

BUTYL ESTERS PRODUCTION FROM CANOLA OIL OVER HETEROGENEOUS BASE CATALYSTS

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Oğuzhan AKIN**

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ABSTRACT

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In this study, transesterification reaction of canola oil with butanol over calcium oxide alumina catalyst was investigated with varying butanol:lipid molar ratios, catalyst amount and reaction time. Catalysts were prepared with the single step sol-gel method, and the activity of synthesized catalysts were investigated for two different forms of catalysts as powder and structured form.

In the case of powdered catalysts, at butanol:lipid molar ratios of 9 and 24 with 6 wt% of lipids as catalyst amount, led to 32% and 45% butyl esters yield in 1 hour. On the other hand, ~70% butyl esters yield has obtained at butanol:lipid molar ratios of 48 and 60 for the reaction time of 1 hour, while 89% yield had achieved when the reaction lasted for 4 hours at butanol:lipid molar ratio of 48. The necessity of mild basic strength and high butanol:lipid molar ratio was found to obtain high butyl esters yield. At high butanol lipid ratios of 48 and 60, it was observed that glycerolysis reaction occurs and promotes reverse transesterification reactions in first 30 minutes of the experiments.

In the case of structured catalysts, lower butyl esters yields than powder catalysts were obtained, yet they eliminated the need for catalysts separation step in the experiments. Reusability tests showed that catalyst activity has decreased due to calcium ion leaching in the first hour of reaction and kept its activity constant for the rest of the reaction.

ÖZET

HETEROJEN BAZ KATALİZÖR ÜZERİNDE KANOLA YAĞINDAN BUTİL ESTERLERİN ÜRETİMİ

Bu çalışmada, kanola yağının bütanol ile birlikte, kalsiyum oksit alüminyum oksit katalizör üzerinde, değişen bütanol:lipid oranları, katalizör miktarı ve reaksiyon süreleri ile transesterifikasyon reaksiyonu incelenmiştir. Katalizörler tek basamaklı bir sol-jel yöntemi ile hazırlanmıştır ve hazırlanan katalizörlerin aktivitesi iki farklı katalizör formu için, toz ve yapılandırılmış form olarak incelenmiştir.

Toz katalizörler için, 9 ve 24'lük molar bütanol:lipid oranlarında ve lipidin kütlece 6%'sı kadar katalizörle, 1 saatte, 32%'lik ve 45%'lik butil ester verimi elde edilmiştir. Diğer bir yandan, 1 saatlik reaksiyon süresi için, yaklaşık olarak %70'lik butil ester verimi, 48 ve 60 molar bütanol:lipid oranlarına elde edilmiştir ve 48 bütanol:lipid molar oranı için reaksiyon süresi 4 saate uzatıldığında %89'luk verim elde edilmiştir. Orta derece bazik kuvvetlik ve yüksek bütanol:lipid molar oranın yüksek butil ester verimi elde etmek için gerekli olduğu bulunmuştur. 48 ve 60'luk yüksek bütanol:lipid molar oranlarında, deneyin ilk 30 dakikasında, gliserolisiz reaksiyonun olduğu ve ters transesterifikasyon reaksiyonunu desteklediği gözlemlenmiştir.

Yapılandırılmış katalizörler için, toz katalizörlere göre daha düşük butil ester verimleri elde edilmiştir fakat deneyler için katalizör ayırma aşamasının gerekliliğini ortadan kaldırmışlardır. Tekrar kullanılabilirlik testleri, reaksiyonun ilk saatinde kalsiyum iyonu salınımından dolayı katalizör aktivitesi düşmüştür ve reaksiyonun geri kalanında aktivite sabit kalmıştır.

TABLE OF CONTENTS

LIST OF TABLES.....	vi
LIST OF FIGURES	vii
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. LITERATURE SURVEY	12
2.1. CaO Catalyst	12
2.2. Biodiesel Synthesis with Butanol	17
CHAPTER 3. MATERIALS AND METHODS	21
3.1. Materials	21
3.2. Methods.....	21
3.2.1. Catalyst Preparation	21
3.2.2. Catalyst Activity.....	23
3.3. Catalyst Characterization	27
CHAPTER 4. RESULTS AND DISCUSSION.....	29
4.1. Crystalline Phases and Basicities of the Catalysts	29
4.2. Catalyst Activity	32
CHAPTER 5. CONCLUSION	39
REFERENCES	40

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 1. Comparison of 1st, 2nd and 3rd generation biofuels.....	4
Table 2. Basicities of CaO obtained from different precursors.....	13
Table 3. Transesterification reaction with butanol in literature.....	20
Table 4. Samples with corresponding reaction conditions.....	24
Table 5. Fatty acid content of canola oil.....	28
Table 6. Total basicity ($\mu\text{mol CO}_2/\text{g catalyst}$) using FTIR.....	30
Table 7. Elemental distribution on structured catalyst.....	32
Table 8. Butyl ester yields as a function of catalyst amount for powder catalysts.....	33
Table 9. Amount of dissolved Ca cation in FABE at butanol:lipid molar ratio of 48 and powder catalyst amount of 6 wt%.....	37
Table 10. FABE yields obtained by structured catalysts.....	38

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1. Global energy consumption.....	1
Figure 2. CO ₂ emission from fuel combustion (World).	2
Figure 3. CO ₂ emission from fuel combustion (Turkey).	2
Figure 4. Biodiesel Production Capacity.	5
Figure 5. Transesterification reaction with methanol.	6
Figure 6. Saponification reaction.	6
Figure 7. Neutralization reaction.	6
Figure 8. Esterification reaction.....	6
Figure 9. Commercial biodiesel production.	7
Figure 10. Transesterification reaction under the presence of base catalyst.	9
Figure 11. Transesterification reaction under the presence of acid catalyst.	9
Figure 12. Transesterification reaction on CaO/Al ₂ O ₃ catalyst.	15
Figure 13. Synthesis of 60%CaO/40%Al ₂ O ₃ catalysts.	22
Figure 14. Powdered and structured catalysts.	23
Figure 15. Experimental steps of activity test.....	25
Figure 16. Experimental set up for structured catalyst.	26
Figure 17. XRD of 60%CaO/Al ₂ O ₃ calcined at 700°C.	29
Figure 18. SEM view and EDX mapping of structured catalyst.	31
Figure 19. Effect of reaction time on different butanol:lipid molar ratios with the powder catalyst amount of 6 wt%.	34
Figure 20. FAME yield as a function of butanol:lipid molar ratio and reaction time for the powder catalyst amount of 6 wt%.	36
Figure 21. Activity of structured catalyst for the butanol:lipid molar ratio of 48:1 with 1 hour of reaction time.....	37
Figure 22. Activity of structured catalyst for the butanol:lipid molar ratio of 48:1 with 4 hour of reaction time.....	38

CHAPTER 1

INTRODUCTION

Major part of energy demand is largely provided by fossil fuels and their derivatives. However, the contribution of petroleum-based fuels to CO₂ emission is severe. Figure 1 shows the global energy consumption and resource change through the years 1978, 1998, and 2018. Thanks to advancing technology in the renewable energy sector, its global share on total energy production have increased from 0.1% to 4.1% whereas, oil dependency decreased from 48.5% to 33.6%. However, the total energy consumption has also drastically increased from 270.5 EJ in 1978 to 578 EJ in 2018. Thus, it could be misleading to conclude energy production from oil has decreased since 1978 because only the share of total energy generation has reduced. In contrast, energy production from oil has increased from 131.2 EJ to 194.2 EJ.

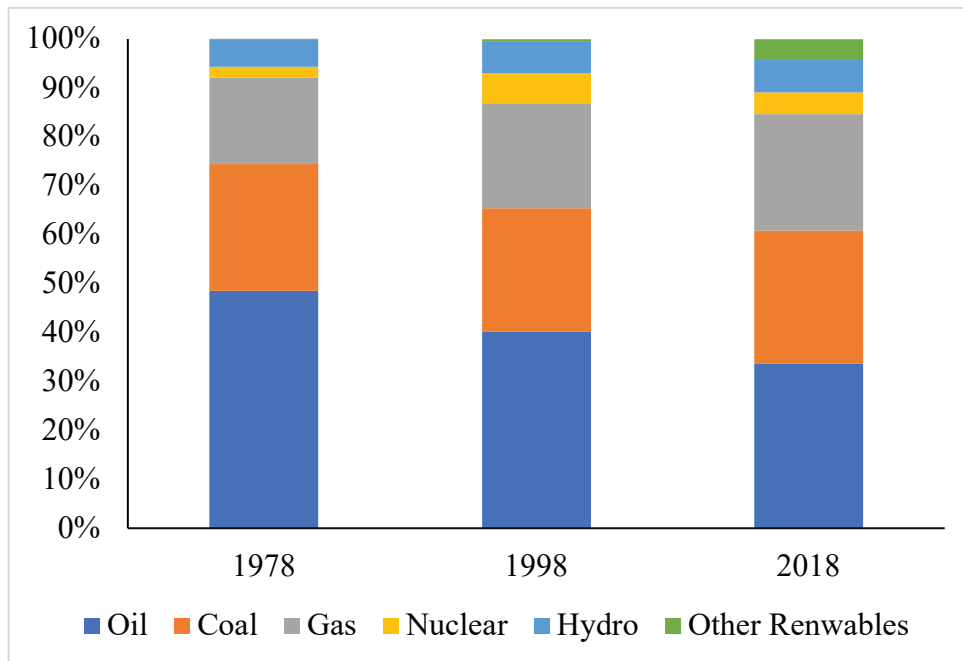


Figure 1. Global energy consumption.

In the past, one of the main motivations for developing renewable energy technologies was the depletion of fossil fuel resources. Recently, its contribution to CO₂ emission became the primary problem. Energy-related CO₂ emission has increased by 87% since 1978. Besides, the carbon intensity of total energy production decreased thanks to the growth of nuclear and renewable energy in total energy production share. Moreover, petroleum and its derivatives are responsible for 45% of total CO₂ emission from energy consumption while 25.87% of petroleum-related CO₂ emission came from distillate fuel oil in the U.S.A. in 2019 (IEA 2020). Increasing CO₂ concentration in the atmosphere causes the greenhouse effect and leading global warming. Therefore, it is critical reducing CO₂ emission caused by petroleum distillates due to their considerable contribution to total CO₂ emission.

