

**ESTERIFICATION OF FREE FATTY ACID
OBTAINED FROM WASTE COOKING OIL OVER
SOLID CATALYST**

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**by
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ABSTRACT

ESTERIFICATION OF FREE FATTY ACID OBTAINED FROM WASTE COOKING OIL OVER SOLID CATALYST

The objective of this study was to investigate effect of reaction temperature, catalyst weight percentage and composition of $\text{Al}_2\text{O}_3/\text{SiO}_2$ on conversion of FFA obtained from waste cooking oil (WCO) to take place esterification reaction by using Box-Behnken design. Statistical analysis demonstrates that catalyst weight percentage and temperature were insignificant statistically. Alumina composition was found as significant parameter at certain conditions by considering statistical analysis. It was seen that conversion of Free Fatty Acid (FFA) increases as composition of Al_2O_3 in Alumina/Silica catalyst increases. %80 Al_2O_3 /20% SiO_2 catalyst was found as promising catalyst since conversion of FFA with the catalyst was 32% at 80°C and 15:1 alcohol to FFA ratio. Besides, it was found that alcohol to FFA ratio affected the conversion reversely. When alcohol to FFA ratio was reduced to 2:1, conversion of FFA increased to 41%. The prepared catalysts were characterized by XRD and TPD analysis. Activity of catalysts were attributed to acidic strength and Bronsted acid sites on the aluminum sulfate in the catalysts.

After screening effects of catalysts and reaction conditions, optimum levels of parameters were used to investigate the esterification reaction of model WCO. This reveals that conversion of FFA was found as 11% at 80°C and 15:1 alcohol to FFA ratio. Finally, the proposed catalyst does not have catalytic activity of hydrolysis reaction of oil at applied conditions.

ÖZET

ATIK YAĞDAN ELDE EDİLEN YAĞ ASİTLERİNİN KATI KATALİZÖRDE ESTERİFİKASYON REAKSİYONU

Bu çalışmanın amacı reaksiyon sıcaklığının, katalizör miktarının ve alümina/silika katalizörünün içindeki alümina kompozisyonunun, atık yağdan elde edilen yağ asitlerinin estere dönüşümüne etkisinin Box-Behnken istatistiksel tasarım yapılarak incelenmesidir. İstatistiksel analize göre katalizör miktarı ve reaksiyon sıcaklığı istatistiksel olarak önemsiz olduğu saptanmıştır. Alümina kompozisyonu arttıkça yağ asitlerinin dönüşümü artmıştır. Bundan dolayı 80%Al₂O₃/20%SiO₂ umut verici bir katalizör olarak görülmüştür. Ayrıca alkol miktarının ters etki yarattığı gözlemlenmiştir. Yağ asitlerinin dönüşümü %32 olarak bulunmuştur Alkol mol miktarı 15 kattan 2 kata indiğinde ise yağ asitlerinin dönüşümü %41'e çıkmıştır. Hazırlanan katalizörler X ışını difraktometresi ve sıcaklık programlı desorpsiyon analizleri yapılmıştır. Katalizörlerin aktivitesi olası alumina sülfat fazında bulunan Bronsted asit yüzeylerine ve asidik güçlerine atfedilmiştir.

Katalizörlerin ve reaksiyon koşullarının taranmasından sonra parametrelerin optimum seviyeleri model olarak alınan atık yağ esterifikasyon reaksiyonu 80°C'de ve 15:1 etil alkol: yağ asidi oranında denenmiştir. Bu da göstermiştir ki yağ asitlerinin dönüşümü 11% bulunmuştur.

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CHAPTER 1

INTRODUCTION

Energy demand increases with increasing population and welfare year by year as seen in the Figure 1. Although energy efficient processes and devices are produced by various sectors, energy demand per person increases due to several reasons including digitalization and individualization. The energy demand is mostly provided by fossil fuels and their derivatives. However, fossil fuels have been being depleted rapidly and lead to severe environmental pollutions, including global warming and acid rains.

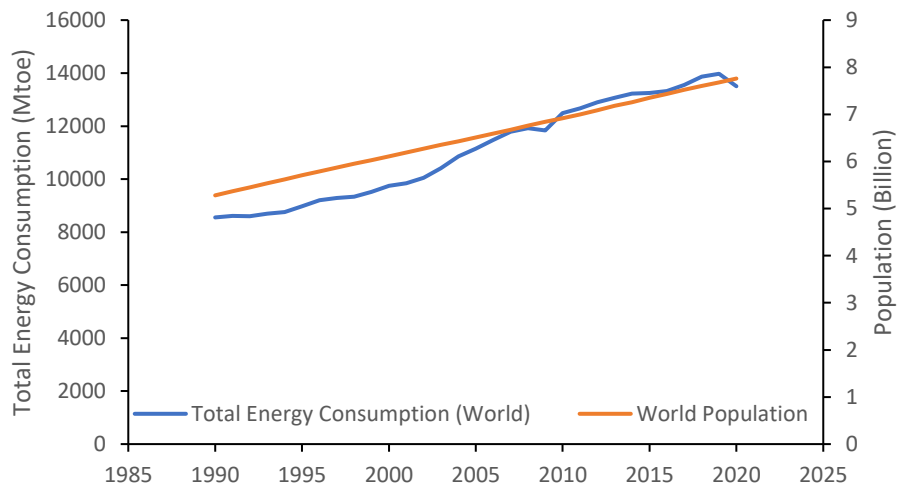


Figure 1. Total Energy Consumption vs Population in the World

(Source: “World Energy Consumption Statistics | Enerdata” n.d.; “Population, Total | Data” n.d.)

The total energy consumption has dramatically increased as seen in Figure 1. Share of Renewable energy in the total energy consumption is approximately 13 in 2019 as seen in Figure 2. Renewable energy has become more attractive for a long time due to the depletion of fossil fuel and concerns about climate change. In addition to these issues, dependency on petroleum can be another reason for most countries where do not have petroleum sources. Moreover, Paris Agreement has urged governments to replace fossil fuels with renewable energy sources including wind, solar and biomass. On the other hand, the share of other renewable energy sources increases, resulting from improvement

of solar and wind energy. Biofuel is distinct from other renewable energy types since it cannot be produced without using biomass. Besides, the share of biofuels is decreased from 10.8 to 9.4. However, total biofuel production capacity increases, resulting in Diesel produced from fossil fuels is one of the most used fuels, but it contributes to environmental impacts resulting from release of SO₂, CO₂ and CO. Therefore, biodiesel is a promising alternative to petroleum diesel since it has carbon neutrality feature resulting from use of CO₂ released into atmosphere while combusting in diesel engine as plant nutrition.

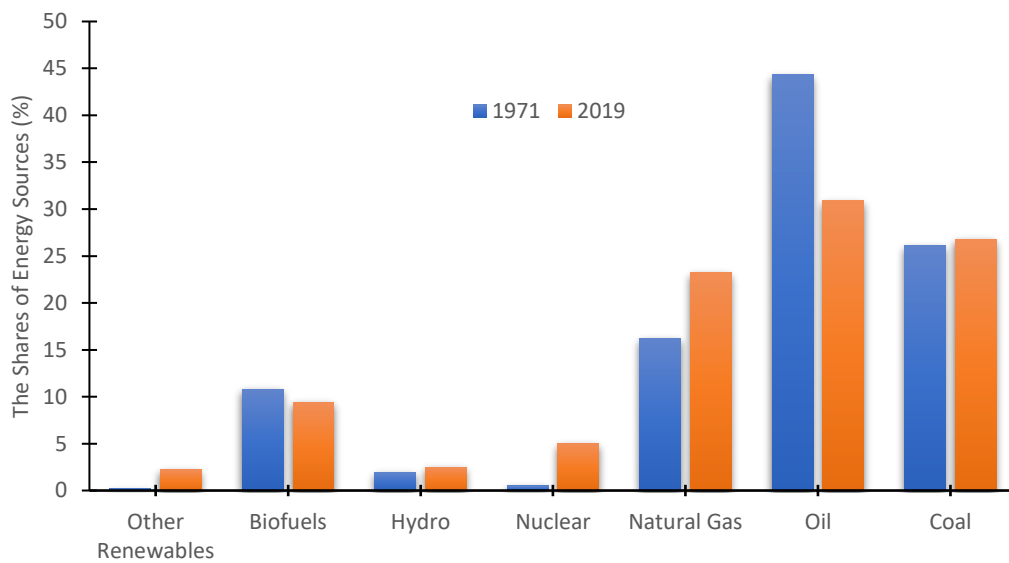


Figure 2. The Shares of Energy Sources
(Source: “IEA – International Energy Agency” n.d.)

The main motivation of tending toward renewable energy is to decrease CO₂ emissions. Figures 4 and 5 demonstrate the CO₂ emissions of worldwide and Türkiye in 2020, respectively. Both graphs of worldwide and Turkey reveals that transport sector is the second most contributing factor to CO₂ emissions while electricity and heat generation sector is the most contributing factor. Increase in CO₂ emissions has urged scientists to develop new technologies including wind, solar and biomass energies. Biomass is different from other renewable energy technologies since biofuels are produced from biomass sources, leading to replacement of traditional fuels with several treatments. In other words, traditional vehicles, fueled by gasoline, LNG or diesel, may be used by means of biofuels whereas they cannot be fueled by solar and wind energy

without any modifications. As a result, transportation sector can be fueled by renewable energy including biodiesel, sustainable aviation fuel or green gasoline.

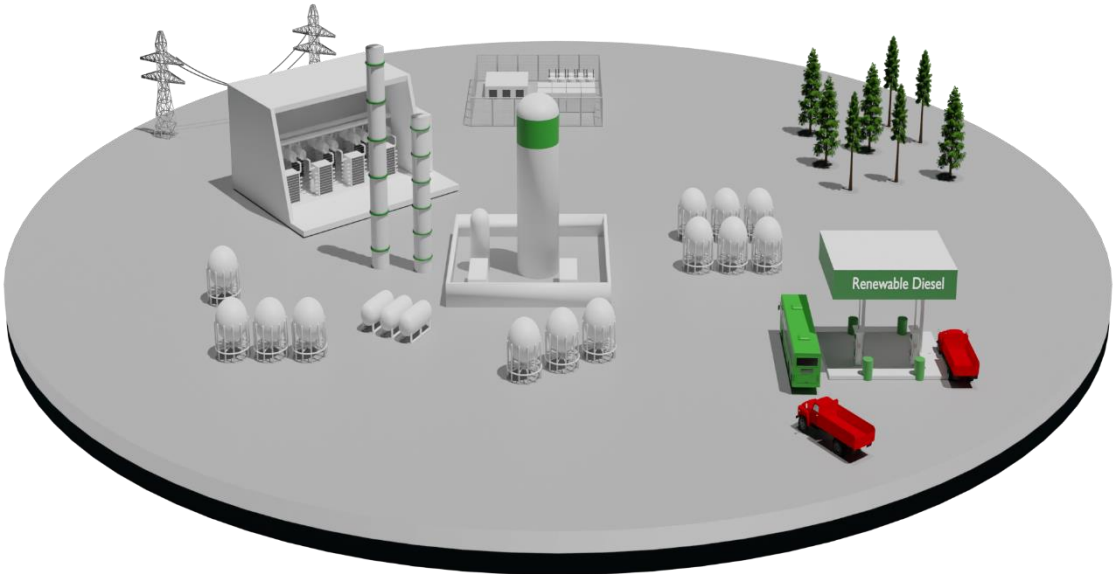


Figure 3. Representation of renewable diesel production plant

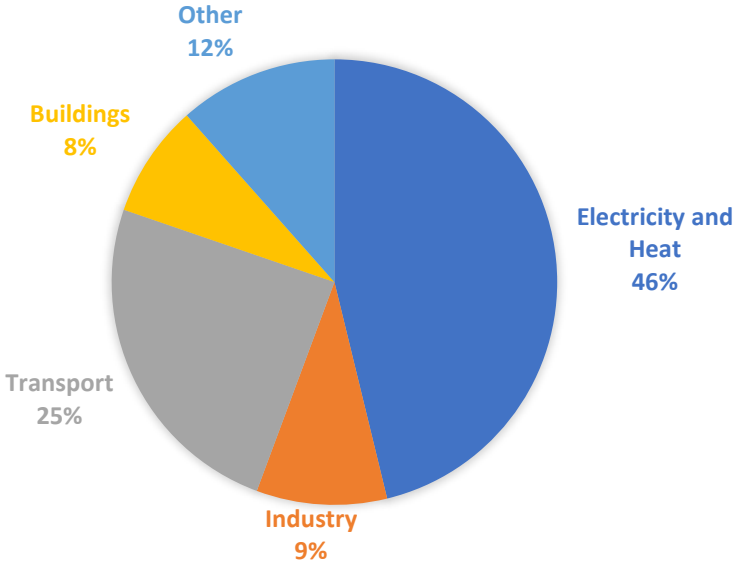


Figure 4. Shares of CO₂ emissions caused by energy consumption in the World (Source: “IEA – International Energy Agency” n.d.)

