipment. As a result, the study's first goal is to figure out and quantify the best conditions for making biodiesel from used cooking oil. However, worldwide we need more energy to start the industrialization process, which comes from fossil fuels and thus contributes to pollution. We must develop renewable energy sources capable of maintaining a healthy environment for future generations if we are to maintain a healthy environment for future generations. Our economy will continue to improve its competitiveness. Biodiesel is a fuel made up of long-chain fatty acid esters derived from a variety of oils, according to ASTM D6751 (vegetable or animal). B100 is a common nickname for it. It must also adhere to certain guidelines (Hansen, 2008).

It has a slew of economic and environmental advantages. Biodiesel was required to undergo Tier I and Tier II health effects testing under the Clean Air Act in 2000, and Solasa et al. (2013) concluded that it was the only alternative fuel to do so successfully. Biodiesel significantly reduced all regulated emissions, indicating that it is unlikely to be harmful to human health, according to these comprehensive assessments. He also discovered that biodiesel contains almost no Sulphur or aromatics, and that it reduces unburned hydrocarbons, carbon monoxide, and particulate matter when used in a conventional diesel engine (that is a reduction in greenhouse gases). Furthermore, biodiesel production has a positive energy balance. Biodiesel is so efficient that every unit consumed in its production generates at least 4.5 units of energy. It has lubricity, is low in toxicity, has a low flash point, has a low environmental impact, and is biodegradable, among other properties that help reduce emissions and benefit the environment (Moser, 2008). Biodiesel has been formally approved and codified as a fuel and a component of fuel additives. The requirement ensures that biodiesel is of the highest quality and readily available in the marketplace. Both ASTM D6751 (ASTM 2008a) and EN 14214 (European Committee for Standardization, CEN) are important fuel standards in the United States and the European Union (Tomes et al., 2011). A significant increase in the amount of time spent synthesizing Biodiesel made from renewable energy sources is a major driving force behind the industry. The biodiesel industry is important to the economy because it creates good, environmentally friendly jobs for citizens and boosts national competitiveness.

## Objectives

The aim of this study was to produce biodiesel from waste soybean oil. This aim was expected to be achieved through the following objectives:

- Preparation and optimization of titanium-supported-magnesium oxide catalyst to catalyze waste cooking oil transesterification to biodiesel.
- Investigate the operating conditions such as effect of time, temperature, hexane co-solvent and alcohol to oil mole ratio that will achieve the highest activity, highest life time and good resistance to reaction medium.
- Study the effect of magnesium oxide catalyst on Titanium support for the optimum production of biodiesel from waste cooking oil.
- Characterize the quality of the biodiesel produced using 1H NMR analysis

## Scope of the Research and Limitations

This study is within the scope listed below:

- Preparation of the calcined support titanium (IV) oxide (TiO2)
- Impregnation of the active Magnesium nitrate on the titanium support to yield the catalyst (MgO/TiO2).
- Characterization of the catalyst produced.
- Catalytic testing to yield fatty acid methyl ester (FAME) at 1 hour reaction time.
- Characterization of the biodiesel produced using HNMR analysis.

**Research Problems/Questions**

This study is set to answer the following questions:

- What are the best conditions for the production of biodiesel from waste cooking oil?
- Can the biodiesel produced from waste cooking oil be characterized by 1HNMR analysis?

## II.     LITERATURE REVIEW

For centuries, the world has been reliant on non-renewable crude oil. This means that the International Energy Agency anticipates a 45 percent increase in global energy consumption between now and 2030. (International Energy Agency, 2008). The world's oil production is currently around 27 billion barrels per year, and at a rate of 2% per year, production will grow exponentially to a maximum of 55 billion barrels per year in 2037. (Cavallo, 2002). Several countries have reported that their maximum oil production capacity is increasing, and with it, global oil production. Many anticipate a decline in oil supplies following the peak. While the World Energy Forum's study made no recommendations for alternative energy sources, it did predict that the majority of the world's oil reserves would be depleted within the next decade (Yacob, 2009). Bentley (2002) predicted that the peak of all hydrocarbons (including oil and gas) would likely be reached in about ten years, and so on. In Figure 2.1, the year 2008 is depicted as the world production peak predicted by OPEC.
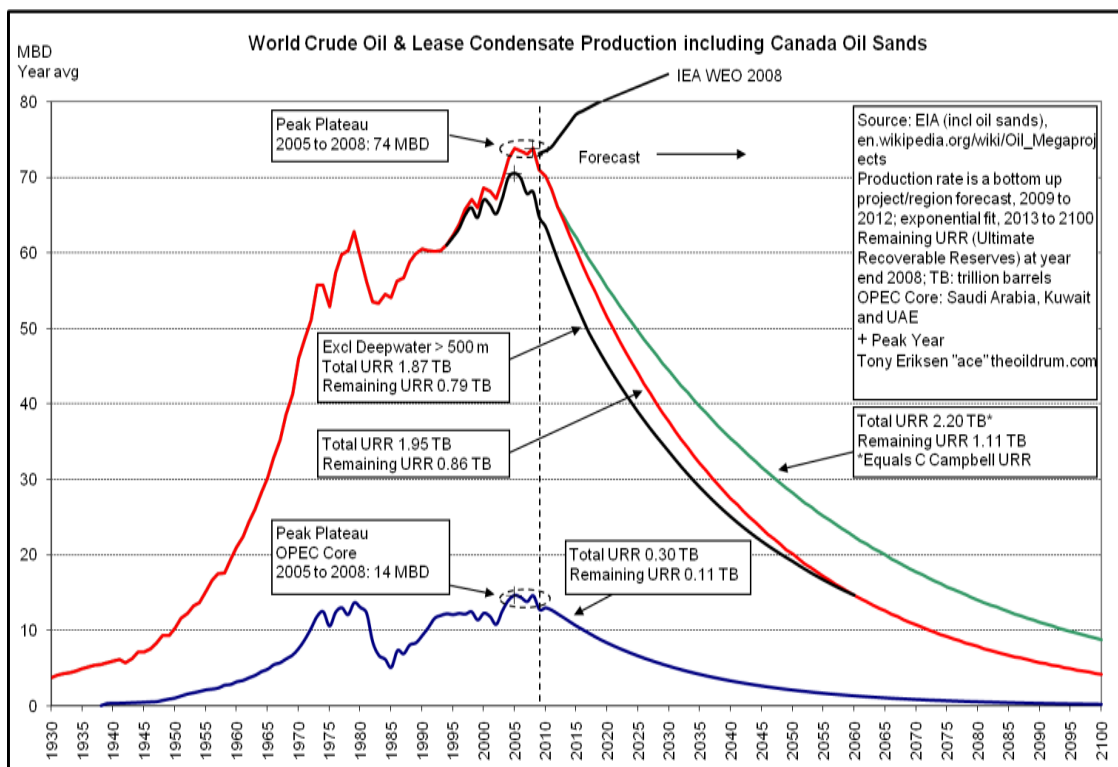