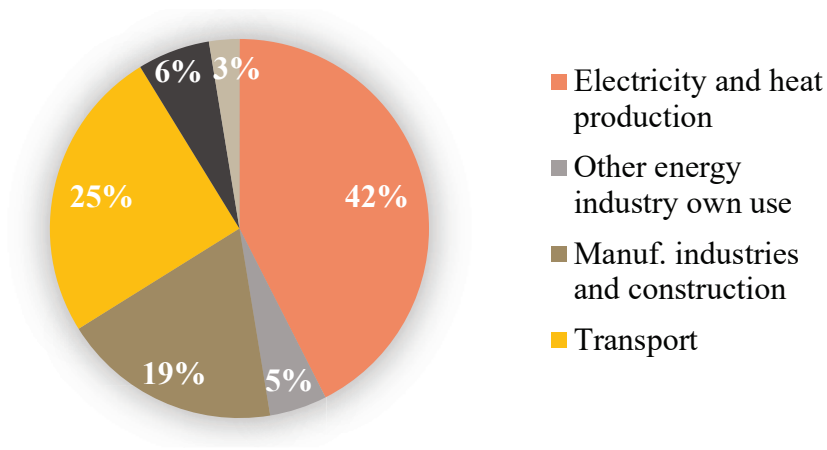


Figure 2. CO₂ emission from fuel combustion (World).

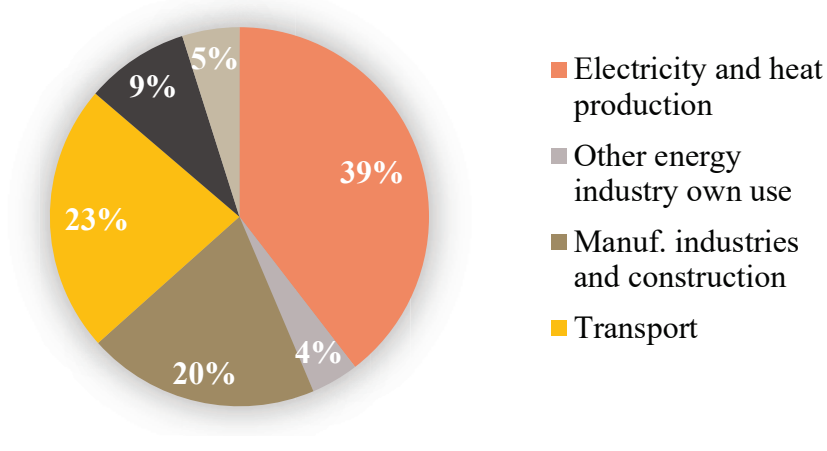


Figure 3. CO₂ emission from fuel combustion (Turkey).

Figure 2 and Figure 3 demonstrate the CO₂ emissions from fuel combustion regarding their usage worldwide and Turkey, respectively. For both cases, electricity/heat production and the transportation sector have the highest contribution to CO₂ emission. One way to reduce CO₂ emissions is by developing alternative energy technologies to reduce dependency on fossil fuels. Alternative energy production technologies have been developed to overcome the CO₂ emission problem, such as solar, wind, and biomass conversion technologies. Several countries have put regulations to promote renewable energy usage and limit CO₂ emissions recently. Although those policies have helped extend alternative energy usage, it is not sufficient to decrease reliance on fossil fuels to desired levels. For instance, recent developments in solar and wind energy technologies have made them economically feasible and improved their share in total energy production from renewable energy. However, both technologies generate energy in heat and electricity and require expensive infrastructural modifications to replace fossil fuels for vehicles requiring fossil fuel to run. Considering that the transportation sector is one of the major contributors to the CO₂ emission as 25% (IEA 2020), it is critically important to produce biofuels that can replace conventional petroleum-derived fuels.

Vegetable oil, bio-alcohol, biogas, and biodiesels can potentially replace fossil fuels. However, using vegetable oil as liquid fuel is not viable due to its different physical and chemical properties compared to conventional fuel leading to motor engine complications. Bio-alcohol, biogas and biodiesel are viable options for fuel and fuel additives. Biogas is suitable to replace and mixed with natural gas by improving its CH₄ content. In comparison, bio-alcohols are used as fuel additives. When the transportation sector is considered, biodiesel has the highest potential to replace conventional diesel. In addition to its usage as a fuel additive, like bio-alcohol, its similar physical and chemical properties with diesel and favorable combustion emission profile make it possible to directly use diesel engine with little to no modification requirements (Thangaraj et al. 2019).

Biodiesel is simply the mono-alkyl esters of long-chain fatty acids produced from vegetable or algal oil. Even though the latter case is more preferable and called third generation fuel, it is not commercially applicable yet, unlike vegetable oil. On the other hand, biodiesel production from vegetable oil is a well-known and widely used method in the industry as well (Borges and Díaz 2012). It has a specific gravity range of 0.873-0.884 kg/m³, kinematic viscosity of 3.8-4.8 mm/s², and a cetane number of 50 – 62,

although it may differ with the derived feedstock (Guo, Song, and Buhain 2015). Moreover, its cloud and flash point of $-4^{\circ}\text{C} - 14^{\circ}\text{C}$, and $110-190^{\circ}\text{C}$, respectively, and energy density of 38-45 MJ/kg improves its compatibility with conventional diesel to an extent of direct replacement (Hoekman et al. 2012).

Biofuels/biodiesels are divided into three groups: first-, second- and third-generation biofuels. First-generation biofuels, starch, sugar or vegetable oil derived biofuels (Alaswad et al. 2015), are well established and being produced on an industrial scale for years (Brennan and Owende 2010). Because of the competition with the food market, it can only meet a limited portion of the growing biofuel need. Its sustainability is debatable due to extensive land requirements and deforestation causing problems (Alaswad et al. 2015, Brennan and Owende 2010). Second-generation biofuels are developed to overcome the problems of first-generation biofuels by using agricultural residues, forest residues and non-edible vegetable oils instead of food crops as feedstock. However, its global production volume is smaller in the world market than the first-generation biofuels since the process requires well-established waste management and transportation systems that are mostly available in developed countries (Brennan and Owende 2010). Third-generation biofuels are marine biomass (algae) derived biofuels that are developed to compensate for the drawbacks of the first- and second-generation biofuels (Brennan and Owende 2010, Alaswad et al. 2015, Enamala et al. 2018). Algae cultivation does not compete with the food market. Moreover, cultivation does not require significant land utilization compared to first- and second-generation feedstocks (Enamala et al. 2018). Large water requirement for algae cultivation preventing it to be a commercially viable feedstock for diesel production. A brief comparison of first-, second- and third-generation biofuels was summarized in Table 1.

Table 1. Comparison of 1st, 2nd and 3rd generation biofuels.

Parameters	1st Generation	2nd Generation	3rd Generation
Land use efficiency	Low	Medium	High
Food vs Fuel Competition	Yes	No	No
Commercial Availability	Yes	Limited	No
Water utilization*	High	Medium	High**
Ability to utilize wastes	No	Yes	Yes
Process complexity	Simple	Complex	Complex

Biodiesel production from vegetable oil or waste vegetable oil is a well-known method in the industry. Initially, high petroleum prices in 2001 shifted attention to biodiesel in the global market and increased the world biodiesel production capacity (Guo, Song, and Buhain 2015). As Figure 4 shows, global biodiesel production capacity significantly increases after 2001 (Balat 2007). Even though petroleum prices are not expensive today, increased awareness on energy security and CO₂ emission kept the importance of biodiesel production. Moreover, several countries have put regulations to promote blending conventional diesel with biodiesel. For instance, the Turkish Energy Regulatory Agency (EMRA) made mandatory to blend biofuel with conventional fuel, in Turkey. According to EMRA, it was compulsory to blend biodiesel with traditional diesel with a ratio of 1% in 2014, and it was increased to 2% in 2015, and it was increased up by 1% in 2016 to reach 3% (Boluk and Koc 2013).

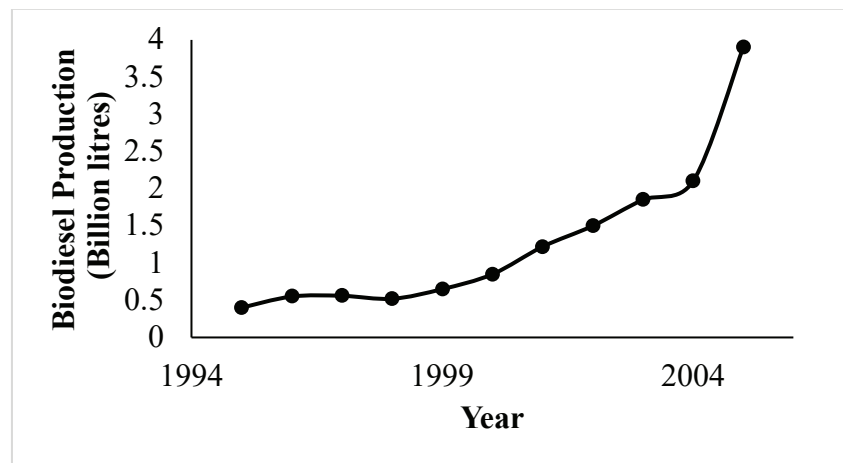


Figure 4. Biodiesel Production Capacity.

On a commercial scale, methanol is the most used alcohol and, KOH and NaOH are the most used basic homogenous catalysts for biodiesel production. Depending on the production capacity, the process can occur in continuous operation or batch operation. For both cases, the catalyst is mixed with methanol to form methoxide, and then the oil is introduced for transesterification reaction to occur, which is shown in Figure 5. Then crude glycerin and crude biodiesel are separated. Since crude biodiesel contains methanol, soap, monoglyceride, diglyceride and triglyceride, it requires a highly water consuming washing step for purification. Soap formation occurs under the presence of water via saponification reaction, as shown in Figure 6. In the case of waste oil (generally

cooking oil) used as the feedstock, presence of free fatty acids (FFA) leads to neutralization reaction, which ends up by soap formation, as seen in Figure 7. Therefore, it is necessary to pretreat waste oil with acid catalyst and methanol to obtain methyl esters via esterification reaction, as shown in figure 7 (Borges and Díaz 2012).