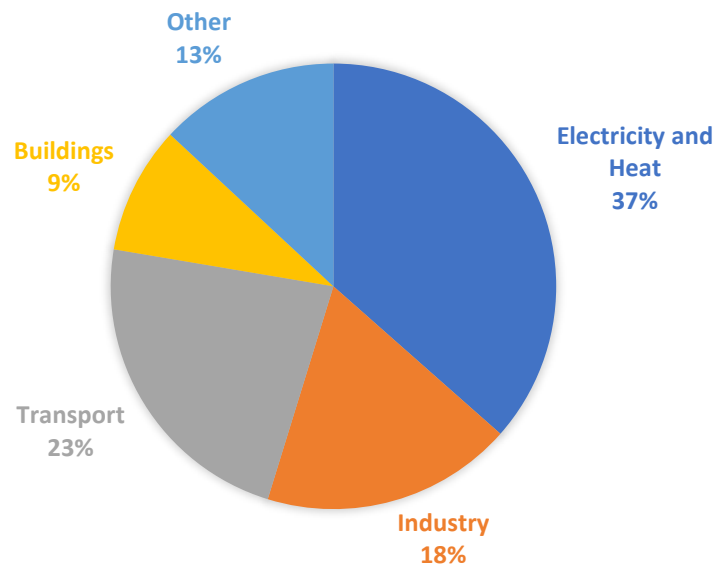


Figure 5. Shares of CO₂ emissions caused by energy consumption in the Türkiye
(Source: “IEA – International Energy Agency” n.d.)

Biofuels are categorized into three groups including first-, second- and third generation biofuels. The first-generation biofuels including starch, bio-alcohol, sugar or vegetable oil are well known processes in industrial scale for years. However, it has competition with the food market, leading to imbalance between need of energy and food. Therefore, the sustainability of the first-generation biofuels is controversial. The second-generation biofuels are put forward to overcome disadvantages of the first-generation biofuels. The third-generation biofuels are expected to use algae, compensating for the disadvantages of first- and second-generation biofuels since algae cultivation does not have competition for food market.

Biodiesel can be produced by two main reactions including esterification and transesterification. Esterification reaction is mostly catalyzed by acid catalyzed, resulting in corrosive problems. Also, it requires longer reaction time than transesterification reactions catalyzed by alkaline solutions. Therefore, transesterification reaction by acid catalyzed is unpreferable for industry. Transesterification reaction by alkaline catalyst is highly preferable for industrial scales. However, waste cooking oil consists of different free fatty acids (FFA). FFA can be conventionally removed by different methods including esterification of FFA by homogenous acid catalyzed, extraction from the waste cooking oil by different solvents or saponification reactions. These methods have several problems about separation, bringing about environmental effects and extra cost.

Biodiesel is fatty acid alkyl esters produced from vegetable oils, fats and algae oil. Although algae oil can be preferable due to the third-generation sources, it is still not commercially applicable unlike vegetable oil and waste cooking oil. On the other hand, biodiesel production from the waste cooking oil and vegetable oil is a commercially well-known process for industrial scale. The best case is probably to use waste cooking oil. As seen in Figure 6, waste cooking oil declared by people is between 13000- and 17000-ton liters.

Methanol is generally preferred by industry to take place transesterification and esterification reactions. However, there are some challenges to produce fully biodiesel. One of them is lowness of miscibility of methanol and oil or FFA, resulting in mass transfer limitations. On the contrary, ethanol is higher miscibility with oil or FFA. Another challenge is producibility of methanol from biomass. On the other hand, ethanol can be produced from different feedstocks including sugarcane, corn, fruits and biomass-carbon compounds. Also, it can be seen that trend of production of ethanol from biomass carbon compounds increases, indicating probability of absence of competition with food market.

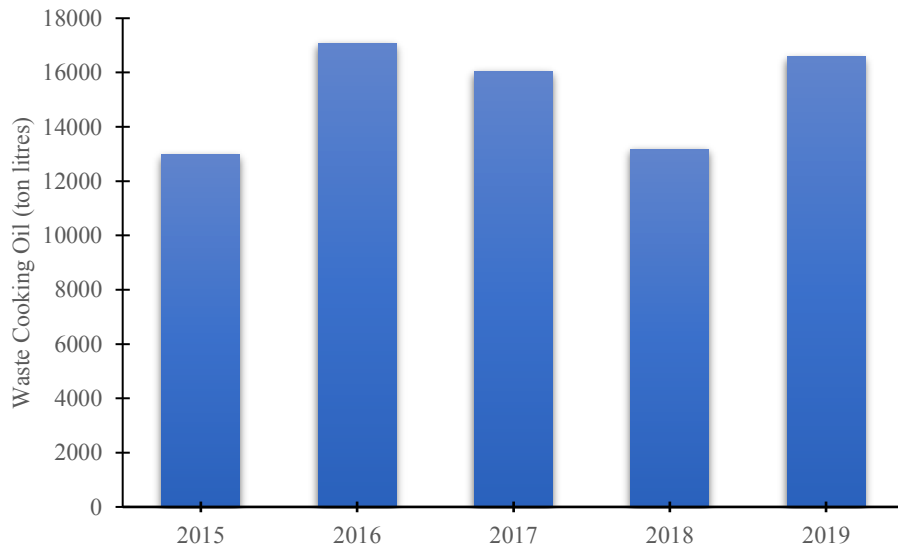


Figure 6. Annual Waste Cooking Oil declared in Türkiye

(Source: Yönetimi Dairesi Başkanlığı, Beyanında Bulunan Tesislerin Yıllara Göre Dağılımı, and Beyanında Bulunan Tesis Sayısı 2018)

Biodiesel can be utilized by different purposes comprising production of renewable diesel, sustainable aviation fuel and gasoline. Renewable diesel can be

traditionally produced by hydrodeoxygenation methods. It can be converted to different fuels including sustainable aviation fuel and gasoline in a biorefinery, resulting in less CO₂ emission generated from fossil fuel and retardation of global warming. The consumption of renewable diesel increases from 82 M liters in 2010 to 7556 M liters in 2020. As seen in Figure 7, the consumption of biodiesel is also increased from 20511 M liters in 2010 to 43216 M liters in 2020, demonstrating incremental trend.

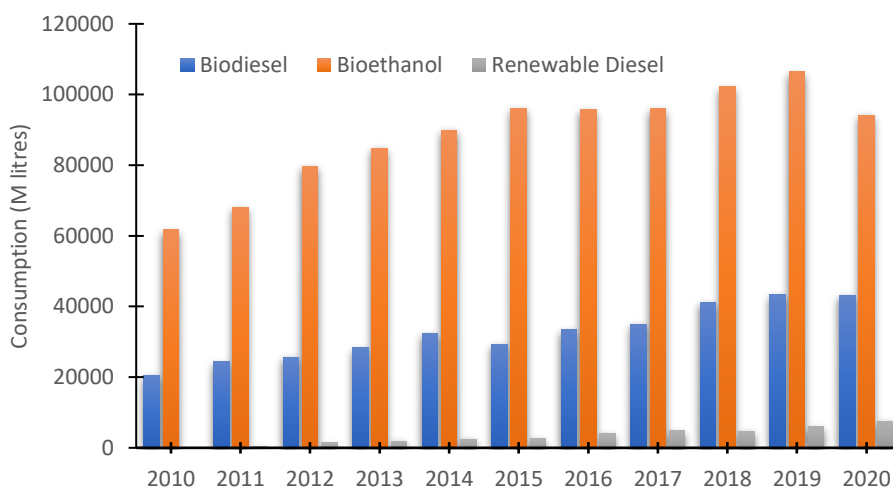


Figure 7. Consumption of Biodiesel, Bioethanol and Renewable Diesel in the World
(Source: “IEA – International Energy Agency” n.d.)

Alcohol and triglyceride molecules are reacted over alkaline catalyst or acidic catalyst to form fatty acid alkyl ester and glycerol molecules, which is called as transesterification reaction. Alkaline catalyst is faster than acidic catalyst to carry out transesterification reaction, resulting from changes in reaction pathway. Transesterification reaction alkaline-catalyzed proceeds with forming nucleophilic alkoxide (Methoxide/Ethoxide) from alcohol which attack the electrophilic part of the carbon, indicating rate determining step for this reaction pathway. Heterogenous alkaline catalyst like CaO catalyst has quite high activity due to the oxygen anion in the present on CaO surface (Marinković et al. 2016).

Transesterification reaction homogenous acid catalyzed proceeds with protonation of carbonyl groups of triglycerides and alcohol attacks protonated carbon to form a tetrahedral intermediate. Then, unstable tetrahedral structure is broken down to generate diglyceride and fatty acid ester. Finally, proton transfers to catalyst for homogenous catalysts (Cheng 2017).

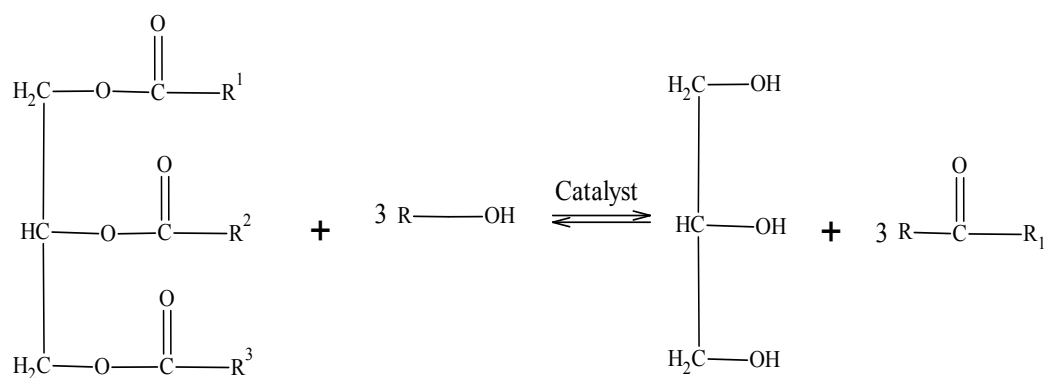


Figure 8. Transesterification Reaction

Esterification reaction proceeds with acidic catalyst especially Bronsted acid. Bronsted acid provides hydrogen or proton to generate carbocation from FFA, which is a rate determining step for this reaction. Then, alcohol attacks the carbocation due to the electron configuration of oxygen in the alcohol. In other words, nucleophilic attack of alcohol to carbocation generation from protonation occurs, facilitating the generation of tetrahedral intermediate. Finally, it generates water and ester (Khan et al. 2021).