**Figure 2.1:** World oil production to 2100 (Source: US Energy Information Administration (US EIA), International Energy Outlook 2011)

Additionally, the US Energy Information Administration (EIA) estimated a maximum daily production of approximately 73.78 million barrels (MBD) in 2008, more than a million barrels above the previous record set in 2005. When Campell's estimate of Total Ultimate Recovery Reserves (URR) is used, it is possible to forecast a decline in production following 2012. And the US Energy Information Administration (EIA) projects that crude oil use as an energy source will increase in the future. As illustrated in Figure 2.2, it is anticipated that reliance on crude oil will decline over time.

In Figure 2.2, you can see how global energy consumption is expected to grow over the next two decades, expressed in millions of barrels of oil equivalent (MBOE). The figures are taken from the International Energy Outlook 2011 published by the US Energy Information Administration (US EIA).
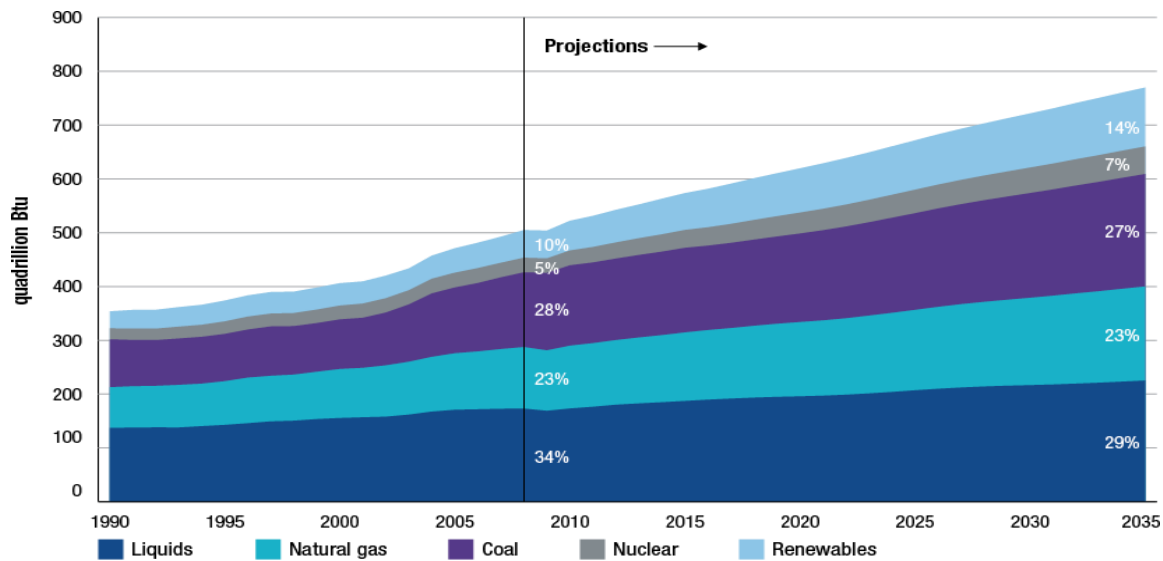
**Figure 2.2:** Annual world energy consumption, by fuel type: 1990 to 2035 (Source: US Energy Information Administration (US EIA), International Energy Outlook 2011).Note: Liquids are made up of petroleum and other liquid fuels including petroleum-derived fuels and non-petroleum-derived liquid fuels

By 2035, crude and other liquid fuels will meet only 29% of global energy demand. Alternative energy sources are expected to grow in popularity, according to experts. Natural gas and coal, as well as anything associated with them Nuclear and renewable energy will both expand; the former with increased support, while the latter will account for approximately 14% of global energy needs by 2035. Additionally, researchers discovered alternative raw materials to liquid fuel that will keep up with the demand for energy supply, according to their research findings. Biodiesel's chemical structure and energy content have garnered considerable attention due to their similarity to conventional diesel (petro diesel). Petroleum, a single fossil fuel, is believed to account for 95 percent of the energy consumed by the world's transportation (Kahn Ribeiro et al., 2007). As more people switch to biodiesel as a substitute for conventional diesel, the number of people reliant on crude oil will decrease. This widespread desire to produce and use biodiesel is global in scope; while the United States leads the way in terms of biodiesel awareness, many European countries have joined the movement. There are no modifications required to run biodiesel in an oil-fueled engine, regardless of the type of petroleum used to make it (Rahim et al., 2012).

## III.    METHODOLOGY

### 3.1  Materials and Methods

This chapter describes the different components and processes involved in the development of the TiO2-supported-MgO catalyst. Every material and every tool for the transesterification reaction is clearly defined in the materials section. The methodology shows exactly how the precursor is being loaded into the reactor to obtain the catalyst. The procedures used to assess catalysts, collect samples, and describe fatty acid methyl esters are also described.

### 3.2  Materials

Magnesium nitrate hexahydrate (Mg (NO3)2.6H2O) (98 percent), soybean oil (99 percent), and an acid with the P code 1000896770 were utilized in this research. It was isolated from an MKBB7610V lot and an acid with the P code 101051834. Finally, 364525-1L of methanol was found inside. Additionally, titanium (IV) oxide or titanium was present in this solution. We obtained all of our reagents directly from Sigma Aldrich in South Africa and used them as-is.

The trans-esterification process was carried out in a Parr reactor with a 300 cm3 capacity and 24 bar pressure inert-nitrogen gas. The researchers created the laboratory-produced oil by adding 5% oleic acid to soybean oil. According to Van Gerpen (2005), widely used cooking oils contain between 2% and 7% free fatty acids (FFAs), animal fats include between 5% and 30% FFAs, and poorer quality feed stocks, such as trap grease, contain up

to 100% FFAs. Additionally, they discovered that the concentrations of free fatty acids in biodiesel feedstock varied significantly. Iqbal et al. (2011) reported that these values ranged from less than 0.05 percent in refined vegetable oils to 0.3-0.7 percent in unrefined vegetable oils, 2-7 percent in restaurant waste grease, 5-30 percent in animal fat, and 40-100 percent in trap grease.