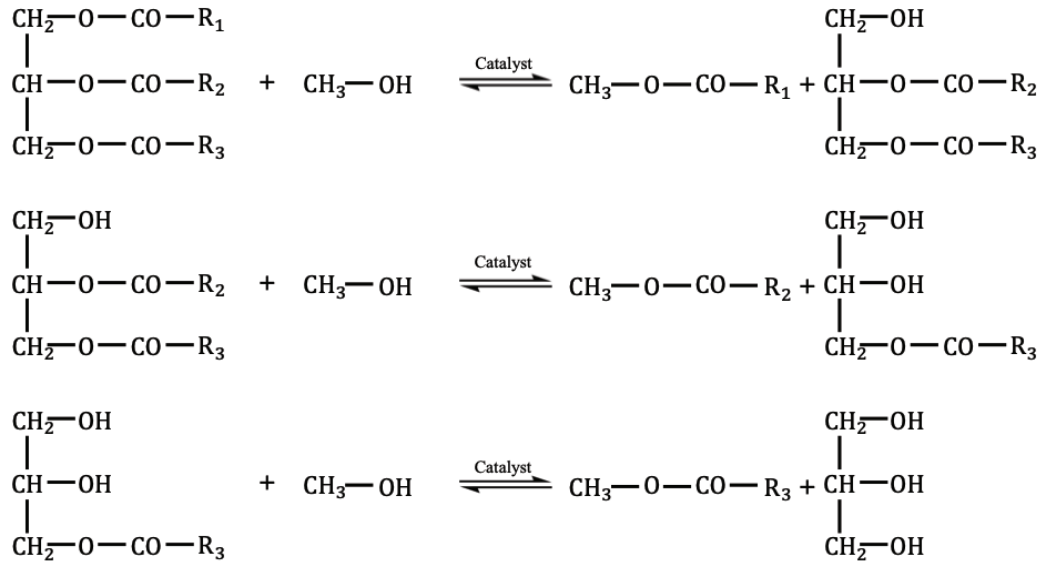


Figure 5. Transesterification reaction with methanol.

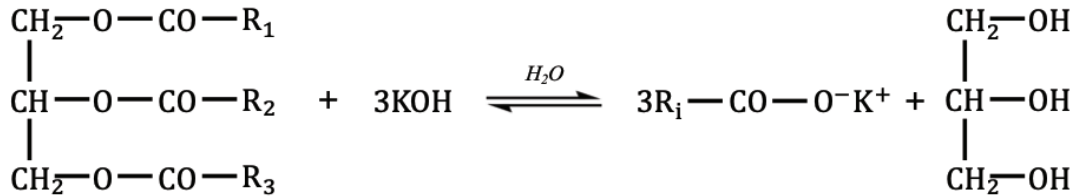


Figure 6. Saponification reaction.

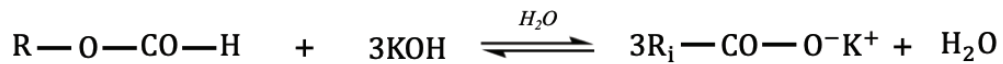


Figure 7. Neutralization reaction.



Figure 8. Esterification reaction.

The abundance and affordable prices of NaOH and KOH make them viable catalysts for commercial scale utilization. However, it brings the need for catalyst separation steps. Usually, crude biodiesel is washed with acid water to neutralize and separate catalysts. However, it not only leads to an increase in water utilization, but it also leads to soap formation. Even though that produced soap might be sold as a byproduct, generated wastewater needs treatment, increasing the overall operation cost. However, NaOH and KOH are soluble in methanol and easily form sodium and potassium methoxides, which catalyze the reaction; the reaction reaches high biodiesel yields in a short time without the need for high reaction temperatures (Borges and Díaz 2012). Heterogenous catalyst usage eliminates the catalyst separation step, and theoretically decreases the overall operational cost and improves the process simplicity (Janaun and Ellis 2010). Commercially homogenous catalysts are used in biodiesel production due to abundancy and low prices of KOH and NaOH. A brief scheme of a commercial biodiesel production process has shown in Figure 9 (Borges and Díaz 2012).

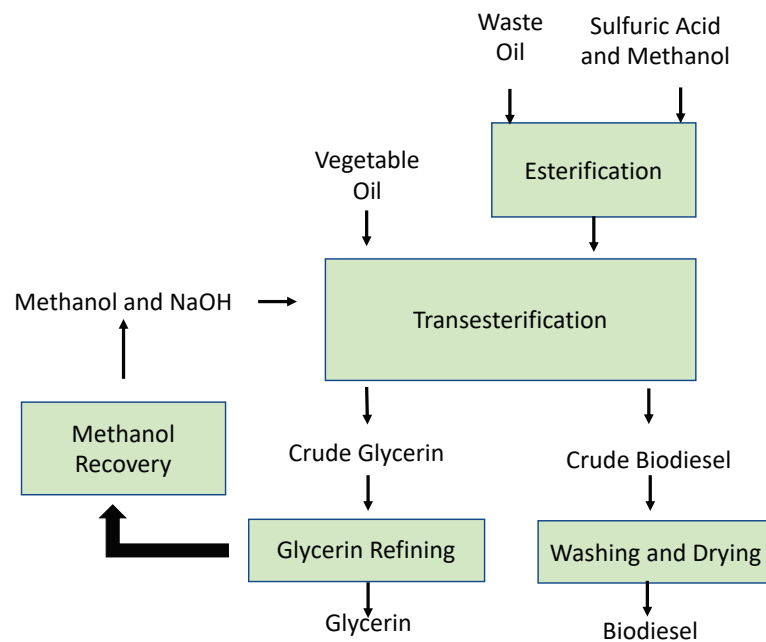


Figure 9. Commercial biodiesel production.

Heterogenous catalyst has many advantages over homogenous catalysts when the biodiesel production process is considered. As previously mentioned, the use of heterogenous catalysts is expected to significantly decrease the cost of catalysts

separation and purification steps. However, another advantage of using heterogenous catalysts is coming from environmental concerns. Homogenous catalysts like NaOH and KOH have the tendency to form soap and contaminates the water used in the washing step, in addition to their limited recovery and reusability in the overall process (Janaun and Ellis 2010). In need of esterification reactions, highly corrosive and hazardous homogenous catalysts like H₂SO₄ and HCl are used (Carmo et al. 2009, Srilatha et al. 2009). In theory, use of heterogenous catalyst also decreases the catalyst disposal to environment, and higher reusability decreases the need of catalyst amount to produce same biodiesel amount produced via homogeneously catalyzed reactions.

Transesterification reactions can be catalyzed in both acidic and basic conditions. Under the basic influence, first, the alcohol is deprotonated by the base, and alkoxides occur. Then, it makes a nucleophilic attack to the carbonyl group of the triglyceride leading to formation of alkyl ester, and the corresponding anion of the diglyceride. Then the anion of the diglyceride protonated by the previously protonated base and all procedure is repeated prior to complete transesterification of triglyceride to glycerine which is shown in Figure 10 (Schuchardt, Sercheli, and Vargas 1998). In the acid catalyzed scenario, acid protonates triglyceride and then alcohol makes a nucleophilic attack where they form an intermediate. Then, protonated alcohol leaves the structure as glycerol by it protonating the previously deprotonated acid. Similarly, all these steps are repeated till the complete transesterification of triglyceride occurs. The mechanism of acid catalyzed esterification has shown in Figure 11 (Meher, Vidyasagar, and Naik 2006). Base catalysts are considered more active than acid catalysts for transesterification reactions since they favor milder temperatures such as 50-60°C, and shorter reaction times unlike acid catalyzed reaction requiring higher temperatures above 100°C. On the other hand, acid catalyzed reactions are not affected by the influence of water presence and FFA content of the feedstock (Lotero et al. 2005). Ideally, bifunctional catalysts that carry both acidic and basic characteristics that simultaneously catalyze esterification and transesterification reactions are the best choice for industrial application, since it allows wider feedstock variety and relatively short reaction time. Nevertheless, basic heterogenous catalysts have high potential to replace commercially used NaOH and KOH since they are the most used catalyst in commercial biodiesel production facilities.

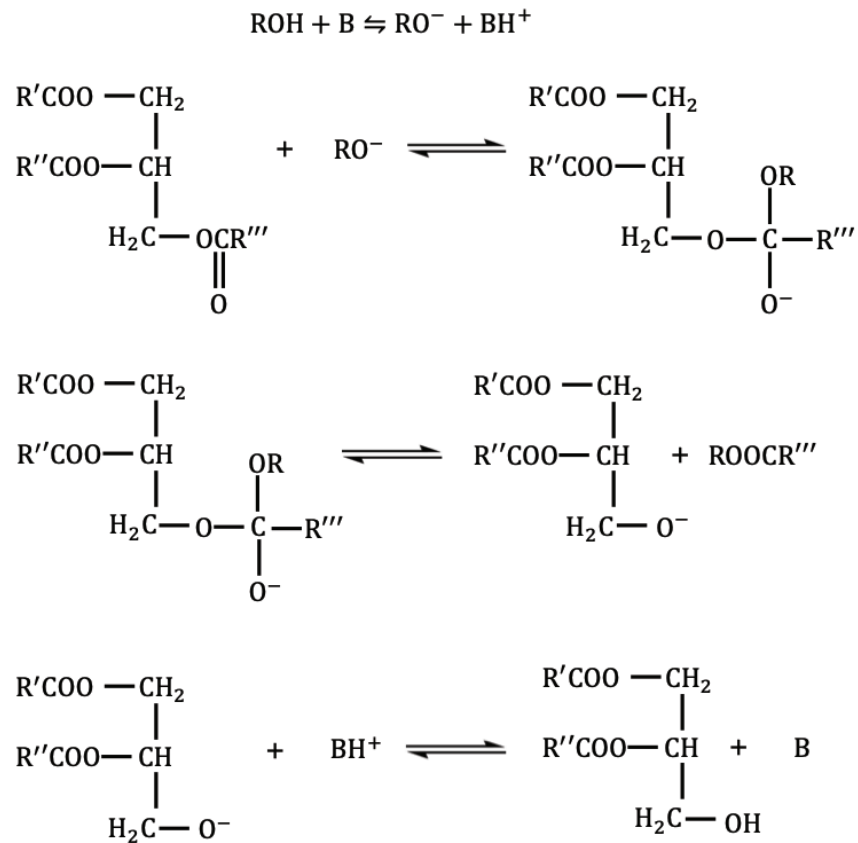


Figure 10. Transesterification reaction under the presence of base catalyst.