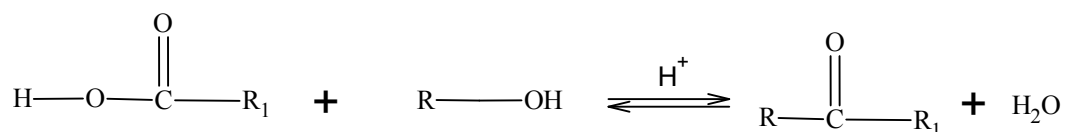


Figure 9. Esterification Reaction

This thesis consists of five chapters. The first chapter contains introduction of the significance of biofuels like biodiesel, biodiesel production, the general principles of esterification reactions. The second chapter involves literature survey about esterification reaction with methanol/ethanol by using homogenous/heterogenous catalysts. In the third chapter, the catalyst preparation method used in esterification reactions and catalyst activity tests were mentioned. The fourth chapter reveals results of experiments and discussions of experiments. In the final chapter, all the results of the study were concluded.

CHAPTER 2

LITERATURE SUVEY

2.1. Esterification of FFA with ethanol by using homogenous catalyst

Esterification of FFA with ethanol over heterogenous catalyst was not studied as extensively as methanol. Most of the studies is about homogenous catalyst like sulfuric acid as it was tabulated in Table 1. For example, Marchetti et al. studied conversion of mixture of sunflower and Oleic acid corresponding to 10wt.% FFA to FAEE by using ethanol in the presence of sulfuric acid as a catalyst (Marchetti and Errazu 2008). They obtained 95% and 96% conversion by using 2.1 wt. % and 5.14 wt.% sulfuric acid at 45°C and 55°C, respectively. This may reveal that equilibrium conversion is close to %95 at 6:1 alcohol to FFA and 45-55°C. Therefore, after 200 minutes, conversion of FFA is not significantly changed. However, if FFA content increases, equilibrium conversion can be enhanced due to increase in the concentration of reactant. Also, at the end of esterification reaction, water was formed, resulting in hydrolysis of oil in acidic medium. Therefore, it should be controlled. Marchetti et al. carried out similar study about conversion of mixture of sunflower oil and oleic acid which is 10.624% FFA content (Marchetti, Pedernera, and Schbib 2011). They obtained 96% conversion of FFA by using 2.261 wt.% sulfuric acid and 6.125 alcohol to FFA at 55°C. It also proves that sulfuric acid as homogenous catalyst is quite active for this reaction. Finally, Murad et al. conducted similar study on conversion of 40 wt.% FFA content, but they used lower catalyst amount and higher temperature than previously studies, indicating that temperature is 70°C and catalyst amount (sulfuric acid) is 0.33 wt.%. This study reveals that when catalyst amount is reduced, temperature should be increased to reach similar conversion (Murad et al. 2018).

Table 1. Studies about esterification of FFA with ethanol using homogenous catalyst

Substrate	FFA content (%)	Temperature (°C)	EtOH: FFA	Reaction Duration (min)	Conversion (%)	Ref
Sunflower oil and Oleic Acid	10	55	6.1:1	180	95	(Marchetti and Errazu 2008)
Sunflower oil and Oleic Acid	10	45	6.1:1	180	96	(Marchetti and Errazu 2008)
Soybean Oil and Lauric Acid	40	70	9:1	200	89	(Marchetti, Pedernera, and Schbib 2011)
Sunflower oil and Oleic Acid	10.7	55	6.125:1	200	96	(Murad et al. 2018)

2.2. Esterification of FFA with ethanol by using heterogenous catalyst

There are several studies on esterification of FFA with ethanol over heterogenous catalyst as seen in Table 2. For instance, Kaur et al. carried out study on conversion of pure oleic acid to FAEE over Ce/ZrO₂-TiO₂/SO₄, revealing that conversion of oleic acid is higher than 98% for 80 minutes at conditions including 75°C, 6:1 alcohol to FFA ratio and catalyst amount as 5wt.% (Kaur and Ali 2015). However, they did not try whether any substance leaching out from heterogenous catalyst can catalyzed or not. Therefore, it may be homogenous catalyzed. Another study by Cordeiro et al. reveals that catalyst produced by them reaches 23.1% conversion by using mixture of palm oil and oleic acid (Cordeiro et al. 2008). This was achieved for 2 hours at 100°C by using 2wt.% catalyst amount, 6:1 alcohol to FFA ratio. Another study by Hykkerud et al. demonstrated that conversion of oleic acid with 90% purity is 34% at 75°C for 3 hours by using Amberlyst 15 while operating conditions including alcohol to FFA ratio and catalyst amount were set as 6:1 and 20%, respectively (Hykkerud and Marchetti 2016). Also, this study reveals that as ethanol to FFA ratio increases from 1:1 to 1:12, conversion of FFA decreases,

resulting in that 1:1 ethanol to FFA ratio gives the highest conversion as 42%. Alvarez et al. reveals that sulfated alumina catalysts produced by using different sulfate precursor including $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , NiSO_4 reaches 40%, 28%, respectively (Álvarez et al. 2009). Sulfated Al_2O_3 catalyst may have $\text{Al}_2(\text{SO}_4)_3$ phase, facilitating the Bronsted Acid as can be seen in Figure 10. However, alumina calcined at 700°C may leach out aluminum sulfate, facilitating the catalytic activity as homogenous catalyst. Results may be attributed to acidity or acidic strength of catalysts. All studies about esterification reaction over heterogenous acidic catalyst did not investigate particle size distribution. However, it may affect significantly.

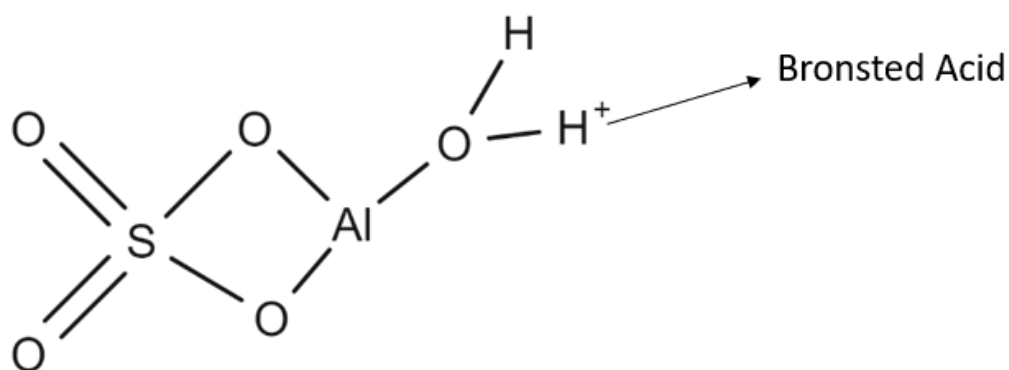


Figure 10. Bronsted acid in sulfated alumina
(Source: Álvarez et al. 2009)

Table 2. Studies about esterification of FFA with ethanol using heterogenous catalyst

Catalyst/Ref	Substrate	Temperature (°C)	EtOH: FFA	Time (h)	Conversion (%)
Ce/ZrO ₂ -TiO ₂ /SO ₄ (Kaur and Ali 2015)	Pure Oleic Acid	75	6:1	1.33	>98
(Zn ₅ (OH) ₈ (NO ₃) ₂ ·2H ₂ O) (Cordeiro et al. 2008)	Palm Oil and Lauric Acid	100	6:1	2	23.1
Amberlyst 15 (Hykkerud and Marchetti 2016)	90% Oleic Acid	75	6:1	3	34
Al ₂ O ₃ /(NH ₄) ₂ SO ₄ (Álvarez et al. 2009)	Pure Oleic Acid	86	10:1	3	40
Al ₂ O ₃ /H ₂ SO ₄ (Álvarez et al. 2009)	Pure Oleic Acid	86	10:1	3	28
Al ₂ O ₃ /NiSO ₄ (Álvarez et al. 2009)	Pure Oleic Acid	86	10:1	3	31

2.3. Esterification of FFA with methanol by using heterogenous catalyst

Resende et al. reveals that HZSM-5 has low activity to convert oleic acid to methyl ester, which is approximately 35% at 100°C for 10:1 alcohol to oleic acid. On the other hand, conversion of oleic acid was increased from 35% to 100% when sulfated La₂O₃ was added to the HZSM-5. The addition of sulfated La₂O₃ to HZSM shows 100% conversion until 15wt.% composition of sulfated La₂O₃. Higher than 15wt.% composition decreased conversion from 100% to 51%. Besides, concentration of Bronsted acid and Lewis acid sites was determined by adsorption of Pyridine and Collidine. Although HZSM-5 has high concentrations of Bronsted acid, it has lowest conversion among other catalysts including sulfated La₂O₃. This may be caused by acidic strengths of catalysts. Also, reusability test was performed three times by authors, demonstrating absence of any activity loss (Resende et al. 2020). Chiang et al. reveals that conversion of FFA was 59% by using sulfated ZrO₂/Al₂O₃ catalyst calcined at 700°C and 20:1 methanol to oil ratio was set. However, conversion of FFA increased to 78% as calcination temperature decreased. This may be caused by leaching out from catalyst,

leading to behaving as homogenous catalyst (Chiang et al. 2020). Another study by Chung et al. shows that different zeolites, including H-beta, H-faujasite, Na type-MFI and MOR with different pretreatments, take place esterification reaction. The activity of different zeolites was attributed to the acidity of zeolites. However, it was not matched. Although acidity of MOR zeolite was significantly higher than MFI zeolite, conversion of FFA was not changed significantly. Therefore, it may be attributed to acidic strength, thus determining turnover frequency which demonstrates genuine activity of catalysts (Chung, Chang, and Park 2008). Srilatha et al. shows that 12-tungstophosphoric acid (TPA) supported on niobium oxide was used to take place esterification reaction. Activity of the prepared catalysts decreased as calcination temperature increased, arising from that homogenous catalyst can be utilized for esterification reaction. Therefore, whether substance leaching out from the prepared catalyst can be catalyzed for esterification reaction or not should be controlled. As calcination temperature increases, sintering also increases, leading to becoming difficulty in leaching out and removing the impurities (Srilatha et al. 2009).

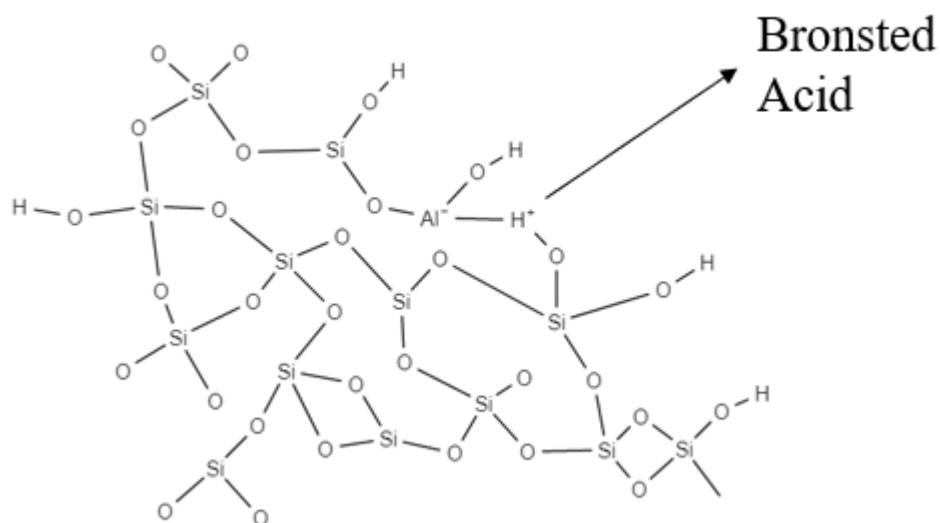


Figure 11. Bronsted acid on the $\text{Al}_2\text{O}_3/\text{SiO}_2$

(Source: “Studies in Surface Science and Catalysis 51 NEW SOLID ACIDS AND BASES Their Catalytic Properties,” n.d.)