### 3.3      Methods

### 3.3.1     Preparation of support - (Titanium IV oxide)

Titanium IV oxide support was produced by dissolving 200 g of titanium powder in 100 ml of deionized water, then combining it with 400 ml of deionized water to get the final mixture. A white liquid was made by mixing and stirring a solution that was then dried at 100 degrees Celsius for 12 hours. The calcined support was placed in an oven at 600 C for 12 hours to remove moisture. The support was crushed and sieved after calcination. The support had particle sizes of 53 to 106 μm and were measured. Calcined titanium IV oxide support that weighed 27.026 g was obtained.

### 3.3.2     Preparation of active MgO

A research team developed a new magnesium oxide catalyst for use in neutralizing chlorine-contaminated water by testing the activity of it with the help of its crystallinity. Therefore, a total of 19.095 g of magnesium nitrate hex hydrate, which is equal to the weight of magnesium oxide necessary to be combined with titanium for the catalyst, is needed.

### 3.3.3     Preparation of the catalyst (MgO/TiO2)

Titanium was added to the TiO2/MgO catalyst during the impregnation process. The process began by completely dissolving 19.095 g magnesium nitrate hexahydrate in 13.5 ml de-ionized water (about half of the titanium mass that had been calcined). The nitrate solution was then added to a beaker containing 27.026 g of calcined titanium support. After 12 hours at 100°C drying in the air, the resulting catalyst mixture (MgO/TiO2) was applied as a paste. It was calcined at 600 degrees Celsius for 12 hours before being calcined in air.

### 3.3.4     Characterization of the Catalyst

Following the catalyst preparation, the characterisation included the following analyses. X-ray diffraction (XRD), X-ray fluorescence (XRF), and Brunauer–Emmett–Teller (BET) are among the methods used in the study.

### 3.3.4.1  XRD analysis

The crystallinity of the catalyst and the support was assessed by using XRD analysis. It exhibits the diffraction angle or crystal structure of the atoms' position. The Rigaku Ultima IV X-ray diffractometer was utilised for the XRD analysis, using the following gear: For this analysis, a standard CuKα (λ = 1.54 Å) radiation source, 30 mA and 40 KV, 1.0000 degree/minutes, 5.0 – 90o scan range with a step width of 0.01o were used. The equation for the diffraction angle provided by Moynihan and Crean (2009) is Bragg's law, and it may be expressed as:

$$N \lambda = 2\, d\, Sign\theta \quad \text{(3a)}$$

Where;

"n" is any integer,

"λ" is the wavelength of the incident X-rays "d" is the inter-planar spacing, and

"θ" is the diffraction angle

The particle sizes (D) of atom in the powder can be estimated from X-ray diffraction data using the Scherrer formula (Obadiah et al., 2012):

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where:

K = Shape Factor

β = FWHM = line broadening at half the maximum intensity

λ = wavelength of x-rays, and

θ = Bragg's diffraction angle

Note that the average particle size (i.e., apparent size) is what results from the Scherrer formula. Powders of materials are mostly made up of particles of various sizes, and thus exist as an aggregation of many particles. It is possible to carry out phase quantifications utilising techniques established by Spurr and Myers, as done in phase analysis (Hanaor and Sorrell 2011). The equations for this technique are given below in c:

$$\frac{WR}{WA} = 1.22 \frac{IR}{IA} - 0.028$$

Where:

WR and WA are the weight fractions of rutile and anatase (WR =1 - WA), IR and IA are the intensity of the rutile (110)

peak at 27.35o of 2θ and the anatse (101) peak at 25.18o of 2θ.

### 3.3.4.2  XRF analysis

A method called XRF was utilised to figure out how much active MgO was placed onto the support. The loaded MgO percentage on titanium, which was set as the goal. Analysis was completed using the EZS001XNV application.

### 3.3.4.3  BET analysis

Micromeritics used the TriStar 3000 machine to do the BET analysis. It evaluates the size, porosity, and pore volume of the catalyst and support with the pores, which helps estimate the surface area. The analysis was done using a sample weight of 210 mg. Before any analysis could be performed, the catalyst was heated to 150 degrees Celsius for 6 hours in order to eliminate moisture and other adsorbed gases from the catalyst surface.

### 3.3.5  Masses of Feedstock for Transesterification Reaction

### 3.3.5.1  Waste cooking oil

From Appendix B on page 90, it follows that: Mass of soybeans oil = 95 g

Mass of oleic acid = 5 g

### 3.3.5.2  Methanol

From Appendix C on page 90, Mass of methanol = 60 g

### 3.3.5.3  Catalyst

Several investigations showed that a solid catalyst (3 wt. %) is the ideal maximum conversion of biodiesel (Kumar et al., 2010). A reaction system using this catalyst is characterised by a high number of active basic sites, since the catalyst always stays in a different phase than the reactants. Smith and Notheisz (2006) have shown that catalyst effectiveness is dependent on the size of the catalyst's pores, pores' volumes, active site concentration, and the quantity of available surface area. Larger holes in the catalyst provide the triglyceride molecules easier access to the active sites, thus favouring the transesterification process. When combined, the catalytic performance of the titanium and magnesium oxides was much improved.

The masses of the feedstock are weighed as follows: Soybeans Oil    = 95 g

Oleic Acid          = 5 g

Methanol            = 60 gCatalyst (MgO/TiO2) = 3 g

### 3.3.6    Hexane co-solvent

Hexane co-solvent to Oil Ratio = > Hexane: Oil = 1: 1 Mass of hexane = Mass of oil = 95 g

Dividing the feedstock masses by three, we have the following Soybeans oil = 31.7 g

Hexane  = 31.7 g

Oleic acid          = 1.7 g

Methanol            = 20 g

Catalyst = 1 g

### 3.3.7    Catalyst Testing

In this experiment, a 300 cm3 Parr reactor was utilised (as shown in Figure 3.1), which was put under a pressure of 24 bar of inert nitrogen gas and was used to keep all reactants at liquid form and in various reaction temperatures. All experiments had a stirrer that was set at 1100 rpm. A PID controller was attached to a K-type thermocouple that monitored the temperature of the reacting medium, while controlling the temperature to the various target temperatures of 100 degrees Celsius, 150 degrees Celsius, and 200 degrees Celsius, respectively. The following ingredients (as specified in the text) were put into the reactor: 60 cm3 of methanol, 95 cm3 of soybean oil, 5 cm3 of oleic acid, and 3 g of catalyst. In the reactor, 95 cm3 of hexane was added alongside the feedstock. Sampling took place at fifteen, thirty, forty-five, and sixty minutes. Every experiment was conducted using identical reaction conditions. The phase separation occurred when the goods were allowed to cool after sampling. Glycerol needs to be extracted first because the solvent separates into two layers of glycerol and methanol on top, and a layer of oil and methyl esters on the bottom. At remove the methanol, the samples were heated in a vacuum drier set to 65oC. To extract the hexane solvent, a vacuum pump (Vacuum Pump (V-700)) was used. Next, 1H-NMR was used to ascertain the waste vegetable oil conversion. The transesterification reaction's catalytic test was performed three times each run.