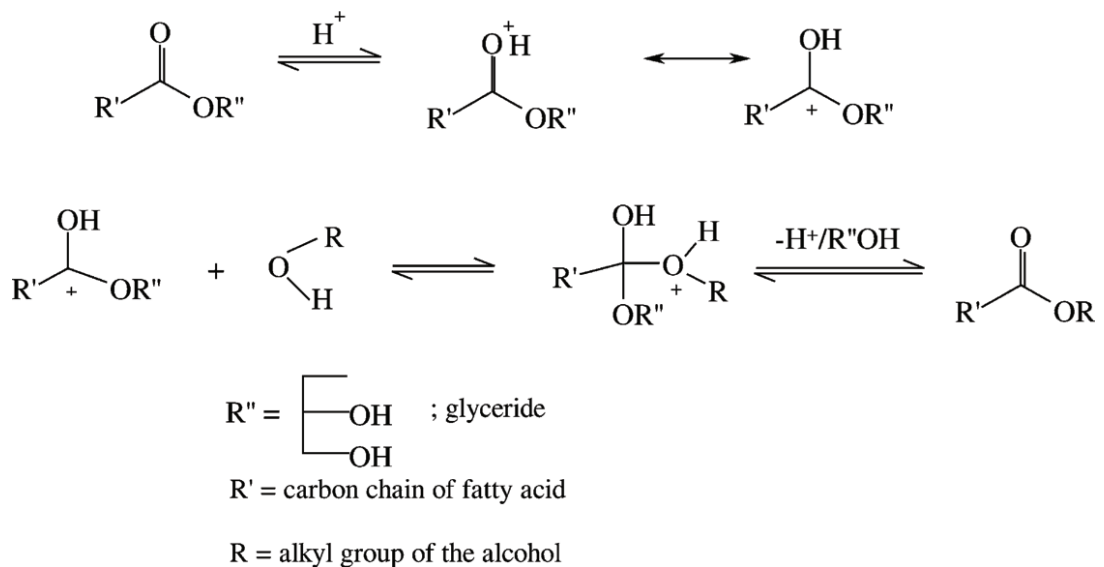


Figure 11. Transesterification reaction under the presence of acid catalyst.

For basic heterogenous catalysts, metal oxides are intensely studied, where CaO is one of the most studied. Besides, calcium oxide is highly active for transesterification

reaction; it also has a long catalyst lifetime. Another advantage of using CaO is relying on its feedstock. It can be obtained from natural sources such as eggshells and mollusk shells which improves the carbon neutrality of the process (Viriya-Empikul et al. 2010). However, CaO synthesis from waste is another topic itself to study. Thus most of the laboratory studies utilize pure CaO or CaO salts for catalyst synthesis (Borges and Díaz 2012).

The choice of alcohol to use in biodiesel production is an important factor for both diesel quality and carbon neutrality of the process. Even though methanol has been widely used and given high conversion and high yield of FAME in biodiesel production (Mahdavi and Monajemi 2014, Zabeti, Daud, and Aroua 2009, Yan, Lu, and Liang 2008, Umdu, Tuncer, and Seker 2009, Cakirca et al. 2019, Teo et al. 2014), it is generally produced from oil or natural gas. Considering the general aim is replacing conventional diesel with biodiesel with lower carbon footprint, the resource of the alcohol used in the process directly affects the carbon neutrality of the process. Hence, it is crucial to use bio-derived alcohols in that manner. Ethanol is produced from biological sources and Leggieri et al. reported that fatty acid ethyl esters (FAEE) have shown better cold-flow properties compared to FAME (Leggieri, Senra, and Soh 2018). Yet, bioethanol itself is also used as fuel additive and has its own market. Nevertheless, fatty acid butyl ester (FABE) exhibits higher combustion energy than both FAME and FAEE (Nimcevic et al. 2000), and improves the cold-flow properties when mixed with the conventional biodiesel due to its lower cloud point (Pappu et al. 2011). Moreover, butanol could be produced from biological sources via acetone-butanol-ethanol (ABE) fermentation (Kujawska et al. 2015). However, butanol usage in biodiesel production is not studied as extensively as methanol and ethanol. Besides, limited researches with transesterification reaction of triglycerides with butanol utilized homogenous catalysts rather than heterogenous catalysts (Nimcevic et al. 2000, Hajek et al. 2017, Colucci, Borrero, and Alape 2005, Ataya, Dube, and Ternan 2008, Leadbeater, Barnard, and Stencel 2008, Likozar and Levec 2014).

As a contribution, the presented study has aimed to produce butyl esters biodiesel from renewable sources in the presence of CaO based heterogenous catalyst. Considering the challenges faced during the catalyst separation in large scale operations, two types of catalysts were prepared as powder and structured catalysts. Therefore, transesterification reaction of canola oil with butanol was investigated over powder and structured

CaO/Al₂O₃ catalyst at 50°C and 1 atm as a function of butanol:lipid molar ratios, the amount of catalyst, and the reaction time.

Presented thesis is composed of five chapters. In the first chapter, the importance of biofuels and biodiesel on CO₂ emission, biodiesel production methods, and the general principle of transesterification reaction was briefly summarized. CaO catalysts with their usage in the transesterification reaction, and advantages of butanol usage and its examples are reviewed in the second chapter. In the third chapter, the catalyst preparation method used in the study was explained in detail as well as how the reactions were executed. In the following chapter, results of the experiments were discussed and tried to make an explanation between catalyst activity and its basic properties. In the final section, the results of the study were concluded.

CHAPTER 2

LITERATURE SURVEY

2.1. CaO Catalyst

As it was previously mentioned, CaO is one of the most studied metal-oxide for transesterification reaction. It is abundant in nature and can be obtained from minerals like limestone and CaCO₃ containing bioresources such as eggshells and seashells. In the case of calcium carbonate containing material, it is usually aimed to remove one mole of CO₂ from the structure to obtain CaO by thermally decomposing it at high calcination temperatures. However, CaO itself has high a tendency to react with CO₂ and moisture in the air leading to the reformation of CaCO₃ and the formation of Ca(OH)₂ (Marinković et al. 2016). Even though obtaining CaO from biological resources has many environmental benefits, most laboratory studies for biodiesel production obtain CaO from calcium salts.

The main property of the CaO that makes it a viable metal-oxide for transesterification reactions is its basic properties. For instance, calcium oxide has an ionic crystal structure where calcium cation is considered as weak acid according to Lewis theory, and conjugated oxygen anion demonstrates strong basic properties. The presence of basic sites on the CaO surface and the basic strength of that sites directly affect the catalytic activity. Simply, those basic sites deprotonate the target compound and start the catalytic reaction. However, number of the basic sites and basic strength of the CaO are strongly influenced by the activation conditions such as, heating rate, calcination temperature and calcination time (Bilton, Brown, and Milne 2012). Alonso et al. studied the basicity of CaO obtained from different precursors for the same calcination temperature and time (800°C and 1 hour) and observed different basicity values for different precursors as shown in Table 2 (Alonso et al. 2010). Therefore, the calcination conditions and the used precursor also affect the basicity of the CaO, which explains the reason for the different basicity values of CaO and CaO mixed catalysts presented in the literature (Marinković et al. 2016).

Table 2. Basicities of CaO obtained from different precursors.

Precursor	Basicity ($\mu\text{mol CO}_2/\text{g of catalyst}$)
Calcium carbonate	101
Calcium acetate	62
Calcium oxalate	63
Calcium hydroxide ^a	61
Calcium hydroxide ^b	15

a: obtained from calcium acetate
b: obtained from calcium nitrate

Even though pure CaO can catalyze the transesterification reaction, its weak mechanical strength limits its commercial scale applications. Therefore, it is possible to enhance its catalyst activity, thermal stability, and mechanical strength by mixing CaO with different support metal-oxide such as Al_2O_3 (Marinković et al. 2016, Pasupulety et al. 2013). In that case, acidity and basicity of used support Al_2O_3 have an effect on the catalyst activity, as well as the synthesis method. For instance, Pasupulety et al. investigated the effect of acidic, basic and neutral Al_2O_3 on the $\text{CaO}/\text{Al}_2\text{O}_3$ catalyzed transesterification reaction (Pasupulety et al. 2013). They used the wet impregnation method for catalyst synthesis and tested their catalyst with soybean oil and methanol to obtain FAME. They found that the highest FAME yield obtained with the catalyst prepared by neutral Al_2O_3 support and proposed that catalyst prepared with neutral Al_2O_3 leads to the formation of an intermediate called calcium diglyceroxide, which facilitates the transesterification reaction and improves the catalyst activity. In addition to that, they observed that beside the catalyst synthesized with basic Al_2O_3 support lead the formation of stronger basic sites on the catalyst surface compared to ones observed on the neutral Al_2O_3 supported catalyst, latter one has given the highest yield (Pasupulety et al. 2013). For instance, Turkkul et al. also suggested that mild basic strength with high basicity favors transesterification reaction and increases the catalytic activity as they observed beside their catalyst had lower basicity compared to pure CaO and Al_2O_3 , it has given significantly higher FAEE yields. They stated that basic strength of the active sites of their catalyst was actually weaker than those found on pure CaO and Al_2O_3 (Turkkul, Deliismail, and Seker 2020).