2.4. Al₂O₃/SiO₂ catalyst

One of the most known acidic catalysts is Al₂O₃/SiO₂ catalyst, possessing high acidity. It has both Lewis and Bronsted acid sites. Bronsted acids in Al₂O₃/SiO₂ catalyst was shown in Figure 11, facilitating H⁺ donor. Also, when composition of silica was increased from 0 to 85, amount of Bronsted acid site was increased. Composition of silica with higher than 85% decreases amount of Bronsted acid site. However, it depends on preparation of catalysts since Lewis acid sites can be slightly converted to Bronsted acid after treatment of catalyst with water (“Studies in Surface Science and Catalysis 51 NEW SOLID ACIDS AND BASES Their Catalytic Properties,” n.d.). Also, pure Al₂O₃ has also Bronsted acid after water treatment, initiating carbonium ion reactions (Richardson James T., n.d.). Therefore, it can be used for esterification reaction.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Silica-alumina ($\text{SiO}_2 / \text{Al}_2\text{O}_3$) catalysts with different compositions which are 20/80 wt.%, 50/50 wt.%, 80/20 wt.% were synthesized by the modified single step sol-gel method for esterification reaction. Aluminum isopropoxide (AIP, Sigma-Aldrich) was used as a precursor, deionized water (DIW) was used as a solvent and sulfuric acid (H_2SO_4 , VWR Chemicals) was used as a peptizer in the alumina synthesis. For silica, tetraethyl orthosilicate (TEOS, Fluka) was used as a precursor, ethanol (EtOH, Sigma-Aldrich), and deionized water (DIW) were used as a solvent, and hydrochloric acid (HCl) was used as a peptizer. Also, $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst as base catalyst for transesterification reaction was produced by using Calcium nitrate tetrahydrate (Fluka R Analytical) with a purity of 99.3%. Nitric acid (HNO_3 , VWR Chemicals) was used as peptizer in the alumina synthesis for $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst.

3.2. Preparation of $\text{Al}_2\text{O}_3/\text{SiO}_2$ Catalyst

The required aluminum isopropoxide (AIP) as alumina precursor and deionized water (DIW) were added to a Schott bottle at 85°C for 1 hour under constant stirring at 950 rpm to take place hydrolysis reaction. After 1 hour, the required amount of H_2SO_4 was added to the Schott bottle and the mixture was again continued to be stirring for 1 hour at 85°C . Meanwhile, the required tetraethyl orthosilicate (TEOS) as silica precursor, DIW and ethanol (EtOH), and peptizer HCl were put into another Schott bottle at the same time and mixed for 1 hour at 75°C under constant stirring at 950 rpm. After 1 hour, the alumina sol and the silica sol were produced and they were mixed and continued to be stirred at 85°C for 1 hour. After the end of mixing period, the mixture was left for gelation at 70°C without stirring to evaporate solvents. Then, the obtained soft gel was left in the dryer at 120°C for overnight and the solvents was completely evaporated, followed by calcination at 900°C for 6 hours with $10^\circ\text{C}/\text{min}$ heating rate under atmospheric conditions. Finally, the calcined catalysts were put to ball milling for 3 hours

to increase surface area of catalyst. $\text{SiO}_2 / \text{Al}_2\text{O}_3$ catalysts were produced for 3 different compositions (20/80 wt.%, 50/50 wt.%, 80/20 wt.%).

3.3. Preparation of $\text{CaO}/\text{Al}_2\text{O}_3$ Catalyst

$\text{CaO}/\text{Al}_2\text{O}_3$ catalyst was chosen to carry out transesterification reaction since previous experiments in our research group proved that $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst has high activity with methanol, ethanol and butanol. Therefore, 60 wt% $\text{CaO}/40\text{wt}\%\text{Al}_2\text{O}_3$ catalyst were produced in this study.

The sol-gel method was used to produce 60 wt% $\text{CaO}/40\text{wt}\%\text{Al}_2\text{O}_3$ catalyst. The first step is that the required amount of AIP has dissolved in the required amount of water at 85°C at 950 rpm for 1 hour in a Schott bottle. In the end of 1 hour, the required amount of nitric acid was put in the mixture of AIP and water. After 1 hour, the required amount of calcium nitrate tetrahydrate was dissolved in the required water. Then, it was added to the mixture. At the end of 1 hour, sol obtained from the previously procedure was left for gelation at 70°C without stirring to remove solvent like excess amount of water. After gel was formed, it has dried at 120°C for 15 hours. Then, catalysts were calcined at 700°C to remove impurities. After that, the calcined catalysts were put to ball milling for 3 hours to increase surface area of the catalyst.

3.4. Catalysts Characterization

3.4.1. Temperature Programmed Desorption

Esterification reaction takes place over acidic catalysts. Temperature Programmed Desorption (TPD) as a chemisorption analysis equipped with Micromeritics AutoChem II 2920 was performed to determine the total amount of acidic sites and acidic strength of the catalysts by using ammonia (NH_3) as a probe base molecule. NH_3 adsorbed on the acidic sites of the catalyst surface is desorbed from the catalyst by increasing temperature, resulting in that amount of NH_3 desorbed from acidic sites of catalyst reveals total acidity and the peaks of signals reveals acidic strengths. Initially, the catalysts are activated by heating up to 700°C with a heating rate of 15°C/min for 40 minutes. Then, the system is cooled to 55°C. At this temperature, adsorption is conducted on

approximately 100 mg of fresh catalyst at a flow rate of 30 cm³ /min of NH₃-He flow for 2 hours. Afterward, desorption originates under He gas flow at a rate of 70 cm³ /min with temperature increasing up to 700°C for 90 minutes. When the chemical bonds between the adsorbent and the adsorbate are broken due to heat, the desorbed molecules enter the He stream and are swept into the detector measuring the gas concentration by considering thermal conductivity. The acidity and acidic strength of the catalysts are determined by processing data containing the signals coming out of the detector, time and temperature values.

3.4.2. X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis was carried out at 40 kV and 45 mA to determine crystalline phases of catalyst. In order to calculate the average crystalline sizes by using the peak broadening of the diffraction peaks, Scherrer equation as seen below was used. The average crystalline size corresponds to d in the formula below while K and λ correspond to Scherrer constant and wavelength, respectively. λ is equal to 0.15406 nm. Also, B is the peak broadening of diffraction peak.

$$d = \frac{K\lambda}{(B \cos \theta)}$$

3.5. Pretreatment of Waste Cooking Oil (WCO)

WCO was filtered to separate residual contaminants including food residuals. Then, it was washed with certain amount of deionized water to remove salt in the oil. The mixture of deionized water and WCO was centrifuged at 8000 rpm at 25°C. Two phase was obtained as upper phase containing WCO and bottom phase containing salty water. Electrical conductivity of salty water was measured until electrical conductivity of the used deionized water becomes close to electrical conductivity of pure deionized water.

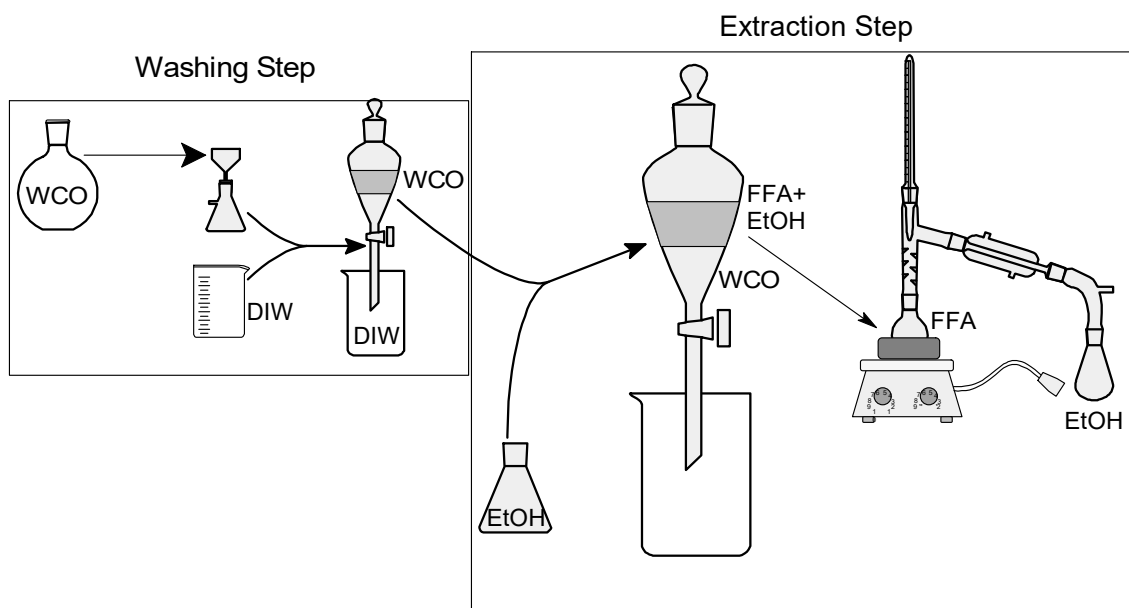


Figure 12. Pretreatment of WCO and extraction of FFA

3.6. FFA Extraction from Waste Cooking Oil (WCO)

WCO is obtained from restaurant in the IZTECH campus. FFA was extracted from WCO by using ethanol. Ethanol was used to not be contaminated by other alcohols including methanol. The certain amount of WCO and ethanol was mixed for 30 minutes. Then, it was centrifuged at 6000 rpm at 25°C for 10 minutes. Two phase was obtained as mixture of ethanol and FFA upper phase and WCO bottom phase. Upper phase was taken and ethanol was evaporated from the mixture of ethanol and FFA by using rotary evaporator at 50°C under vacuum. Then, FFA was obtained from the WCO.

3.7. Catalyst Activity Test

Catalyst activity was tested by carrying out the esterification reaction of FFA obtained from the WCO with ethanol to obtain FAEE in a batch reactor for 3 hours at different temperatures including 80°C, 100°C and 120°C. Alcohol to lipid ratio and stirring rate was kept constant as 15:1 and 1100 rpm. Also, catalyst weight percentages with respect to mass of FFA were 10%, 15% and 20%.

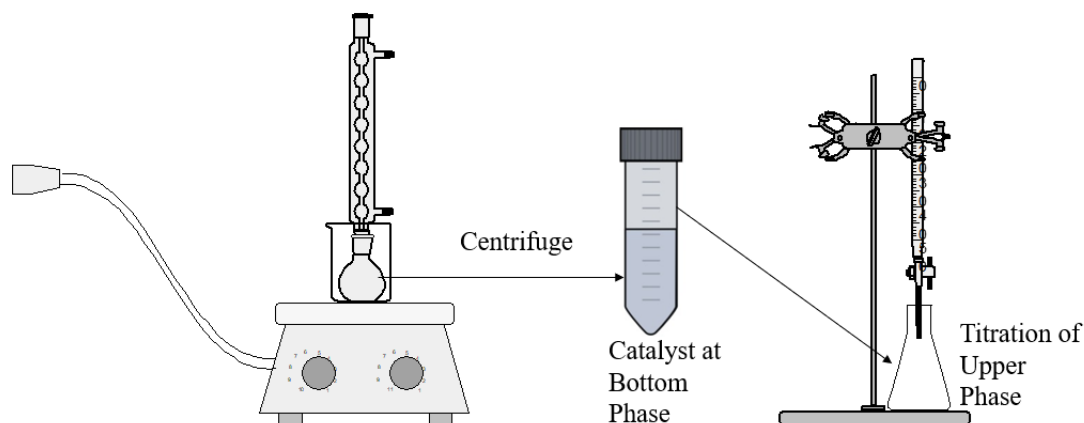


Figure 13. Representation of catalysts tests

Firstly, the previously prepared solid acid catalyst prior to reaction was dried in the batch reactor for 1 hour to remove moisture from the catalyst at 120°C. Then, FFA was added to the batch reactor, followed by adding certain amount of ethanol. The reactor was placed in the oil bath at certain temperatures including 80°C, 100°C and 120°C at 1100 rpm. After reaction duration was completed, the sample in the reactor was centrifuged at 8000 rpm at 25°C for 15 minutes to remove solid catalyst from reaction medium. At the end of centrifuge, two phases were obtained. Upper phase consisted of FAEE, FFA and ethanol owing to miscibility of each chemical while bottom phase consisted of solid catalyst. Upper phase was titrated by using NaOH solution with 0.25 Molar to determine the conversion of FFA to FAEE. Conversion was determined by titration method. Also, error percentage of conversion and titration were calculated as 10.7% and 7.6%, respectively.

$$\text{Conversion of FFA} = \frac{\text{Total initial FFA moles} - \text{Final Total FFA moles}}{\text{Total initial FFA moles}}$$

3.7.1. Esterification Reaction of Model WCO

Mixture of canola oil and FFA obtained from waste cooking oil was used to constitute model of waste cooking oil. To get waste cooking oil with 20wt.% FFA, the required amount of FFA was added to certain amount of canola oil. Then, acidic catalyst was used to perform esterification reaction by using 15:1 ethanol to FFA ratio at 80°C.