**Figure 3.1:** Parr reactor for the laboratory preparation of biodiesel

### 3.3.8    1H-NMR Analysis (Product Analysis)

Figure 3.1 depicts the Parr reactor that was used to test the supported catalyst on waste frying soybean oil and methanol. Proton nuclear magnetic resonance was used to determine the biodiesel yield/conversion (1H-NMR). Using the 1H-NMR, we were able to build a chart of the chemical shifts, where the peaks correspond to the protons present in the sample. The progression of the reaction is measured with two important peaks that appear at the protons' signal of 3.6 ppm and 2.3 ppm, corresponding to the methoxy group and methylene group respectively (Knothe, 2001). Figure 3.2 illustrates the location of the protons described here.
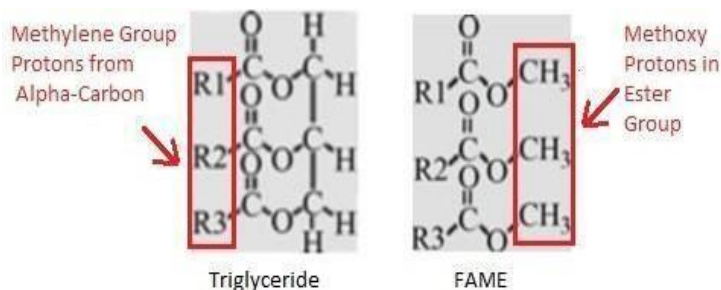


**Figure 3.2:** Protons of interest in $^1$H NMR Analysis of biodiesel samples

The proportion of waste soybean oil converted into biodiesel was determined using a formula proposed by Knothe in 2001, as follows:

$$C = (2\ A_{ME}\ /\ 3\ A_{\alpha\text{-}CH2}) \times 100\%\quad (3d)$$

Methyl ester conversion/yield, which is given by C, is computed using the area from the integration value of the methyl ester protons ($A_{ME}$) and the methylene protons ($A_{\alpha\text{-}CH2}$).

Using Knothe's formula (shown in equation 3d), the biodiesel conversion was determined. The experiments also yielded the same biodiesel conversion results in two out of three rounds of each process. In this study, a

transesterification process with identical biodiesel conversion numbers was used. This gave rise to the following sentence:

At 100oC, 60 minutes without co-solvent

$$C = (2 \times 0.14 \,/\, 3 \times 0.65) \times 100 = 14.4\%$$

# IV.    DISCUSSION

## 4.0   Results and Discussion

### 4.1   Titanium-Supported-Magnesium Oxide Catalyst (MgO/TiO2)

X-ray Fluorescence (XRF) study, Brunauer–Emmett–Teller (BET) analysis, and X-ray diffraction (XRD) analysis were used to evaluate the (MgO/TiO2) catalyst following section 3.2.3. The conclusions and findings are provided and elaborated upon.

### 4.1.1  XRF analysis

Table 4.1 displays the results of XRF scans, which showed the MgO concentration in the catalyst was near to 10 percent and very close to the goal of 10 percent. The catalyst had much more TiO2 (99.39%) than the calcined blank titanium (IV) oxide support. When magnesium nitrate is mixed with the support and dried, its atomic weight rises to 10.87 percent. The proportional percentage of MgO species in the catalyst is determined by its XRF-assessed loading of 10.87 wt.% MgO. The discrepancies between the goal content of 10% MgO (11% MgO was attained) reveal an actual gain in MgO content of . (0.87). Even though it demonstrates an increase in MgO species on the TiO2 support, which is an indication of successful impregnation and subsequent nucleation of the active MgO species. As Schwarz et al. (1995) showed, certain precursor support interactions are driven by chemical or physical forces (like surface hydrolysis, ligand substitution, ion exchange, and electrostatic attraction). Moreover, they believe that a precursor-support interaction could result in a support carrying more substance than would be expected if all of the dissolved substance stayed in the pore filling solution.

**Table 4.1: XRF analysis results for samples calcined at 600ºC**

| Component | XRF of Calcined Support ($TiO_2$) | XRF of Calcined Supported Catalyst ( $MgO/TiO_2$) |
|---|---|---|
| $Na_2O$ | 0.01 | 0.00 |
| $MgO$ | 0.01 | 10.87 |
| $Al_2O_3$ | 0.02 | 0.00 |
| $SiO_2$ | 0.23 | 1.06 |
| $K_2O$ | 0.20 | 0.25 |
| $CaO$ | 0.01 | 0.00 |
| $TiO_2$ | 99.39 | 87.66 |
| $Fe_2O_3$ | 0.13 | 0.16 |

### 4.0.1  BET analysis

As Table 4.2 shows, the blank calcined TiO2 support and the catalyst with 10% active MgO both have specific characteristics. It's clear that solid materials' active sites, as well as the metal dispersion and surface density thereof, are a direct function of a physical characteristic called specific surface area.

**Table 4.2:** BET analysis results for samples calcined at $600^{O}C$

| Sample Name | Calcined support (TiO2) | Calcined catalyst(10 wt. %MgO/TiO2) |
|---|---|---|
| Surface area  ($m^2/g$) | 8.94 | 6.25 |
| Pore volume ($cm^3/g$) | 0.035 | 0.031 |
| Pore size (Å ) | 195.42 | 156.40 |

The calculated surface area of the calcined tetracyanoplatinic oxide support (TiO2) was 8.94 m2/g. The specific surface area of the titanium supported magnesium oxide catalyst (MgO/TiO2) decreased from 18.8 m2/g to 6.25 m2/g after it was impregnated with 10 wt. % magnesium oxide (MgO) and calcinated at 600°C for 12 hours. Another difference was that the pore volume of the blank support and the catalyst decreased, with the former's from 0.035 cm3 to 0.031 cm3. Perhaps the magnesium oxide particles are getting in the way of the support's pores, reducing the catalyst's surface area and pore volume. A good study conducted by Baroutian et al. (2010) supports the belief that active sites will become stronger on the catalysts. A BET study of the alumina-supported vanadium oxide catalysts (VOx/γ-Al2O3) also led to a similar conclusion, as noted by Al-Ghamdi (2013) when he employed these catalysts in the propane oxidative dehydrogenation (ODH) process. He explained the small drop in the catalysts' surface area and pore volume as due to the presence of VOx species, which occupied part of the micropores in the alumina matrix.