Figure 12 demonstrates the reaction mechanism of transesterification of triglyceride on the $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst with methanol. The proposed mechanism follows

the Langmuir-Hinshel-wood-Hougen-Watson theory, where reactants are adsorbed on the catalyst surface, react with each other, and the product is desorbed from the catalyst surface. The key step is considered to be alcohol (methanol) deprotonation on the catalyst surface to form an alkoxide intermediate due to basic site. Triglyceride also is adsorbed on the surface and interacts with the basic site to form another intermediate. These two intermediates then interact with each other and lead to diglyceride and FAME formation, simultaneously regenerating the catalyst. Then, free diglyceride in the reaction medium again is adsorbed on the catalyst surface and form another intermediate that interacts with alkoxide intermediate to produce monoglyceride and FAME in similar manner. Finally, monoglyceride goes through the same reaction steps, and glycerol and FAME occur as the final products (Pasupulety et al. 2013, Marinković et al. 2016).

Unlike esterification reactions, transesterification reaction occurs at milder temperatures with shorter reaction time, and it has been studied for a variety of vegetable oils with various heterogenous catalysts. (Sajjadi, Raman, and Arandiyani 2016). Traditionally, KOH and NaOH are used as homogenous catalysts due to their low cost and high activity. However, the homogenous catalyst usage brings excessively water-consuming treatment steps to the overall process, such as separation and neutralization of the waste catalyst (Yan et al. 2010). Due to its low solubility in the reaction mixture and high tolerance to water and FFA presence in oil, the development of calcium oxide based heterogenous catalysts with various supports has been studied in literature to overcome the drawbacks of using homogenous catalysts (Yan et al. 2010). Mahdavi and Monajemi managed to convert ~92% of the cotton seed oil into ethyl ester biodiesel at 95°C by using CaO-MgO/Al₂O₃ solid base catalyst (Mahdavi and Monajemi 2014). They tested different CaO-MgO (8:2) loading on Al₂O₃ from 10 wt.% to 25 wt.% and observed that increase in CaO-MgO loading on Al₂O₃ actually decreased the CaO-MgO dispersion on the catalyst surface which prevented the formation of active basic sites for CO₂ to adsorb on. TPD profile of their results showed that the catalyst with 10 wt.% CaO-MgO (8:2) loading provided the highest basicity with neat CaO-MgO (8:2) catalyst, and it has given the highest ethyl ester biodiesel yield. The TPD profile also showed that neat CaO-MgO catalyst had higher basic strength as the desorption temperature was shifted to higher temperatures even though peak intensity was nearly similar with the 10 wt.% CaO-MgO/ Al₂O₃ catalyst. However, they did not execute the reaction with neat CaO-MgO so the effect of basic strength was not investigated (Mahdavi and Monajemi 2014).

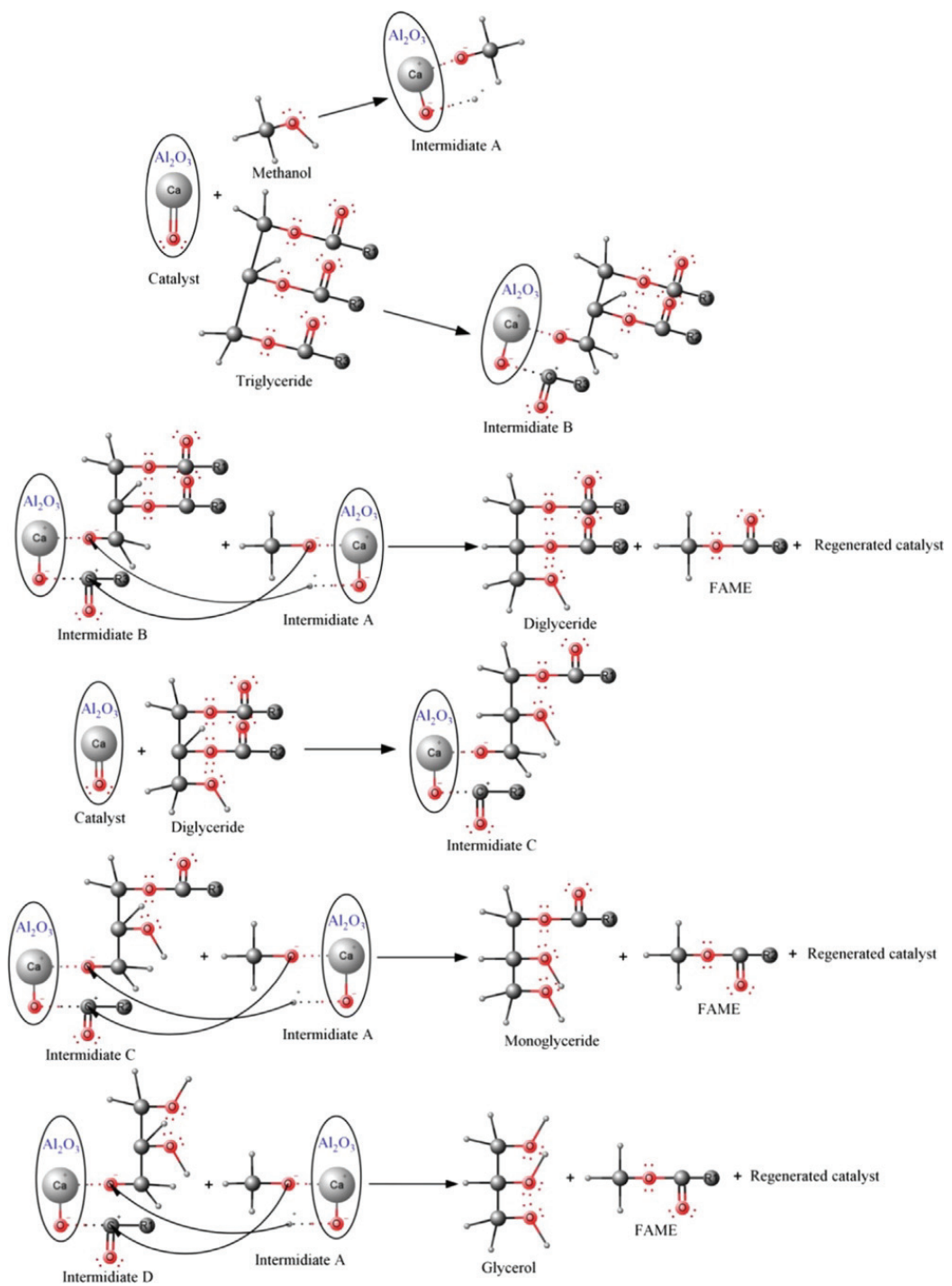


Figure 12. Transesterification reaction on $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst (Source:Sajjadi 2016).

Zabeti et al. achieved the synthesis of CaO/Al₂O₃ catalyst to convert palm oil into methyl ester biodiesel with a yield of 95% at 65°C (Zabeti, Daud, and Aroua 2009). They studied precursor loading and the calcination temperature effect on the basicity of the catalyst. They found that the calcination temperature has a more significant effect on the basicity of the catalyst and stated that increasing the CaO loading after a certain amount decreases the CaO dispersion on the catalyst surface and consequently decreases the basicity of the catalyst. Their experimental model showed a direct correlation between the basicity and the catalytic activity, yet the effect of basic strength was not investigated (Zabeti, Daud, and Aroua 2009). Yan et al. has reached the 92% conversion for methyl ester biodiesel production from rapeseed oil at 64.5°C with CaO/MgO catalyst (Yan, Lu, and Liang 2008). They tested the effect of different CaO loading amounts on catalyst activity. According to them, 16 wt.% CaO loading has given the highest methyl esters yield and basicity and demonstrated the highest basic strength. Therefore, they suggested that both high basicity and basic strength positively affected the catalyst activity. However, their TPD results showed that 20.4 wt.% CaO loaded catalyst has also demonstrated a similar CO₂ desorption profile with smaller intensity, and the desorption temperature was slightly shifted to lower temperatures. Despite that temperature, shift indicates lower basic strength, the difference between the peak intensities was much more significant. It makes it hard to evaluate the effect of basic strength between those two samples as the effect of basicity was clearly the dominant one (Yan, Lu, and Liang 2008).

There are also several studies that utilize algae oil as feedstock to obtain biodiesel in the presence of heterogenous CaO based catalyst. Transesterification of *Nannochloropsis oculata* with methanol over CaO/Al₂O₃ catalyst at 50°C and 1 atm was studied by Umdu et al. and, biodiesel yield was reported as 97%(Umdu, Tuncer, and Seker 2009). They compared the activity of Al₂O₃ supported CaO and MgO catalysts with pure CaO and MgO catalysts. It was stated that the use of Al₂O₃ as support improved the catalyst activity. They observed basicity itself was not enough to explain high catalytic activity as their catalyst with lower basicity actually has given higher methyl esters yield than the one tested with catalyst showed higher basicity. Thus, they checked the basic strength of their catalysts and saw that high basicity with high basic strength was outperformed by the catalyst with lower basicity and milder basic strength. Hence, they concluded that basic strength also has a strong influence on catalyst activity, and high basic strength had a negative influence on the catalytic activity (Umdu, Tuncer, and Seker

2009). Çakırca et al. used CaO/dolomite as catalyst to produce methyl ester biodiesel from *C. protothecoide* oil and achieved to obtain fatty acid methyl ester (FAME) yield of 90% in 3 hours at 65°C (Cakirca et al. 2019). They tested the effects of different levels of CaO loading on dolomite and different alcohol:lipid molar ratios on the transesterification reaction. They stated that as the CaO loading increases, the CaO phases on their catalysts increase which improves the catalytic activity. On the other hand, they have found the optimal alcohol:lipid ratio as 6:1 as the further increase in alcohol amount decreased the methyl esters yield. They explained that behavior by stating catalyst became more dilute in reaction medium and reaction became kinetically slower (Cakirca et al. 2019). Teo et al. investigated the transesterification of *Nannochloropsis oculata* over calcium methoxide catalyst with methanol and obtained 92% biodiesel yield at 60°C (Teo et al. 2014). They have also studied the effect of alcohol:lipid molar ratio and they achieved high methyl ester yields with high alcohol:lipid ratio of 60, which is ten times higher than the alcohol ratio used in the study of Çakırca et al. (Teo et al. 2014, Cakirca et al. 2019). Recently, Turkkul et al. studied transesterification of *Spirulina sp.* and *Nannochloropsis oculata* microalgal lipids over CaO/Al₂O₃ catalyst with ethanol to produce ethyl ester biodiesel and they managed to obtain 90-99% biodiesel yield in 30 min. at 50°C (Turkkul, Deliismail, and Seker 2020). They also obtained high ethyl esters yield at high alcohol:lipid molar ratio of 48. They compared the activity of their CaO/Al₂O₃ catalyst with pure CaO and Al₂O₃ catalyst. Even though both pure CaO and Al₂O₃ catalyst had higher basicity than CaO/Al₂O₃ catalyst, they showed lower activity and it was correlated to milder basic strength of CaO/Al₂O₃ catalyst. Another key finding of their study is that at high butanol molar lipid ratio, between the reaction time of 30 and 60 minutes, they observed a decrease in ethyl esters yield which was explained by the possible occurrence of glycerolysis reaction which led to reverse reaction (Turkkul, Deliismail, and Seker 2020).