3.8. Box Behnken Design for Statistical Analysis

In normal conditions, multiple experiments should be conducted to understand the relationship between a variable and its response on the experiments, which is called as factorial experimental design. However, it can be overcome with less experiment by using Box Behnken design, facilitating time and cost effectiveness. This method enables us to determine the relationship between multiple variables and their effects on the experimental response statistically. Box-Behnken experimental design is one of response surface methodologies. Each factor was coded as -1, 0, +1. Center points were used while analyzing experiments. Since center points of experimental results are used effectively, number of experiments is decreased, enabling screening the experimental results. Thus, significant parameters can be determined, resulting in ability to focusing other parameters or proceeding experiments in detail. Also, confidence interval was selected as 95% and double tails.

CHAPTER 4

RESULTS AND DISCUSSION

FAEE production over $\text{Al}_2\text{O}_3/\text{SiO}_2$ catalysts was studied by changing the reaction temperature and catalyst weight percentage. Liquid product was characterized by GC-MS and conversion of FFA was calculated by considering the titration. The prepared catalysts were characterized by TPD and XRD to determine acidity/acidic strength and crystalline size.

4.1. Analysis of Variance Studies for Conversion of FFA

In order to determine the significance of parameters studied in the experiments, ANOVA test was carried out for experiment set with confidence interval value set as 95%. Table 3 gives ANOVA test results. P-value is a key parameter to investigate whether any parameter affects the response or not. Parameters possessing lower p-values ($p < 0.05$) indicate strong interactions between the parameter and response. Parameters possessing higher p-values ($p > 0.05$) should be excluded from the empirical model due to the fact that interactions between the parameters and response does not have significant relationship. As can be seen in Table 3, reaction temperature and catalyst weight percentage have p-values of 0.922 and 0.291, respectively, making them insignificant. Thus, the most important parameter used in the experiment set becomes compositions of $\text{Al}_2\text{O}_3/\text{SiO}_2$. Catalyst weight percentage was found to be insignificant since catalyst powder may probably be agglomerated in the reaction medium, resulting in decrease in surface area of catalyst. From our fundamental knowledge, the relationship between catalyst weight and reaction rate may show concave down which second derivative is smaller than 0. In other words, conversion increases rapidly up to certain catalyst weight. Thus, the catalysts weight may increase, but conversion may not be increased significantly. Finally, conversion appears remaining constant. The range of catalyst weight percentage studied in this thesis may be linear relationship. Therefore, conversion and catalyst weight percentage show linear relationship. If catalyst weight percentage can be studied in the range of 2 and 10%, thereby facilitating significant parameter in this case. Besides, temperature was found to be insignificant. However, it should affect the

conversion of FFA. It may be caused by bubbling of ethanol at higher temperatures than its boiling point. FFA and ethanol cannot be come in contact with catalyst at the same time. Temperature (120°C) may also affect reverse reaction which is hydrolysis of ester. Therefore, it can be insignificant parameter for esterification reaction at these conditions. Also, residual plots for conversion were controlled to demonstrate whether residuals are normally distributed or not as can be seen in Figure A.1. Apart from the residual plots, main effects for conversion of FFA graph were seen in Figure A.2.

The most promising composition was seen as 80%Al₂O₃/20%SiO₂ catalyst. It has highest conversion as seen in the Figure 14. When Al₂O₃ composition increases, conversion of FFA also is increased. Therefore, model WCO of simultaneous esterification and transesterification reactions were catalyzed by considering these conditions.

Table 3. Results of ANOVA

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	0.04331	0.004812	1.6	0.261
Linear	3	0.029855	0.009952	3.3	0.079
Temperature	1	0.000031	0.000031	0.01	0.922
Alumina/Silica	1	0.025979	0.025979	8.62	0.019
Catalyst Weight Percent	1	0.003846	0.003846	1.28	0.291
Square	3	0.00858	0.00286	0.95	0.462
Temperature*Temperature	1	0.000331	0.000331	0.11	0.749
Alumina/Silica*Alumina/Silica	1	0.002339	0.002339	0.78	0.404
Catalyst Weight Percent*Catalyst Weight Percent	1	0.006665	0.006665	2.21	0.175
2-Way Interaction	3	0.004874	0.001625	0.54	0.669
Temperature*Alumina/Silica	1	0.00346	0.00346	1.15	0.315
Temperature*Catalyst Weight Percent	1	0.000062	0.000062	0.02	0.889
Alumina/Silica*Catalyst Weight Percent	1	0.001352	0.001352	0.45	0.522
Error	8	0.024114	0.003014		
Lack-of-Fit	3	0.00912	0.00304	1.01	0.46
Pure Error	5	0.014994	0.002999		
Total	17	0.067424			

Table 4. Results of experiments

	Reaction Temperature (°C)	Alumina/Silica (%/%)	Catalyst Weight Percent (%)	Conversion (%)
Exp1	100	80/20	20	34±3.6
Exp2	120	80/20	15	32±3.5
Exp3	80	50/50	10	16±1.7
Exp4	120	20/80	15	16±1.7
Exp5	100	20/80	10	15±1.6
Exp6	100	50/50	15	29±3.1
Exp7	120	50/50	20	25±2.7
Exp8	100	50/50	15	22±2.4
Exp9	100	50/50	15	21±2.2
Exp10	80	80/20	15	32±3.5
Exp11	100	20/80	20	18±1.9
Exp12	100	50/50	15	32±3.5
Exp13	100	50/50	15	19±2
Exp14	80	20/80	15	28±3
Exp15	80	50/50	20	19±2
Exp16	100	50/50	15	21±2.2
Exp17	100	80/20	10	24±2.5
Exp18	120	50/50	10	24±2.5

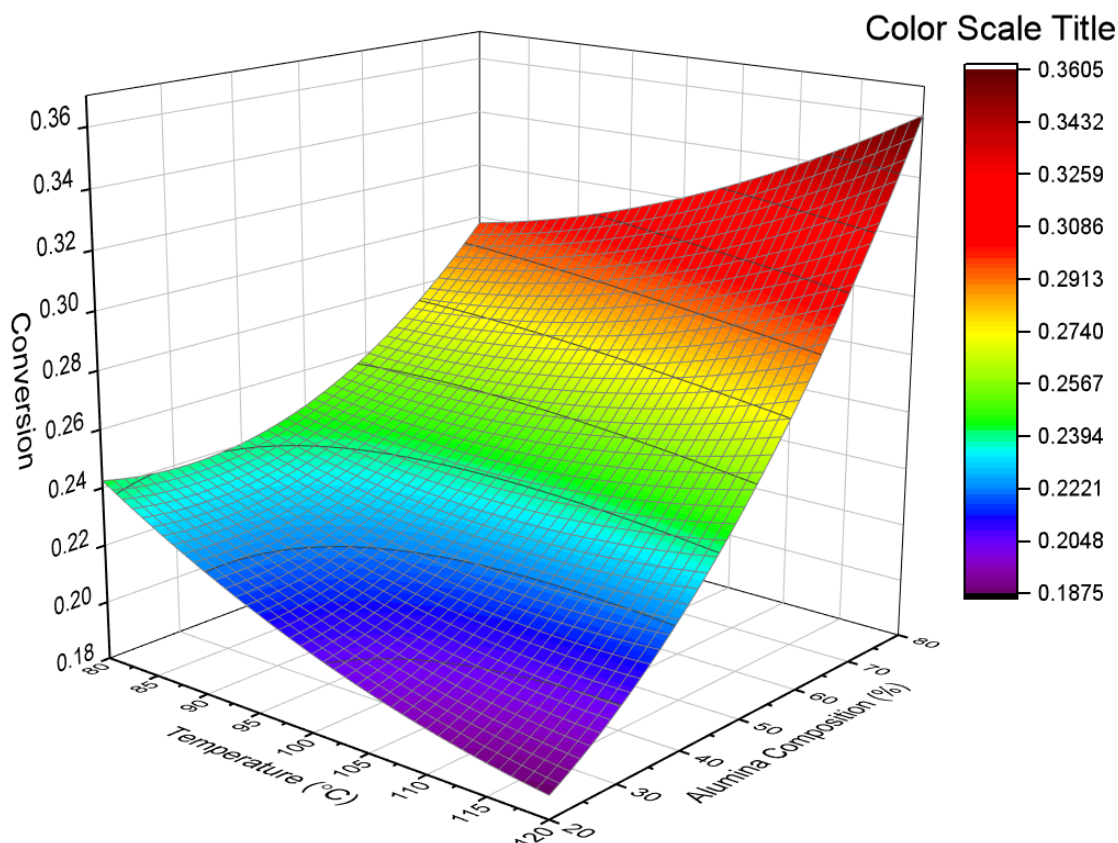


Figure 14. Behavior of conversion of FFA at constant catalyst weight percentage (15%)

Conversion of FFA increases significantly as alumina composition in alumina/silica catalyst increases as can be seen in Figure 14. Conversion of FFA decreases as temperature increases from 80°C to 120°C for alumina composition set as 20%. However, conversion of FFA increases slightly as both of alumina composition and temperature increases. Although regression of fit is low as 68%, behavior of response was plotted to observe behavior of responses since there is not data enough to simplify model. Therefore, any model was not suggested in this thesis.

Conversion of FFA increases as catalyst weight percentage increases for 80% alumina composition as can be seen in Figure 15. Conversion of FFA increased as catalyst weight percentage increased from 10% to 15%, which may be said that it is statistically increasing. However, when catalyst weight percentage increased from 15% to 20%, it can be said that conversion of FFA remained constant. If catalyst weight percentage levels were selected as 5%, 10% and 15%, then it would be seen that it is a significant parameter statistically.