### 4.0.1  XRD analysis

XRD is used to learn about the unit cell's unit particle size and shape for any chemical. It provides broad data on the qualitative and quantitative analyses of compounds (identifying phases and calculating lattice parameters and phase fractions). Because of this, the diffraction pattern details any anomalies, which provides information on the location of atoms and allows for further evaluation. It also enables people to easily determine the crystal type of solid mixes. Figure 4.1 shows the diffraction patterns obtained from the blank TiO2 support and the catalyst (10 wt. percent MgO/TiO2).
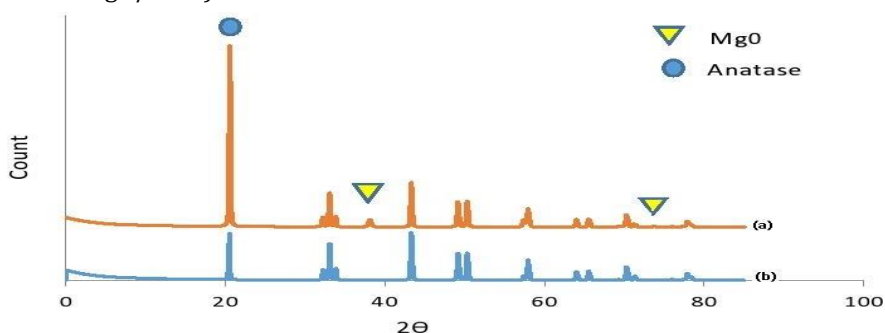


**Figure 4.1:** XRD Patterns for (a) TiO2-supported-MgO catalyst and (b) blank TiO2

The XRD diffraction patterns of the 10% MgO/TiO2 catalyst appear in the image on the left, while those of the blank TiO2 support appear on the right. Both patterns seem similar, with anatase at 2θ's main peaks of ca. 20, 32, 43, 48, and 50. Additional diffraction peaks were observed at diffraction angles of 37o and 78.7o, respectively, on the XRD pattern for the catalyst (pattern a) compared to the calcined blank support. It's also similar to what Corma et al. (2000) found: MgO samples emit XRD diffraction peaks at 2θ = 37o, 42.9o, 64o, 67o, and 78.6o. The Bragg's angle 37o had the highest value of the catalyst's concentration, and that measurement helped compute the MgO crystallite size using the Scherrer equation (equation 4a).

$$D = \frac{k\lambda}{\beta \cos \theta} \qquad (4a)$$

Where:

K = Shape Factor

β = FWHM = line broadening at half the maximum intensity

λ = wavelength of x-rays, and

θ = Bragg's diffraction angle

A value of 25.7 nm was discovered for the average crystallite size (with K = 0.9 and λ = 0.15 nm). In addition, anatase was detected as the only component of the blank calcined TiO2 support through XRD quantitative analysis. This percentage varies as the catalyst was discovered to contain 79.32% anatase and 20.7% periclase, but lacking rutile particles, when it was incubated and calcined at 600 degrees Celsius. As indicated in Table 4.1, SiO2, which is an impurity, hinders the transition of anatase to rutile particles since it is present in the composition.

### 4.0    NMR ANALYSIS

In order to measure the waste vegetable oil conversion, 1H-NMR analysis was conducted at several reaction durations and temperatures. A magnetic resonance frequency analysis was utilised to measure fatty acids in biodiesel, because the signal strength of proton nuclear magnetic resonance (1H-NMR) is linked to the amount of hydrogen nuclei in the molecule (Irmawati et al., 2014). In contrast, a typical NMR spectra obtained after 60 minutes of reaction at 200 degrees Celsius with the addition of hexane as a co-solvent appears as follows.
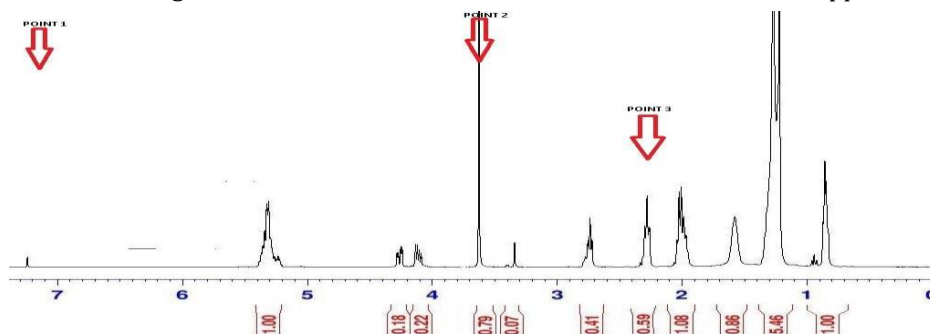


**Figure 4.2:** $^{1}$H NMR spectrum of sample collected after 60minutes of reaction at 200$^{o}$C
with hexane as co-solvent.

For methyl esters, protons on the neighbouring α-CH2 groups (2.3 ppm) are associated with the production of methyl esters while the protons on methyl esters (3.6 ppm) are associated with synthesis of methyl esters. The presence of two distinct peaks in methyl esters may confirm methyl ester synthesis in biodiesel. It is the integration values that indicate how many protons are in each chemical group (and, thus, peak). The integration values also reflect the location of the protons in the various chemical groups. (Madyira et al., 2012) To determine the % conversion of biodiesel after 60 minutes of reaction at 200oC, the sample calculation was produced using equation (3d) as cited by Knothe, (2001). This required integrating the sample results of the calculated peak area and known areas (a).

C = (2 x 0.79 / 3 x 0.59) x 100 = 89.3%

Additionally, Table 4.3 shows that there are many tables in Appendix E on page 92 that detail the various percentage conversions.

Point 1 is the solvent peak at 7.20 ppm, point 2 is the methoxy group peak of FAME at 3.6 ppm, and point 3 is the methylene group peak of the triglyceride at 2.6 ppm.