2.2. Biodiesel Synthesis with Butanol

Butanol use in biodiesel synthesis was not studied as extensively as methanol and ethanol; most of the studies include butanol was utilized homogenous catalysts as it was briefly summarized in Table 3. For instance, Nye et al. studied the used frying oil conversion into biodiesel by using butanol under the presence of KOH and H₂SO₄

catalysts (Nye et al. 1983). They obtained 59.5% and 78.1% butyl esters yields for KOH and H₂SO₄ catalysts, respectively. However, the reaction conditions were considerably harsh compared to studies conducted nowadays. Alcohol:lipid molar ratio was chosen as 3.5, which is nearly equal to the stoichiometric ratio. The reaction temperature and time were 105°C and 40 hours for acid catalyzed reactions, while 50°C and 24 hours were used for base catalyzed reactions. Moreover, frying oil was used as triglyceride source, which is high in FFA content; thus, it is expected to observe poor catalytic performance from KOH which could only provide 59.5% butyl esters yield in one day of reaction time. On the other hand, they conducted the same reaction with methanol. Both methanol and butanol have given similar yields for acid catalyzed reaction, yet in the case of base catalyzed transesterification reaction, methanol has given 91.9% of methyl esters yield, which can indicate the ease of methoxide formation compared to butoxide formation (Nye et al. 1983). Nimcevic et al. conducted a similar study with rapeseed oil. They used higher alcohol:lipid molar ratios and lower reaction time, yet they could not achieve high butyl esters yield with KOH catalyst (15.4%), whereas they have obtained high butyl esters yield (97.5%) with H₂SO₄ catalyst. Hence, they claimed that it was not possible to produce a high amount of biodiesel from butanol under the presence of alkali catalysts. In the acid catalyst case, they had to elevate the reaction temperature to boiling temperature of the butanol to obtain high butyl esters yields (Nimcevic et al. 2000). On the other hand, Freedman et al. conducted a similar study with soybean oil and sodium methoxide as the catalyst. They obtained high butyl esters yield of ~95% with butanol:lipid molar ratio of 6:1 at 114°C (Freedman, Pryde, and Mounts 1984). Similarly, Colucci et al. managed to obtain 92% butyl ester conversion in their study where they used soybean oil as the triglyceride source and KOH as the catalyst, in 2 hours at 60°C with butanol:lipid molar ratio of 6:1 (Colucci, Borrero, and Alape 2005). They also executed the reaction with methanol and ethanol under similar reaction conditions, and both alcohols have given the same biodiesel yield as 99%. They claimed that the acidity of the alcohol directly affects the alkoxide formation as it reacts faster with sodium when the acidity of alcohol is higher. They have supported their claim by checking the pK_a values of the alcohols and showed that both methanol and ethanol had a similar pK_a value while the butanol has the highest as 15.5, 15.9, and 19.2, respectively (Colucci, Borrero, and Alape 2005).

The study published by Hajek et al. investigated the transesterification reaction of rapeseed oil by butanol with KOH catalyst. They used high butanol:lipid molar ratios up to 15:1, and they managed to obtain a high conversion, above 90%. Interestingly, they stated that temperature did not have a significant effect on the reaction as they conducted the experiments at 30°C and 80°C. They claimed that equilibrium conversion is already high and achieved at 30°C, so the temperature increase did not make a significant change (Hajek et al. 2017). On the other hand, Jha et al. showed different behavior in their study as they claimed that the increase in temperature from 75°C to 105°C, improved their butyl esters yield; although the highest yield they obtained was in the range of 55-60% (Jha, Gupta, and Kumar 2007). Leadbeater et al. studied the “butobiodiesel”, which is butyl esters, production from plant oil with microwave assisted heating (Leadbeater, Barnard, and Stencel 2008). They used KOH as the catalysts, and thanks to microwave heating, they managed to obtain 80% and 90% of oil conversions in 1 minutes of reaction time at 50°C and 120°C, respectively. Even though microwave heating is different in principle from conventional heating, results showed that temperature increase had an effect on the reaction and gave higher butyl ester yields which contradict the findings presented in the study of Hajek et al. (Hajek et al. 2017, Leadbeater, Barnard, and Stencel 2008).

To the best of my research, only Navas studied the butyl ester production from plant oil under the presence of basic heterogeneous catalysts (Navas et al. 2018). They used soybean and castor oil as the plant oil and synthesized $\text{CaO}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Al}_2\text{O}_3$ and $\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts for the reaction. Initially, they have tested the catalytic activity with methanol and soybean oil, and they obtained 55%, 60% and 41% methyl esters yields, respectively, at 60°C in 6 hours with methanol:lipid molar ratio of 6:1. When they conducted the experiments with castor oil with same conditions, they obtained lower yields as 39% and 24% for the $\text{MgO}/\text{Al}_2\text{O}_3$ and $\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts, respectively which was correlated to different fatty acid compositions of the two oil as castor oil has the higher free fatty acid content. Interestingly, when the castor oil was used for butyl ester synthesis with the same reaction conditions with the reaction temperature of 80°C, it has given significantly higher yields as 97% and 85% for $\text{MgO}/\text{Al}_2\text{O}_3$ and $\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts; while the soybean oil was used, butyl esters yields were decreased to 50% and 46%, respectively. It was stated that the high miscibility of butanol in castor oil might improve the conversion. Unfortunately, they did not execute the butanol used reactions with $\text{CaO}/\text{Al}_2\text{O}_3$. However, they obtained higher biodiesel yields with butanol compared

to methanol, and they claimed that higher pK_a value of butanol facilitated its deprotonation, and consequently the alkoxide formation in contrary to Colucci's claim (Navas et al. 2018, Colucci, Borrero, and Alape 2005). On the other hand, it should be taken into account that, in the study of Navas (Navas et al. 2018), the reaction temperatures for methanol and butanol were different; thus, direct comparison between them can be misleading to make certain comments.

Nevertheless, the general lack of study on butyl esters production with heterogeneous catalysts is preventing the potential of butanol as alternative alcohol from being fully understood, which become one of the main motivations of this study.

Table 3. Transesterification reaction with butanol in literature.

Ref.	Oil	Catalyst	ButOH:Oil	Temperature (°C)	Time	Yield
(Nye 1983)	Frying oil	KOH	3.5	105	24 h	59.5%,
(Nimcevic 2000)	Rapeseed	KOH	6	117	5 h	15.4%
(Freedman 1984)	Soybean	CH ₃ NaO	6	114	1 h	96-98%
(Colucci 2005)	Soybean	KOH	6	60	2 h	92%
(Hajek 2017)	Rapeseed	KOH	15	30 and 80	4 h	>90%
(Jha 2007)	Jatropha	NaOH	21	75-90	4 h	55-60%
(Navas 2018)	Soybean	MgO/Al ₂ O ₃ ZnO/Al ₂ O ₃	6	80	6 h	97% 85%

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

60 wt% CaO loaded Al₂O₃ catalysts were synthesized in this study. Calcium nitrate tetrahydrate (Fluka ® Analytical) with a purity of 99.3% was used as CaO precursor. For alumina synthesis, alumina isopropoxide (AIP) (Fluka ® Analytical) with the purity of 98% was used. 65 vol% Nitric acid (HNO₃) solution was used as peptizer in the catalyst synthesis. For the structured catalyst synthesis, porous alumina ceramics calcined at 1525°C were received from Prof. Dr. Muhsin ÇİFTÇİOĞLU.

For the transesterification reaction, commercially available canola oil (Yonca Inc.) was used as the triglyceride source. For the washing step, hydrochloric acid (HCl) 3 vol.% solution was used.

3.2. Methods

3.2.1. Catalyst Preparation

Previous studies conducted on CaO loading in our research group showed that 60 wt% CaO loading had shown high activity for transesterification reaction for methanol and ethanol. Therefore, CaO loading ratio was chosen as 60 wt% (Turkkul, Deliismail, and Seker 2020, Yalman 2012).

60 wt% CaO/40%Al₂O₃ catalysts were prepared by using the sol-gel method. First, the necessary amount of AIP has dissolved in calculated amount of water at 85°C under constant stirring at 1100 rpm for 1 hour in a schot bottle. Then, the calculated amount of nitric acid was added to the mixture and continued to be stirring at 1100 rpm at 85°C for 1 additional hour. Meanwhile, the necessary amount of calcium nitrate tetrahydrate was dissolved in distilled water under room temperature. 1 hour after the

addition of nitric acid, calcium nitrate solution was poured into the alumina sol and then they were stirred for 1 hour at 1100 rpm and 85°C. Then obtained mixture was left for gelation at 70°C without any stirring to remove the excess amount of water by slow evaporation. After the completion of gelation, the obtained gel has dried at 120°C for 14 hours. For the calcination step, Yalman showed that 60wt% CaO loaded CaO/Al₂O₃ catalysts calcined at 700°C has given high biodiesel yield (Yalman 2012), which was also supported by the study of Turkkul (Turkkul, Deliismail, and Seker 2020). Thus, the catalysts were calcined at 700°C for 6 hours, and they were grounded and sieved to less than 325 mesh sizes to be used in the transesterification reaction. The whole process is briefly shown in Figure 13.