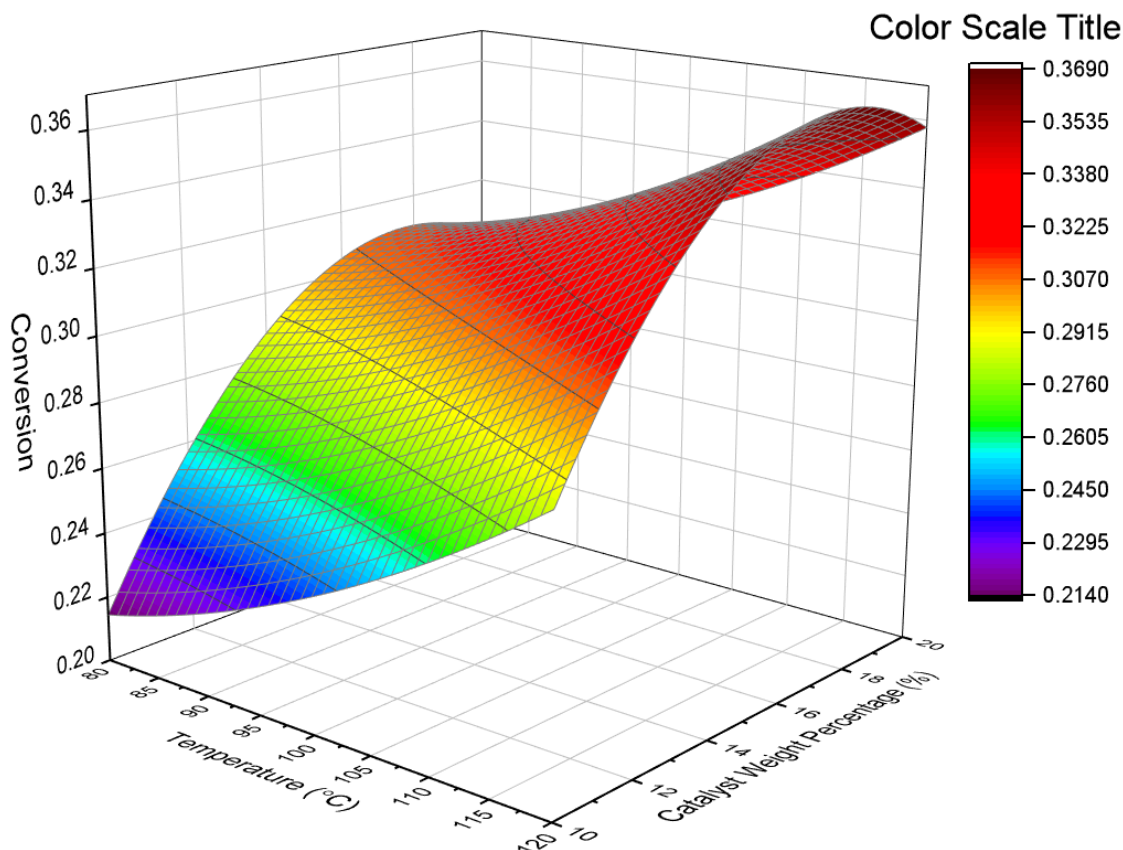


Figure 15. Behavior of conversion of FFA at constant Al₂O₃ composition (80%)

4.2. Results of Additional Experiments

When alcohol to FFA ratio was reduced from 15:1 to 6:1, conversion of FFA increased, resulting from that concentration of ethanol may affect the reaction rate. That is, concentration of ethanol can be denominator at reaction rate expression. This phenomenon was encountered in the literature survey, indicating that alcohol to FFA ratio affects reversely. This depends on catalyst owing to dependency of reaction rate on catalyst type. Also, this result reveals that separation of excess alcohol could be cost effective.

Whether substance leaching out from catalyst, including aluminum sulfate, behaves homogenous catalyst or not was controlled to set up new experimental procedure. It was found not to take place esterification reaction for homogenous catalytic activity. Conversion of canola oil with 20% FFA was found as 11% at same conditions with highest conversion of pure FFA as 33%, resulting from mass transfer limitations. Also, concentration of FFA was reduced, resulting in decrease in reaction rate. That is,

canola oil may behave inert. This hypothesis was demonstrated that canola oil and maximum water which can be obtained from the esterification reaction was performed with prepared acidic catalyst to understand whether hydrolysis of oil takes place or not. It was seen that hydrolysis of oil does not take place at 80°C.

4.3. Control of Homogenous Reaction

After pure FFA was titrated by using NaOH solution, FFA and ethanol was mixed and heated up 80°C and 120°C for 3 hours, revealing that volumes of 0.25 M NaOH solution used in titration part are 3.05 ml and 3 ml, respectively. As can be seen in Figure 16, they have no statistically difference, indicating that there is no conversion of FFA statistically. Also, ICP-OES analysis was used to determine amount of aluminum of leaching out from heterogenous catalyst, indicating that 8 ppm aluminum was leached out from the catalyst. This amount of aluminum did not show catalytic activity.

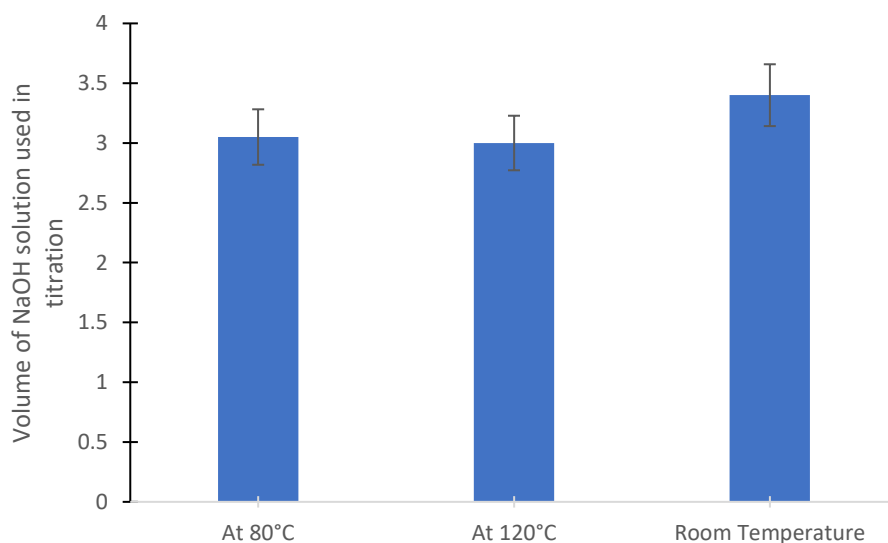


Figure 16. Control of homogenous reaction

4.4. Effect of Alcohol to FFA Ratio on Conversion of FFA

After screening effect of reaction temperature, alumina composition and catalyst weight percentage, alcohol to FFA ratio was investigated as can be seen in Figure 17. Results reveal that conversion of FFA was increased from 32% to 41% as ethanol to FFA ratio decreased. It may be caused by increment of concentration of FFA. Conversion of

FFA was increased from 32% to 38% as ethanol to FFA ratio was decreased from 15:1 to 6:1, which has no statistically difference. However, it was increased from 32% to 41% as ethanol to FFA ratio was decreased from 15:1 to 2:1, which has statistically difference. Besides, conversion of FFA with esterification reaction taking place at 120°C was increased from 32% to 44% as ethanol to FFA ratio was reduced from 15:1 to 6:1, which has statistically difference. This may also be caused by increase in the concentration of FFA, which may indicate that reaction rate is proportional to concentration of FFA. One of the reasons may be that ethanol behaves as a common solvent to increase the miscibility of mixture of products like water and ester since mixture of water and ethyl ester is lowly miscible.

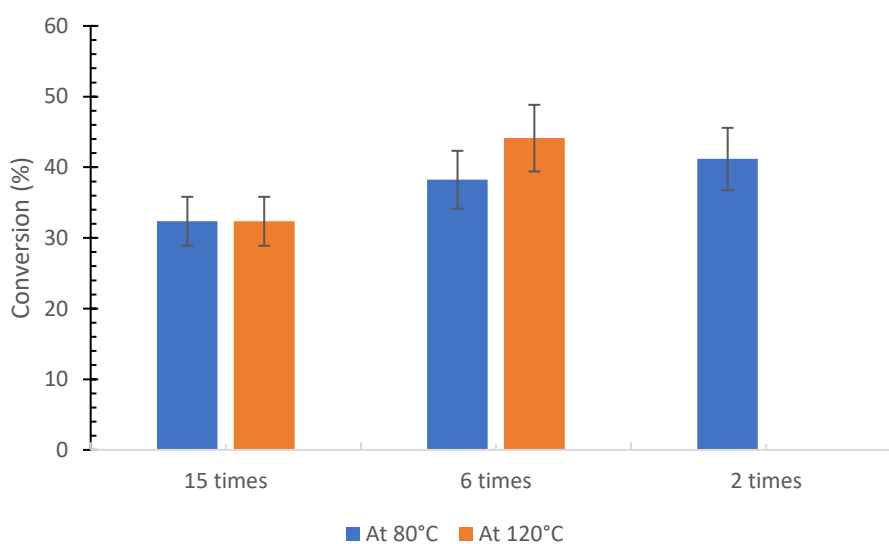


Figure 17. Effect of alcohol to FFA ratio on conversion of FFA

4.5. Temperature Programming Desorption

Table 5. TPD results of catalysts used in this study

Catalyst	Maximum Desorption Temperature(°C)	Acidity ($\mu\text{mol NH}_3/\text{g catalyst}$)	Peak Width of NH_3 Desorbed (°C)
80wt.%Al₂O₃/20wt.%SiO₂	246	511.72	75-527
	540		519-605
	679		642-681
50wt.%Al₂O₃/50wt.%SiO₂	245	747.62	88-579
	683		591-684
20wt.%Al₂O₃/80wt.%SiO₂	176	421.28	65-492
	677		522-677

Table 5 shows the results of TPD of catalysts. All prepared catalysts have both weak and strong acid sites. 50/50 Al₂O₃/SiO₂ catalyst has highest acidity, but present acid sites cannot have catalytic activity to take place esterification reaction. For this reason, acidic strength can be considered by comparing the catalytic activity. If acidic strength is high, this can lead to strong adsorption, resulting in inability to take place reaction. If acidic strength is low, this causes weak adsorption, bringing about that there is enough time to take place reaction. Of all catalyst compositions, 80/20 Al₂O₃/SiO₂ catalyst has highest conversion. It may be caused by medium acidic strength as maximum peak temperature (540°C). The peak width of NH₃ desorbed of 80/20 Al₂O₃/SiO₂ catalyst has range of 519-605, facilitating the more active sites. This means that if this active site can be increased, turnover frequency may be increased for esterification reactions. On the other hand, 20/80 Al₂O₃/SiO₂ catalyst have lowest acidity among the prepared catalysts and has weaker acidic strength, not making available to undergo esterification reaction. Also, TPD graphs can be seen in Figure A.3-A.5.

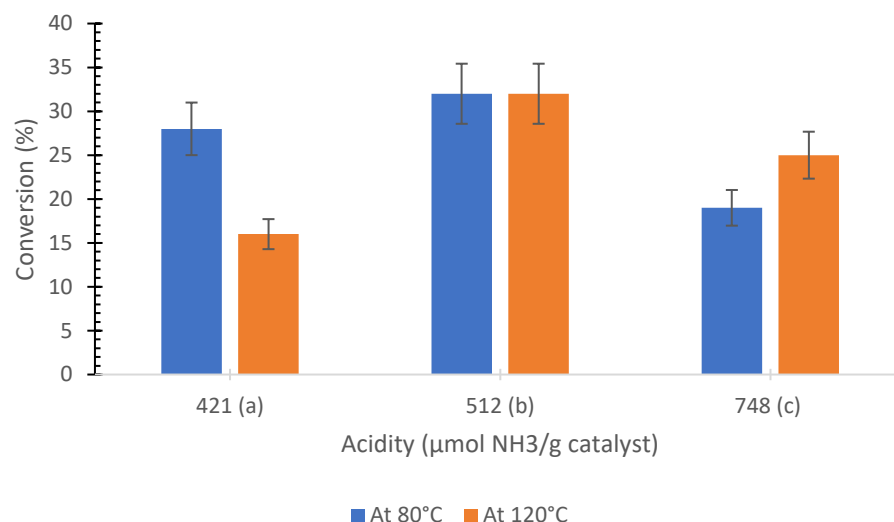


Figure 18. Volcano curve for FFA conversion (%) as a function of acidity (a) 20%Al₂O₃/80%SiO₂ (b) 50%Al₂O₃/50%SiO₂ (c) 80%Al₂O₃/20%SiO₂

Figure 18 shows the volcano curve for FFA conversion as a function of the acidity of the prepared catalysts. The graph demonstrates that there is no correlation between acidity and conversion of FFA. As mentioned before, acidic strength may be more significant than acidity. Also, conversion of FFA by using catalyst with low acidity decreases as temperature increases, which may result from acidic strength at 176°C. That is, it may possess activity for esterification. However, reactant may be desorbed from the catalyst without completing reaction when reaction temperature increases from 80°C to 120°C. Conversion of FFA by using catalyst with medium acidity remains constant as reaction temperature increases, which may originate from the acidic strength at 246°C. Synergetic effect of acidic strengths at 246°C and 540°C may be more effective to take place esterification reaction. As reaction temperature increases from 80°C to 120°C, activity of acidic strength at 246°C may be decreased due to desorption of reactant from catalyst. Therefore, activity of the catalyst may remain constant. On the other hand, conversion of FFA by using the catalyst with highest acidity is lower than other catalysts and conversion of FFA increases as reaction temperature increases, which may arise from the lowness of acidic strength at lower temperatures since the prepared catalysts have heterogenous surface including different acidic strength. Therefore, reactant may not be desorbed as reaction temperature increases, resulting in higher conversion at higher temperature.