**Table 4.3:** Biodiesel yield using methanol and hexane as co-solvent with 10 wt. % MgO/TiO2 as catalyst

| SOLVENT | TEMPERATURE (Degrees) | FAME PROTON Signal At 3.6 ppm | METHYLENE PROTON Signal At 2.3 ppm | TIME (Minutes) | CONVERSION (Percentages) |
|---------|-----------------------|-------------------------------|-------------------------------------|----------------|--------------------------|
| Methanol | 100 | 0.02 | 0.61 | 15 | 2.2 |
| | 100 | 0.03 | 0.64 | 30 | 3.1 |
| | 100 | 0.06 | 0.63 | 45 | 6.3 |
| | 100 | 0.14 | 0.65 | 60 | 14.4 |
| | | | | | |
| | 150 | 0.44 | 0.63 | 15 | 46.6 |
| | 150 | 0.45 | 0.62 | 30 | 48.4 |
| | 150 | 0.53 | 0.62 | 45 | 57.0 |
| | 150 | 0.61 | 0.63 | 60 | 64.6 |
| | 200 | 0.45 | 0.62 | 15 | 48.4 |

| | 200 | 0.45 | 0.61 | 30 | 49.2 |
|---|---|---|---|---|---|
| | 200 | 0.78 | 0.70 | 45 | 74.3 |
| | 200 | 0.72 | 0.64 | 60 | 75.0 |
| | | | | | |
| Methanol + Hexane | 100 | 0.53 | 0.66 | 15 | 53.5 |
| | 100 | 0.64 | 0.71 | 30 | 60.1 |
| | 100 | 0.72 | 0.62 | 45 | 77.4 |
| | 100 | 0.65 | 0.54 | 60 | 80.3 |
| | 150 | 0.51 | 0.62 | 15 | 54.8 |
| | 150 | 0.71 | 0.65 | 30 | 72.8 |
| | 150 | 0.65 | 0.54 | 45 | 80.2 |
| | 150 | 0.78 | 0.64 | 60 | 81.3 |
| | | | | | |
| | 200 | 0.53 | 0.64 | 15 | 55.2 |
| | 200 | 0.75 | 0.63 | 30 | 79.4 |
| | 200 | 0.79 | 0.65 | 45 | 81.0 |
| | 200 | 0.79 | 0.59 | 60 | 89.3 |

Using the integration generated peaks to determine the length of methyl-ester chains was discovered during the experimentation. Irmawati et al. (2014) presented 1H-NMR peak assignment that has been used to determine the average amount of carbon and hydrogen atoms in biodiesel. Table 4.4 summarises the results.

**Table 4.4:** ^{1}H-NMR peaks assignment (Irmawati et al., 2014)

| Functional group | Chemical shift δ (ppm) |
|---|---|
| Terminal methyl group | 0.80 − 1.00 |
| Backbone $CH_2$ | 1.22 − 1.42 |
| β–Methylene proton | 1.55 − 1.69 |
| α–Methylene group to one double bond | 1.93 − 2.10 |
| α–methylene group to ester | 2.31 |
| Methyl group to ester | 3.67 |
| Olefinic proton | 5.27 - 5.41 |

A factor is discovered that is used to find the number of hydrogen atoms in other groups, which is done by dividing the methylium (CH3) area, as Table 4.5 shows. It is known that the methylium (CH3) area has three hydrogen atoms and one carbon in their chain, and the factor is used to divide this area to give three hydrogen atoms.

**Table 4.5:** Summary estimates of H and C atoms in produced biodiesel

| Functional group | Methine: (CH) | ($CH_3$) | | Methylene ($CH_2$) | | | | Total |
|---|---|---|---|---|---|---|---|---|
| Chemical shift δ (ppm) | 5.2-5.4 | 3.6 | 0.9 | 2.3 | 2 | 1.5 | 1.2 | |
| Area | 1 | 0.79 | 1.0 | 0.59 | 1.08 | 0.86 | 5.46 | |
| H/C ratio | 1 | 3 | 3 | 2 | 2 | 2 | 2 | |
| H | 3.8 | 3.0 | 3.8 | 2.2 | 4.1 | 3.3 | 20.7 | 40.9 |
| C | 3.8 | 1.0 | 1.3 | 1.1 | 2.1 | 1.6 | 10.4 | 21.2 |

The molecular formula for the biodiesel sample was determined to be C21H41O2 based on these calculations. Arora et al. developed a method that calculates the ratio of polyunsaturated to monounsaturated fat, which they presented in their 2010 paper.

**Monounsaturated integral = Total alkene integral - 2 X polyunsaturated integral          (4b)**

In the H-NMR spectrum, the integral signal is located at 5.1–5.6 ppm, and that is where the total alkene integral is located. Polyunsaturated integrals are situated at the signal area, which may be found between 2.6 and 2.8 ppm. Using data in Appendix I, we discovered that the ratio of polyunsaturated fats to monounsaturated fats was 2.28. As a result, the estimation of the polyunsaturated fat content of this sample is 2.28 times that of the monounsaturated fat content.

### 4.3     Catalytic Result over TiO2-Supported-MgO Catalyst

### 4.3.1   Effect of reaction temperature on biodiesel yield

The temperature of the trans-esterification process and the yield of the biodiesel product are both greatly affected by changes in temperature. More viscous oils will see an increase in reaction rate and reaction time due to a temperature rise, which allows for a quicker response (Encinar et al., 2010).
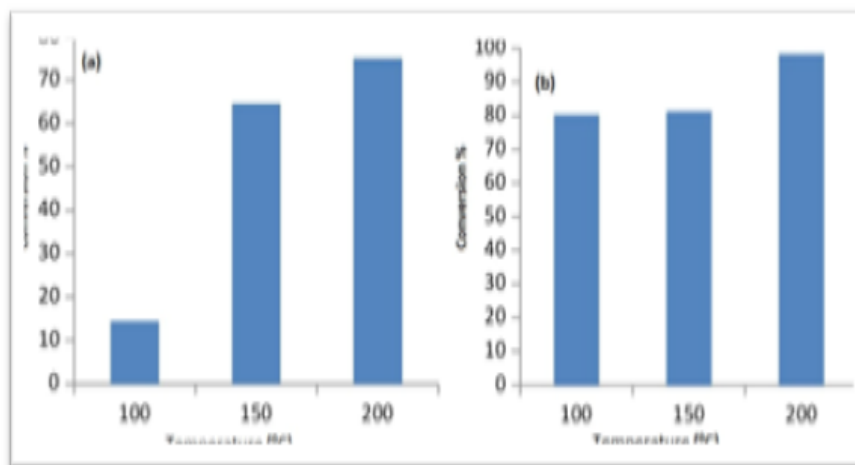


**Figure 4.3:** Effect of temperature on waste oil conversion (alcohol to oil mole ratio of 18:1; Hexane to oil mole ratio of 1:1; catalyst amount of 3 wt.% with respect to oil at 60 minutes reaction time). (a) without hexane co-solvent (b) with hexane co-solvent