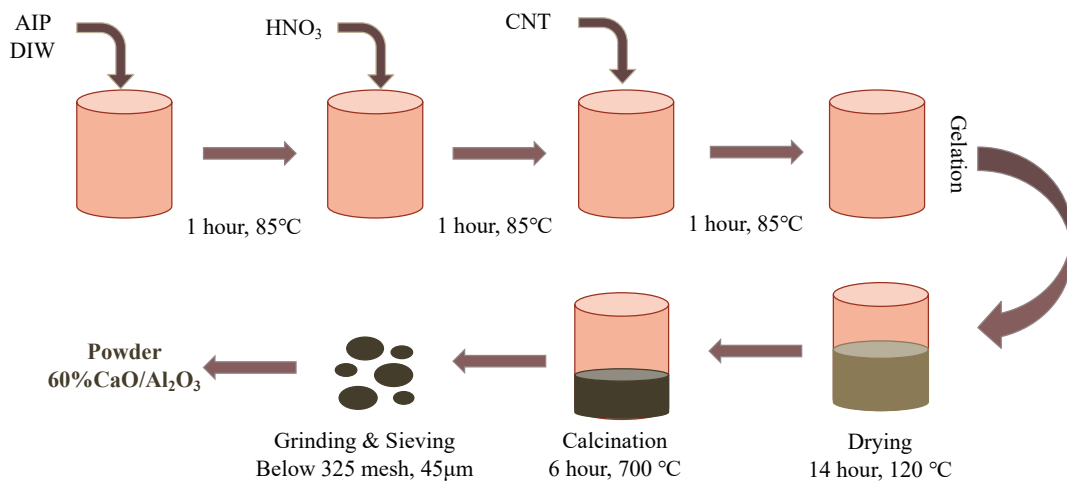


Figure 13. Synthesis of 60%CaO/40%Al₂O₃ catalysts.

For the structured catalyst, catalysts were prepared by following the same steps. The only difference was grinding the dried gel to obtain powder form before the calcination. Then the powder was poured onto the surface of the previously wetted alumina ceramic plate received from Prof. Dr. Muhsin ÇİFTÇİOĞLU, and carefully pressed onto the surface with the tip of the spatula. Then the ceramic was placed into the oven and calcined at 700°C for 6 hours. Both prepared structured and powdered catalyst are shown in Figure 14.

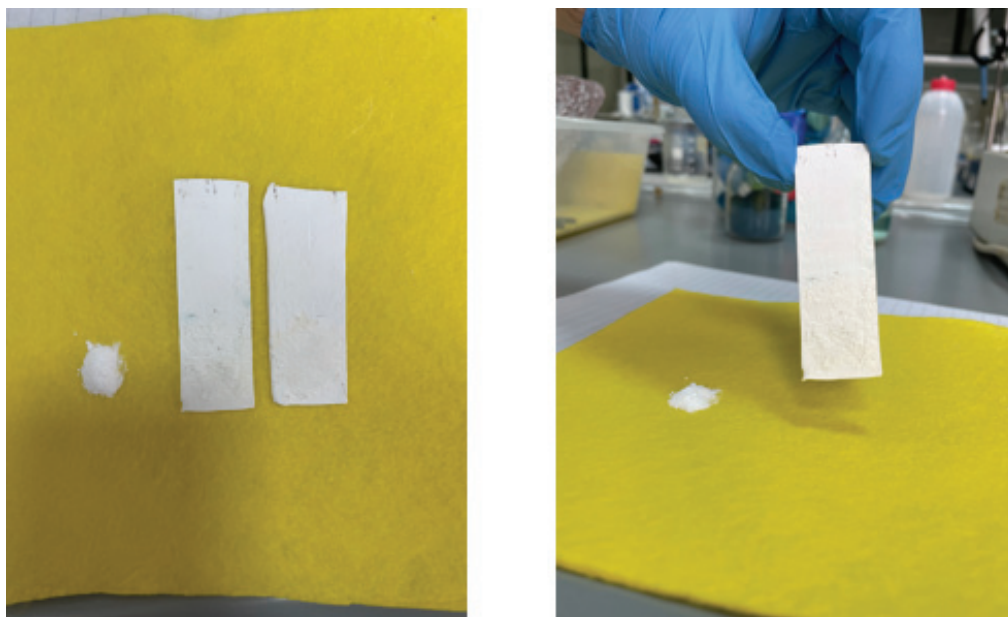


Figure 14. Powdered and structured catalysts.

3.2.2. Catalyst Activity

Catalyst activity was tested by conducting the transesterification reaction of canola oil with butanol to obtain FAME in a batch reactor at 50°C and 1 atm with following reaction conditions; 9:1, 24:1, 48:1 and 60:1 butanol:lipid molar ratios; 6.0 wt%, 9.0 wt% and 12.0 wt% of the lipids as the catalyst amount; and 10 minutes, 30 minutes, 60 minutes and 240 minutes of the reaction time. Experimental steps are summarized in Figure 15 and sample naming according to the reaction conditions were given in Table 4.

First, the previously prepared catalyst was calcined for 1 hour prior to reaction and placed into schott bottle, then the calculated amount of butanol was added, and they were mixed at 900 rpm for 10 minutes at 50°C to obtain butoxides on the catalyst surface. To avoid heat transfer resistance, the calculated amount of canola oil has also been heated up to 50°C, and then it was poured into the catalyst and butanol mixture, then they were mixed at 900 rpm at 50°C for corresponding reaction time. After the reaction was completed, the sample was centrifuged at 6000 rpm and at 25°C for 10 minutes to separate the catalyst from the reaction medium. At the end of the reaction, since butanol, FAME, oil and glycerol were miscible with each other, a single-phase mixture was obtained after it was separated from the catalyst. Nevertheless, the sample was washed with 3 vol%

hydrochloric acid with a reaction medium:acid solution volume ratio of 1:1 at room temperature and 1000 rpm for 1 hour to prevent homogenously catalyzed transesterification reactions due to possible CaO leaching from the catalyst. At the end of the washing step, the sample was centrifuged at 6000 rpm and 25°C for 10 minutes again, and three different phases were obtained as: butanol and butyl esters rich upper phase, oil rich middle phase, and glycerol containing acid solution rich bottom phase.

Table 4. Samples with corresponding reaction conditions.

Sample Name	Butanol:Lipid (Molar)	Catalyst Amount (%wt)	Reaction Time (min)
CB_9_6_30	9	6	30
CB_9_6_60	9	6	60
CB_9_6_240	9	6	240
CB_9_9_60	9	9	60
CB_9_9_30	9	9	30
CB_24_6_30	24	6	30
CB_24_6_60	24	6	60
CB_24_6_240	24	6	240
CB_48_6_10	48	6	10
CB_48_6_30	48	6	30
CB_48_6_60	48	6	60
CB_48_12_60	48	12	60
CB_48_6_240	48	6	240
CB_60_6_10	60	6	10
CB_60_6_30	60	6	30
CB_60_6_60	60	6	60
CB_60_12_60	60	12	60
CB_60_6_240	60	6	240

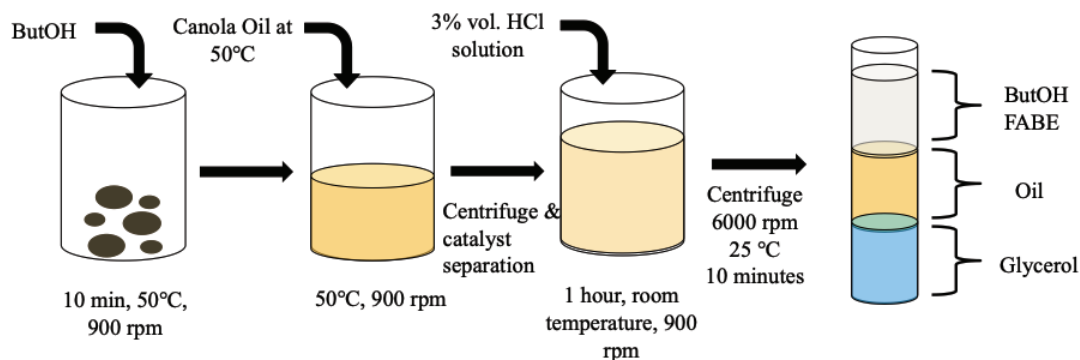


Figure 15. Experimental steps of activity test.

A similar procedure was also applied for the activity test of structured catalysts. They were calcined at 700°C for 1 hour prior to reaction. They were hung on the top of schott bottles where their catalyst covered ends sticking into butanol filled reaction medium. Again, it was kept in the butanol for 10 minutes at 50°C to obtain butoxides on the catalyst surface. However, to avoid magnetic stirrer harming alumina ceramics, the stirring pace was decreased to 500 rpm. After that, oil, preheated to 50°C, was introduced to the reaction medium and they were mixed for the corresponding reaction time. At the end of the reaction, ceramic plates were removed from the schott bottles and the mixture was directly acid washed without the need of centrifuging. The experimental setup for the structured catalyst is presented in Figure 16.

FABE content has been determined by GC analysis. GC analysis was conducted by using an Agilent 6890 N Gas Chromatograph with an FID detector. DB-WAX 122e7032 column with a 60 m of column length, 0.25 mm of column diameter, and 0.25 mm of film thickness has been used in the analysis. The isothermal analysis method was used; the temperature was 250°C for the injection part while it was set to 225°C for the column. Helium flow was adjusted to 32 cm/s while the split ratio was set at 150. FABE yield has been determined in two different ways.