4.6. X-Ray Diffraction Analysis

The crystalline phase and average thickness of the crystalline were determined by using X-Ray Diffractometer to understand the reasons of differences of catalytic activity of catalysts. The crystalline phases in the catalysts were determined by using Powder Diffraction File of International Centre for Diffraction Data (JCPDS-ICDD 2000).

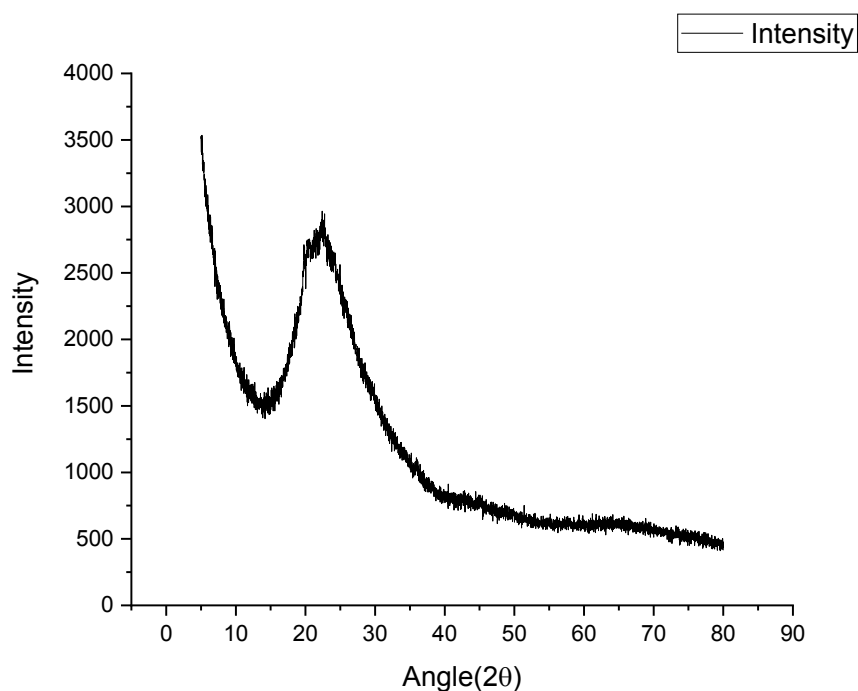


Figure 19. X-Ray Diffraction spectra of 80% SiO₂/20% Al₂O₃

XRD graph as seen in Figure 19 demonstrates amorph structure. However, pattern of intensity could be parallel to the SiO₂ crystal since XRD graph shows broad peak at 21.984°. Therefore, SiO₂ phase can be occurred in the catalysts, but it has amorph structure. This catalyst may have Al₂O₃, Al₂(SO₄)₃ and aluminum silicate phases, but crystal sizes of these phases may be smaller than 3-5 nm which is below detection limit for XRD (Cullity 1978). SiO₂ phase may hinder growth of these crystals.

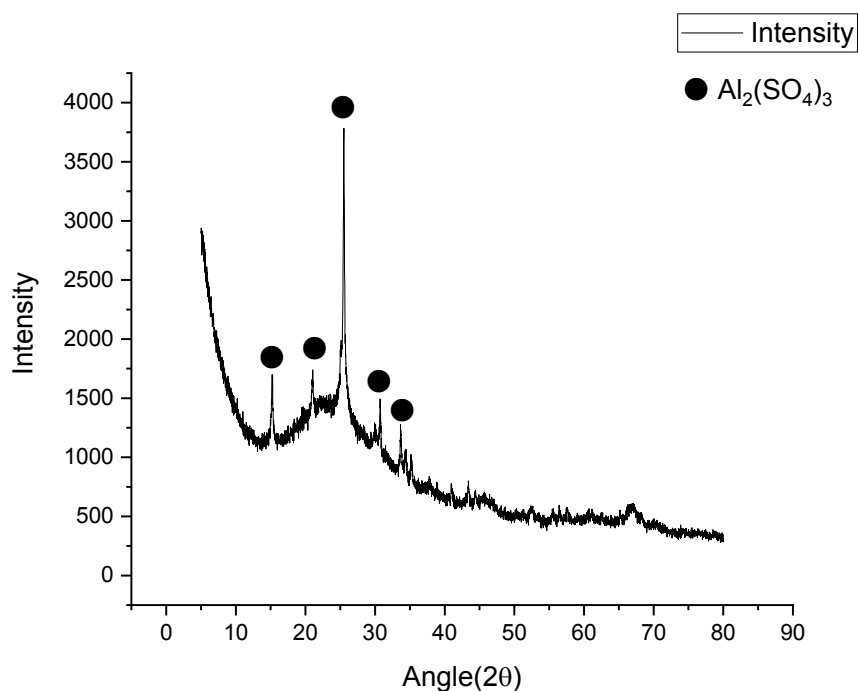


Figure 20. X-Ray Diffraction spectra of 50% SiO₂/50% Al₂O₃

Diffraction peaks of Al₂(SO₄)₃ corresponds to 15.2°, 21°, 25.4°, 30.6°, 33.7°. Al₂(SO₄)₃ phase occurred when composition of Al₂O₃ increased from 20% to 50% as seen in Figure 20, which may result from presence of SiO₂. In other words, decomposition temperature of Al₂(SO₄)₃ is approximately 770°C thermodynamically. However, it is kinetically controlled due to presence of SiO₂. Non-crystal phase may be still in the catalyst. This may lead to more catalytic activity. Besides, the crystallite size of Al₂(SO₄)₃ was calculated as 40 nm, which may result in more stable than lower crystallite size, thereby decreasing the catalytic activity.

The diffraction peaks of 32°, 37.7°, 45.9°, 60.8° and 66.9° are corresponding to η-Al₂O₃. When composition of Al₂O₃ increased from 50% to 80%, Al₂(SO₄)₃ is not observed as seen in Figure 21, which may result from the decomposition of Al₂(SO₄)₃. However, crystals with lower than 3-5 nm may be present. To determine the crystals with lower than 3-5 nm, low-angle XRD can be deployed (Cullity 1978). Besides, the average crystallite size of η-Al₂O₃ was calculated as 6 nm. This catalyst as shown in Figure 22 has highest activity among the prepared catalysts, which may arise from nonstable phase of Al₂(SO₄)₃. It should possess alumina-silicate, facilitating Bronsted acid. Regardless of alumina-silicate phase, Al₂(SO₄)₃ may be more active site. Also, alumina-silicate phase and aluminum sulfate phase have a synergetic effect on esterification reactions. In other

words, additional activity may be generated from small crystalline of aluminum sulfate growth in the catalyst.

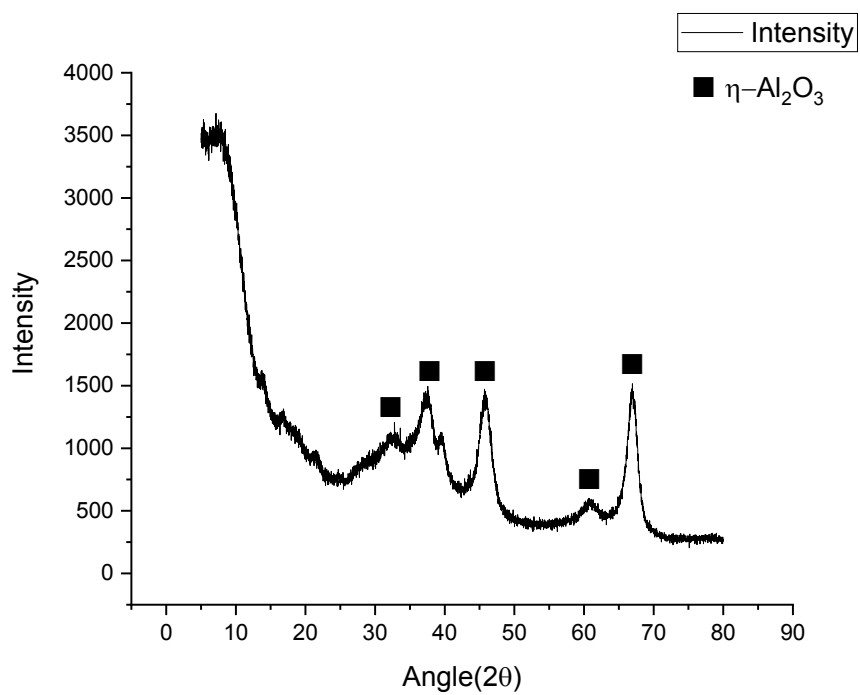


Figure 21. X-Ray Diffraction spectra of 20% SiO₂/ 80% Al₂O₃

CHAPTER 5

CONCLUSION

In this study, heterogenous $\text{Al}_2\text{O}_3/\text{SiO}_2$ catalyst with different compositions was used to undergo esterification reactions at different temperatures including 80°C , 100°C and 120°C . Experimental design was applied to the study to investigate effects of reaction temperature, composition of Al_2O_3 and catalyst weight percentage on conversion of FFA. $80\%\text{Al}_2\text{O}_3/20\%\text{SiO}_2$ catalyst can be promising catalyst for esterification reaction, which conversion of FFA reached conversion of 32% at 80°C and 15:1 ethanol to FFA ratio for 3 hours. Conversion of FFA increased significantly as alumina composition increased, attributed to several inferences including Bronsted acid in $\text{Al}_2(\text{SO}_4)_3$ and medium acidic strength (maximum peak temperature is 540°C). Also, $80\%\text{Al}_2\text{O}_3/20\%\text{SiO}_2$ has unique acidic strength among the prepared catalysts. This may be most active site. Substance leaching out from catalyst does not have any catalytic activity as done experiments. XRD analysis was performed to understand crystalline phases. $20\%\text{Al}_2\text{O}_3/80\%\text{SiO}_2$ has amorph structure. $50\%\text{Al}_2\text{O}_3/50\%\text{SiO}_2$ and $80\%\text{Al}_2\text{O}_3/20\%\text{SiO}_2$ catalysts have $\text{Al}_2(\text{SO}_4)_3$ and $\eta\text{-Al}_2\text{O}_3$, respectively.

After ANOVA, temperature and catalyst weight percentage were found to be insignificant. Alumina/Silica ratio was found to be significant. Therefore, model WCO was performed by considering the optimum conditions, revealing that conversion of FFA is 11%. Finally, $80\%\text{Al}_2\text{O}_3/20\%\text{SiO}_2$ as promising catalyst does not take place hydrolysis reaction of oil as considered experiments done. In addition, effect of alcohol to FFA ratio was investigated, revealing that conversion of FFA increases from 32% to 41% significantly as alcohol to FFA ratio was reduced from 15:1 to 2:1.