Because of this, a rapid, favourable biodiesel yield occurs between 150 and 200 degrees Celsius after the reaction, restricted by mass transfer, starts at 100 degrees Celsius. Using a 10 percent mixture of MgO/TiO2 catalyst at 100°C, converting waste cooking oil into oil with a ratio of 18:1 is at 14.4 percent after 60 minutes (Figure 4.3a). After 60 minutes, using 150 degrees Celsius raised the waste oil conversion rate to 64.6 percent. After 60 minutes, the conversion rose to 75.0 percent when the reaction temperature was raised to 200°C (Figure 4.3a). Nevertheless, it has certain characteristics with using hexane as a co-solvent. After 60 minutes, a titanium-supported magnesium oxide catalyst recorded an oil conversion rate of 80.3 percent after 10 wt. % of titanium, at 100oC, and with a hexane to oil mole ratio of 1:1. At 150 and 200 degrees Celsius, the oil conversion rose by 81.3 percent and 89.3 percent, respectively. It's clear that higher temperatures provide more biodiesel output when the TiO2-supported-MgO catalyst is used. All in all, temperature impacts are due to:

- As temperature increases, viscosity of waste vegetable oil decreases and this improves the mass transfer of reactants to the active sites in the catalyst
- As more energy is added to the system, effective number of collusions increases and this helps to overcome the activation energy barrier
- More waste vegetable oil eventually dissolves in methanol improving methanol-oil immiscibility which also improves the mass transfer in the catalyst;

### 4.3.1 Effect of reaction time on biodiesel yield

The reaction time improves the biodiesel production according to Figure 4.4. A specific example of the catalyst efficiency is as follows: In a lab experiment, the three percent of a titanium-supported-magnesium oxide catalyst at 150 degrees Celsius with a methanol to oil ratio of 18:1 and under operating conditions achieved conversion results of 46.6, 48.4, 57.0, and 64.6 percent in fifteen, thirty, forty-five, and sixty minutes respectively (Figure 4.4a). At 150 °C, the same titanium-supported-magnesium oxide catalyst with 3% weight of magnesium oxide, the rate of conversion goes up to 54.8%, 72.8%, 80.2%, and 81.3% of oil conversion within 15, 30, 45, and 60 minutes respectively when the alcohol-to-oil ratio is 18:1 and the ratio of hexane to oil is 1:1. (Figure 4.4b).
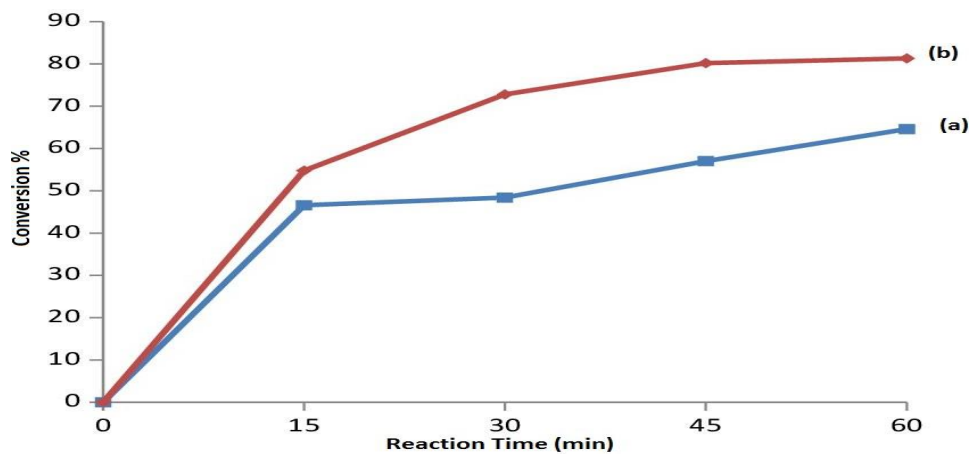


**Figure 4.4:** Effect of reaction time on waste oil conversion (alcohol to oil mole ratio of 18:1, Hexane to oil mole ratio of 1:1; catalyst amount 3 wt. % with respect to oil and reaction temperature of $150^{o}$C).(a) without hexane co-solvent (b) with hexane co-solvent.

Transesterification yield was greater, but a similar pattern was seen at a reaction temperature of 200oC (as shown in Figure 4.5) even though the transesterification yield was considerably higher. It can be observed that at 200 degrees Celsius with a 3 percent catalyst concentration, 18:1 methanol to oil ratio, and a 15-minute duration, the conversion rate is 48.4 percent; 30 minutes, 49.2 percent; 45 minutes, 74.3 percent; and 60 minutes, 75.0 percent (Figure 4.5a). Although using hexane as a co-solvent at 200 degrees Celsius resulted in a decent FAME yield (55.2, 79.4, 81.0, and 89.3 percent) in the fifteen, thirty, forty-five, and sixty-minute timeframes, it is a poor yield when compared to a similar experiment where no co-solvent was used.
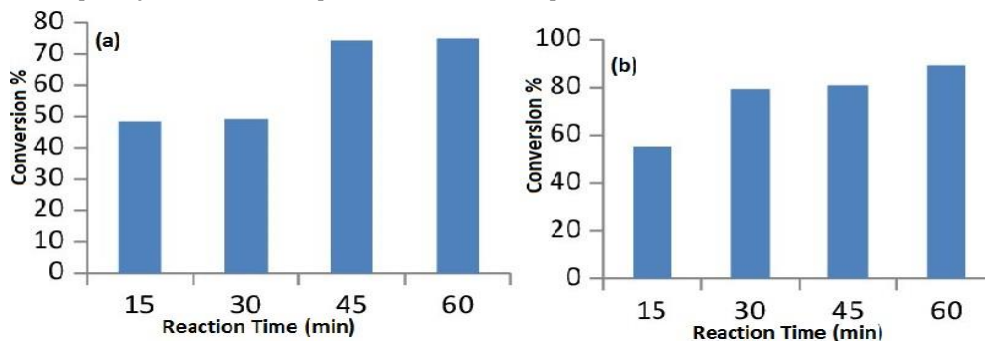


**Figure 4.5:** Effect of reaction time on waste oil conversion (alcohol to oil mole ratio of 18:1; Hexane to oil mole ratio of 1:1; catalyst amount 3 wt.% with respect to oil and reaction temperature of $200^{o}$C) (a) without co-solvent (b) with hexane as co-solvent

But, this research looked at just a one-hour reaction period, and longer reaction durations would provide more optimal waste oil conversion. At the allotted time slots, hexane was used to create a reaction for a 15, 30, 45, and 60 minute timespan, and 150-degree temperature in which the biodiesel conversion at those points was 54.8, 72.8, 80.2, and 81.3 percent, respectively. Thus, after 45 minutes, a biodiesel conversion rate of 80.2% has been reached. Better processing times caused the rise in the amount of oil converted to fuel. The biodiesel

conversion rate after 60 minutes was 81.3%, and the result was obvious. Increasing the response time pushes the percentage conversion closer to equilibrium conversion. Similarly, the equilibrium trend found (Figure 4.5a) did not need hexane as a cosolvent (percentage conversion of biodiesel: 74.3% and 75.0% at 45 and 60 minutes at 200 C).