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APPENDIX A

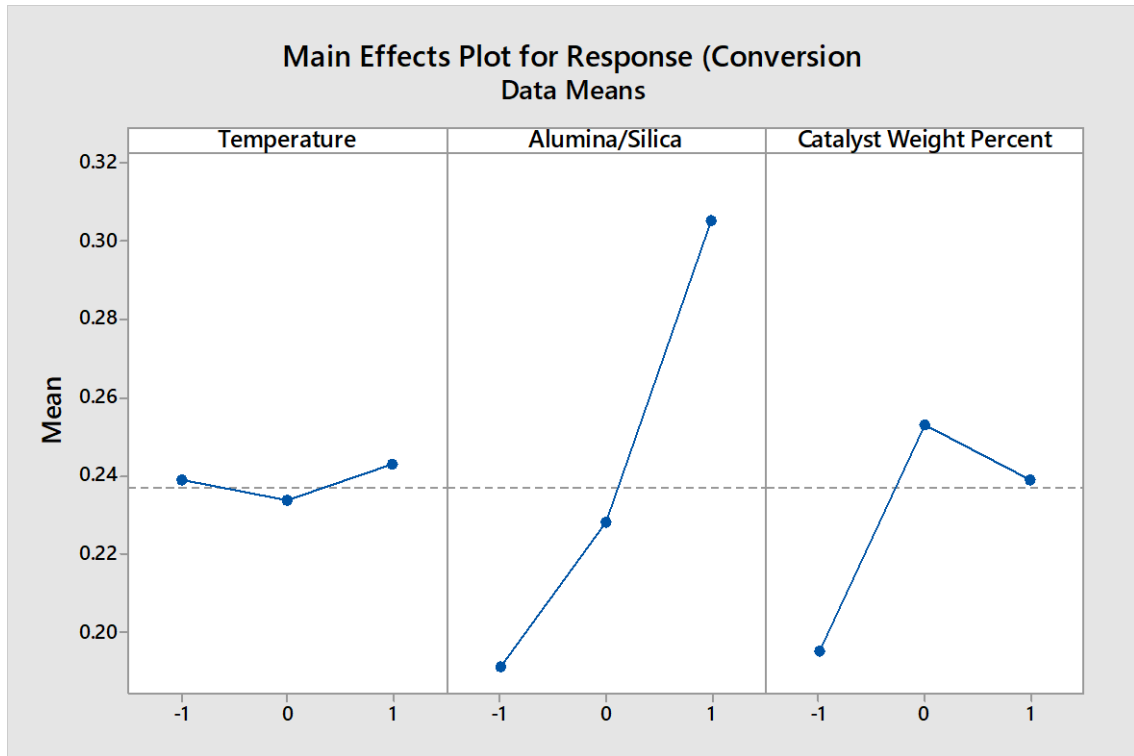


Figure A. 1. Main effects plot for conversion

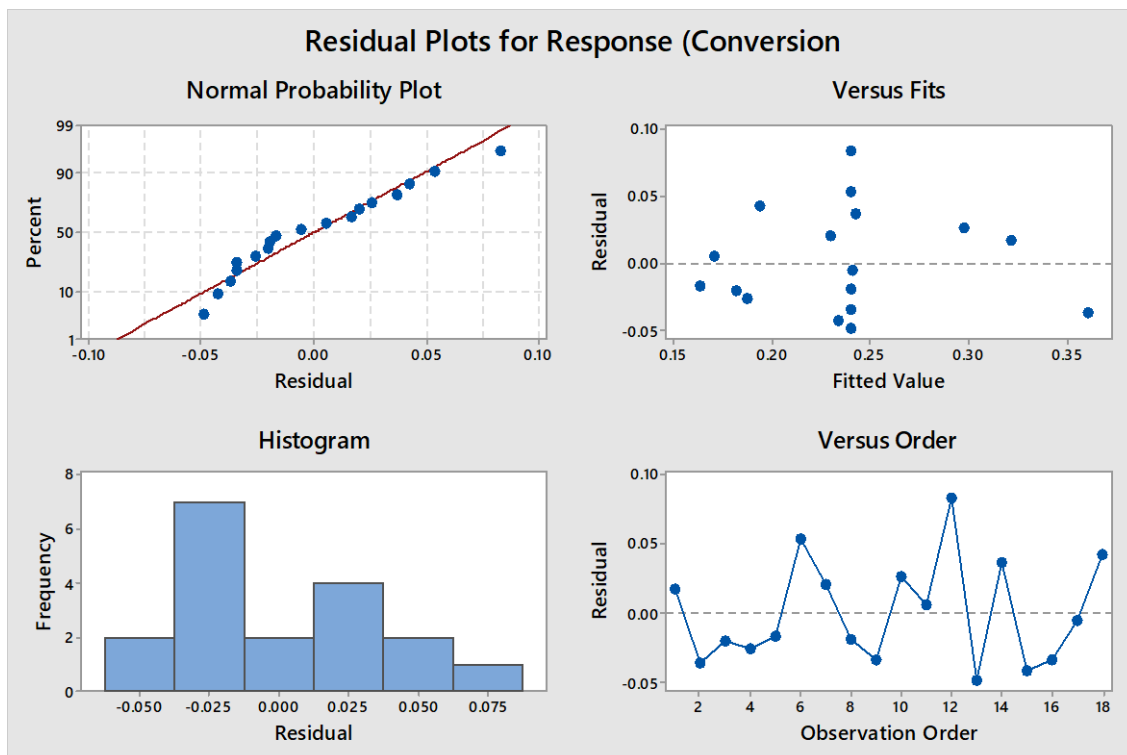


Figure A. 2. Residual plots for conversion

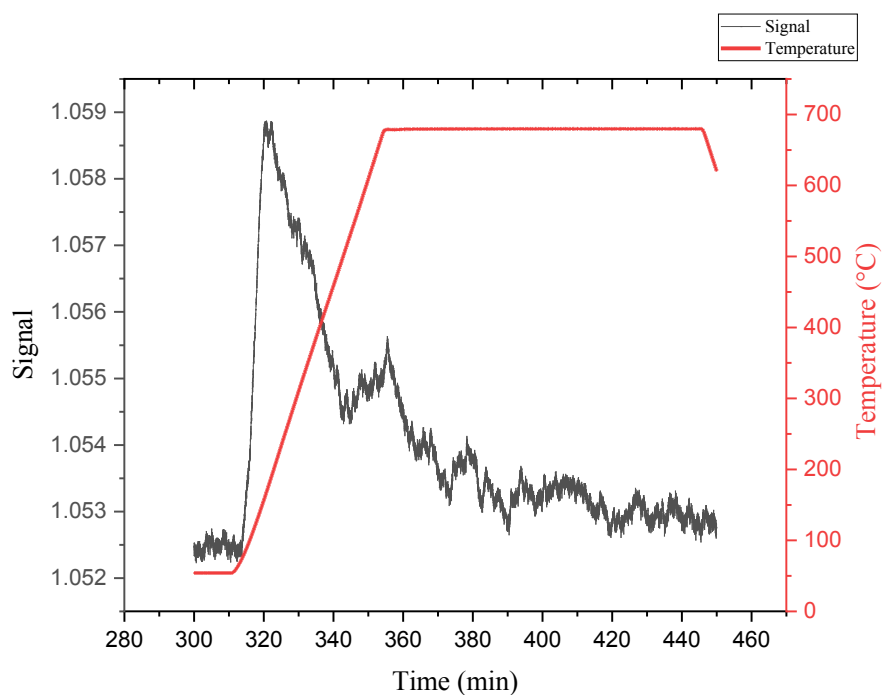


Figure A. 3. TPD behavior of 20/80 $\text{Al}_2\text{O}_3/\text{SiO}_2$

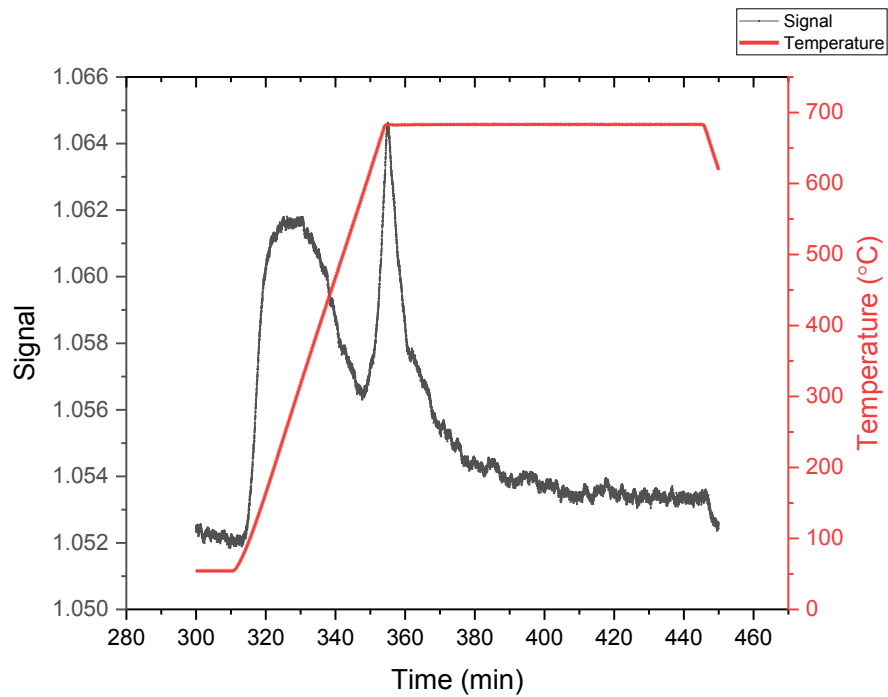


Figure A. 4. TPD behavior of 50/50 Al₂O₃/SiO₂

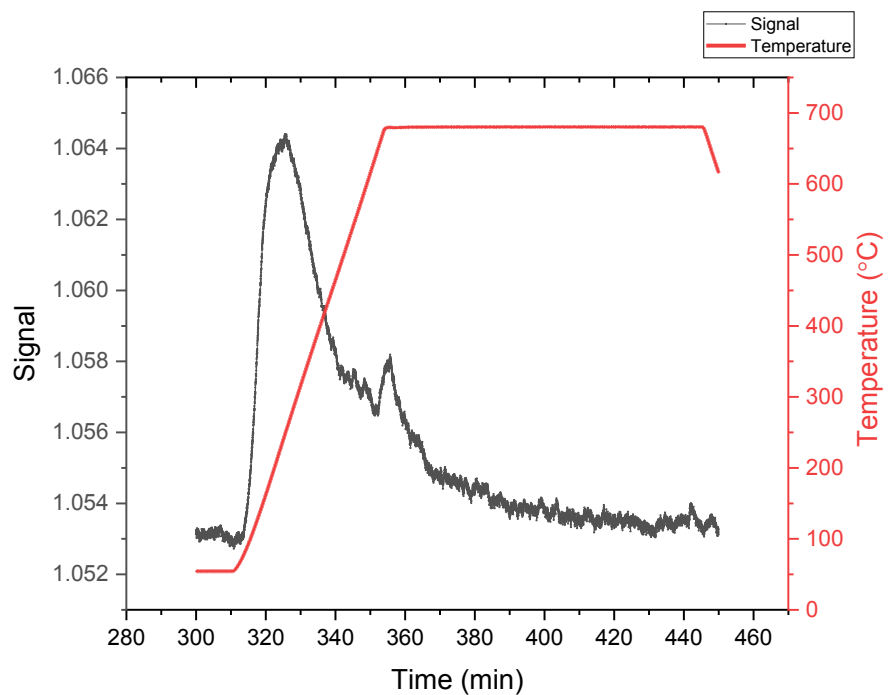


Figure A. 5. TPD behavior of 80/20 Al₂O₃/SiO₂