Transesterification has been run across prolonged reaction times by certain researchers. In the experiment by Sadrameli et al. (2012), a KOH catalyst was loaded on γ-Al2O3 support, the ratio of methanol/oil was 15:1, and the reaction duration was adjusted from 1 to 5 hours. The study was designed to run a transesterification process. It seems that his work revealed that the best biodiesel yield is attained with 3 hours of response time, while the yield was not substantially greater after 4 hours.

### 4.3.1   Effect of co-solvent on biodiesel yield

The transesterification process will be helped along by the presence of a co-solvent that promotes miscibility of the reactants and the catalyst. In transesterification reactions, the addition of a co-solvent will help the transesterification rate rise and boost the methyl ester yield (Yin et al., 2008). To get around the problem of immiscibility, this research employed the solvent hexane. In this way, more of the methanol has the ability to go to the oil/catalyst active sites because of the increased solubility. This has the benefit of increasing the collision efficiency and therefore also the trans-esterification reaction rate.

**Table 4.6:** Yields measured using methanol and hexane co-solvent

| MeOH:Oil:Cosolvent (Molar ratio) | Temperature (°C) | Time (Minutes) | Methyl Ester Yield (%) |
|---|---|---|---|
| 18:1:0 | 100 | 60 | 14.4 |
| 18:1:0 | 150 | 60 | 64.6 |
| 18:1:0 | 200 | 60 | 75.0 |
| 18:1:1 | 100 | 60 | 80.3 |
| 18:1:1 | 150 | 60 | 81.3 |
| 18:1:1 | 200 | 60 | 89.3 |

At temperatures of 100, 150, and 200 °C, the conversion of waste vegetable oil to biodiesel is 14.4, 64.6, and 75.0 percent with no co-solvent. An increase in oil conversion was seen when hexane co-solvent was used: 80.3%, 81.3%, and 89.3% at 100, 150, and 200oC, respectively. The use of hexane co-solvent improved the transesterification process by improving the solubility of waste oil and methanol, which were successfully mixed within a short time period. Kim et al. (2004) concluded that a co-solvent should be used in the reaction in order to enhance the miscibility of the reagents (alcohol and oil), which would help the reaction and reduce the time it takes to achieve the greatest conversion. Yin et al. (2008) found that a 3 percent yield improvement resulted from the use of hexane while heating the test material to 300 degrees Celsius in 30 minutes. A maximum ester yield of 85 percent was achieved when he included 2.5 percent of hexane into the reaction mixture. In addition, Lingfeng et al. (2007) found that after improving their best catalyst (Na/NaOH/γ-Al2O3, 1.0g catalyst, 9:1 methanol to oil molar ratio) with the addition of hexane as a co-solvent, they achieved a biodiesel yield of 94%.

### 4.3.1   Effect of methanol/oil mole ratio on biodiesel yield

One of the most significant factors for the conversion of waste oil to methyl esters is the methanol to oil mole ratio. In reality, the trans-esterification process needs more methanol than is necessary to fulfil the stoichiometric requirement to get high biodiesel yields. Trans-esterification processes catalysed by heterogeneous catalysts are notorious for being sluggish; yet, in certain cases, their speed may be increased. A three-phase system of oil-methanol-catalyst consists of a heterogeneous catalyst including titanium to promote MgO/TiO2 that hampers mass transfer and reduces contact between the active MgO catalyst and the reactants. The reaction is much slower because of reduced mass transfer, which occurs when mass transfer is restricted. This is a contributing factor to the biodiesel output, which is lower when using 100oC to convert waste oil (see

Figure 4.3a). Researchers believe that in order to guarantee that all the triglycerides are converted, the triglycerides need to be mixed with a significant quantity of alcohol. The fact that higher temperature (as previously mentioned) gives a larger surface area for effective contact between reactants and catalyst to achieve a higher oil conversion explains why the researchers chose a methanol to oil ratio of 18:1 in their investigation. Several reports have shown that the ratio of methanol to oil varies. Modi (2010) found that to transform a heterogeneous reactive system to a homogeneous one, it took excessive methanol to dissolve the oil entirely.

The FAME production doubled, jumping from 38 percent to 79 percent, when the methanol-to-oil molar ratio rose from 6 to 25. However, He et al. (2007) found an ester yield reduction to 77% at a methanol/oil molar ratio of 65, having the exact opposite outcome from our experiment. He said that once the system was consistent, the FAME yield would not increase further, but the amount of ester production will go down.

## V.    CONCLUSION

(MgO/TiO2) catalyst was made in this research by soaking a titanium (TiO2) support in magnesium nitrate and then drying and heating it at 600 degrees Celsius. XRD examination demonstrates that although anatase to rutile transition was hindered, the reason is silicon dioxide impurity, as identified by XRF analysis. Trans-esterification of waste cooking oil with methanol into biodiesel was studied using different reaction times and temperatures with a catalyst under 24 bar of inert-nitrogen gas pressure. The reaction time and temperature were shown to directly influence the conversion. In one hour, the trans-esterification reaction had a beneficial impact on transesterification rates, with yields being higher thanks to the use of hexane as a co-solvent. The research shows that the trans-cooperation esterification's with the hexane solvent-to-oil mole ratio of 1:1 and a temperature of 200oC and reaction duration of 1 hour yielded a waste oil conversion of 89.3 percent. We have a positive comparison here in terms of waste oil conversion percentage; although we have only achieved about 25% with just methanol as the solvent, we will easily exceed 75% in the future. To find out the length of fatty acid methyl-ester (FAME) produced, a spectra generated using 1H-NMR was utilized.

## VI.    RECOMMENDATIONS

Trans-esterification process should be done at a higher temperature with more time to decrease methanol and maximise the usage of hexane as a co-solvent in future research. It is crucial to research, develop, and utilise different heterogeneous solid catalysts to make the manufacturing of biofuel affordable. Because it is supported, the supported catalyst has better catalytic activity, selectivity, and stability than most other catalysts.

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