Figure 16. Experimental set up for structured catalyst.

In the first method, Fabe yield was determined from the remaining oil at the end of the reaction. Theoretically, 1 g of canola oil produces 1.207 g of Fabe in the case of 100% oil conversion, as given in Table 3. In that manner, the oil phase obtained after washing step left in the oven at 120°C for 4 hours to evaporate little amount of butanol that it contains, and it weighted. Then consumed oil and produced Fabe yield was calculated through equations (1-2). After the calculation of obtained Fabe yield, the result has divided to maximum achievable Fabe yield, 1.207 g, and multiplied by 100 to obtain Fabe yield as a percentage (%) as given in equation 3.

$$\begin{aligned} \text{Initial amount of oil (g)} - \text{Amount of oil obtained form middle phase (g)} \\ = \text{Amount of oil consumed during reaction(g)} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Amount of Fabe produced (g)} \\ = 1.207 \times (\text{Amount of oil consumed during reaction(g)}) \end{aligned} \quad (2)$$

$$\text{Fabe Yield (\%)} = \frac{\text{Fabe yield (g)}}{1.207 \text{ (g)}} \times 100 \quad (3)$$

In the second method, the sample giving the highest Fabe yield has been taken as a reference, which is CB_48_6_240. The amount of Fabe obtained from the transesterification reaction was calculated via equations 1 and 2. Then, the calculated amount was correlated to are under the curve obtained from GC analysis by dividing

FABE yield to GC area to obtain reference FABE Yield:Area ratio. GC areas of all other samples were then multiplied by that reference ratio to determine their corresponding FABE yields, as shown in equations 4 and 5. After that, by using equation 3, yields were calculated as a percentage. For error calculation, experiments were repeated 6 times at single point with the confidence interval of 95%.

$$\text{Reference Ratio} = \frac{\text{Reference FABE yield}}{\text{GC Area of reference sample}} \quad (4)$$

$$\text{FABE yield of sample} = \text{Reference Ratio} \times \text{GC Area of sample} \quad (5)$$

3.3. Catalyst Characterization

X-ray diffraction (XRD) analysis (Philips X'pert Pro XRD) was conducted at 40kV and 45mA to determine crystalline phases present on the catalyst. Scherrer equation given below was used to calculate average crystalline sizes from the peak broadening of the diffraction peaks. Average crystalline size was represented as d , K was Scherrer constant, λ was the wavelength and equal to 0.15406 nm, B was the peak broadening of diffraction peak determined by the full width at half maximum of the peak and θ was the main diffraction angle of the peak given in degree.

$$d = \frac{K\lambda}{(B\cos\theta)} \quad (6)$$

FTIR analysis was done prior to determining the basicity and basic strengths of the catalysts. CO₂ was used as the probe molecule, and the amount of irreversibly adsorbed CO₂ has given the total amount of basic sites on the catalysts surface, while adsorption wavenumbers were used to compare the basic strengths of the active sites on the catalyst surface (Kozo Tanabe 1990). For leaching analysis, ICP test was conducted to determine Ca ion in the reaction medium for the reaction times of 1 hour and 4 hours. SEM (Scanning Electron Microscope) was used to investigate the morphology of the structured catalysts and EDX (Energy dispersive X-ray) analysis was conducted to determine the CaO/Al₂O₃ catalysts covered areas on alumina ceramics.

Table 5. Fatty acid content of canola oil.

Fatty Acid	Molecular Weight (g/mol)	Percentage wt. %
Palmitic acid (C ₁₆ H ₃₂ O ₂)	256.4	3.9
Stearic acid (C ₁₈ H ₃₆ O ₂)	184.5	1.1
Oleic acid (C ₁₈ H ₃₄ O ₂)	282.5	64.4
Linoleic acid (C ₁₈ H ₃₂ O ₂)	280.5	20.4
Linolenic acid (C ₁₈ H ₃₀ O ₂)	278.4	9.6
Total MW	277.27	99.4
FABE	Molecular Weight (g/mol)	Percentage wt. %
Buthyl palmitate (C ₂₀ H ₄₀ O ₂)	312.53	3.9
Buthyl stearate (C ₂₂ H ₄₄ O ₂)	340.58	1.1
Buthyl oleate (C ₂₂ H ₄₂ O ₂)	338.56	64.4
Buthyl linoleate (C ₂₂ H ₄₀ O ₂)	336.55	20.4
Buthyl linolenate (C ₂₂ H ₃₈ O ₂)	334.53	9.6
Total MW	334.66	99.4
Fatty Acid / FABE	Converted Oil (g)	Produced FABE (g)
Palmitic acid / Buthyl palmitate	3.92	4.78
Stearic acid / Buthyl stearate	1.11	2.04
Oleic acid / Buthyl oleate	64.79	77.65
Linoleic acid / Buthyl linoleate	20.52	24.62
Linolenic acid / Buthyl linoleate	9.66	11.61
Total	100.00	120.70

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Crystalline Phases and Basicities of the Catalysts

Alumina-calcium oxide catalyst (60 wt% on CaO on Al₂O₃) were synthesized and characterized in our previous study done in our research group. It is also recommended to check for the study of Turkkul et al. (Turkkul, Deliismail, and Seker 2020). Diffraction patterns observed on Figure 17 were corresponding to CaO, Ca(OH)₂, CaCO₃, Al₂O₃, 2CaO.Al₂O₃.8H₂O and 3CaO.Al₂O₃.3CaCO₃.3H₂O crystalline phases where latter two were hydrated form of mixture of the other crystalline phases. The average crystallite sizes of CaO, Ca(OH)₂ and CaCO₃ were determined as 43.9 nm, 27.4 nm, 39.59 nm, respectively via Scherrer equation. It was not possible to calculate the average crystallite sizes of Al₂O₃, 2CaO.Al₂O₃.8H₂O and 3CaO.Al₂O₃.3CaCO₃.3H₂O due to their overlapping diffraction peak.

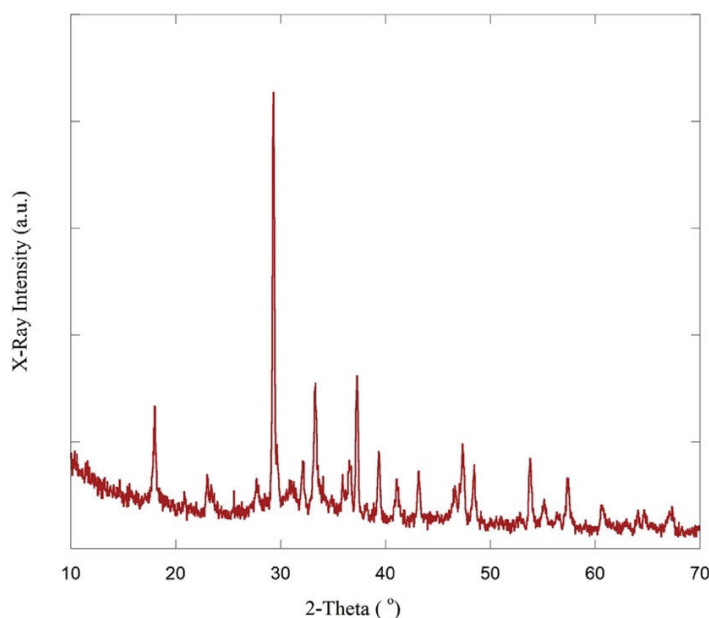


Figure 17. XRD of 60%CaO/Al₂O₃ calcined at 700°C (Source: Turkkul 2020).

Total basicity and CO₂ adsorption maximum wavenumber of powdered 60 wt% CaO/Al₂O₃ catalyst and pure CaO catalyst are summarized in Table 6. Total basicity of 60 wt% CaO/Al₂O₃ determined as 41 μmol CO₂/g catalyst while pure CaO was calculated as 192.6 μmol CO₂/g. Even though basicity of pure CaO was higher than the 60 wt% CaO/Al₂O₃ catalyst, it did not lead to any FBE yield or oil conversion. Similarly, pure Al₂O₃ did not lead any FBE yield even though it has a basicity of 47.1 μmol CO₂/g of catalyst (Turkkul, Deliismail, and Seker 2020). According to the FTIR results, strongest adsorption wave number of pure CaO occurred at a center wavenumber of 1454 cm⁻¹, while the strongest adsorption wave number of 60 wt% CaO/Al₂O₃ catalyst was observed at 1432 cm⁻¹, indicating that 60% CaO/Al₂O₃ catalyst had weaker basic strength than pure CaO. Moreover, lack of bidentate and unidentate carbonate species and dominant presence of bicarbonate species on 60 wt% CaO/Al₂O₃ were correlated to the reason for its lower basic strength compared to pure CaO where unidentate carbonate species were dominant. Thus, even though 60% CaO/Al₂O₃ catalyst had lower basicity than pure CaO, its relatively milder basic strength was thought to be the reason for high canola oil conversion to fatty acid butyl esters.

Table 6. Total basicity (μmol CO₂/g catalyst) using FTIR.

Catalysts calcined at 700°C	Total Basicity (μmol CO₂/g of catalyst) using FTIR	FTIR CO₂ adsorption maximum wavenumber (1/cm)
60% CaO/Al ₂ O ₃	41	1266
		1333
		1432
		1635
		1798
Pure CaO	192.6	2513
		1074
		1424
		1484
		1653
		1794

Different sites of structured catalysts were examined through SEM and EDX elemental analysis. An example of SEM view of structured catalyst was shown in Figure 18. The darker sides in the raw picture are corresponding to alumina ceramic without catalyst covering whereas grey areas are corresponding to CaO/Al₂O₃ catalyst. Even the EDX results shows that darker sides contain Al and O atoms without Ca presence and lighter sides contains Ca, Al and O atoms. Since oxygen is present in both molecular structures of Al₂O₃ and CaO it has appeared all around the mapping. Similarly, both ceramic and synthesized catalysts contain Al. Thus, it also appeared everywhere on the surface. Therefore, Ca atoms are the indicator of where the catalysts are covering the alumina ceramics and it perfectly matches with the lighter areas observed on the raw picture.

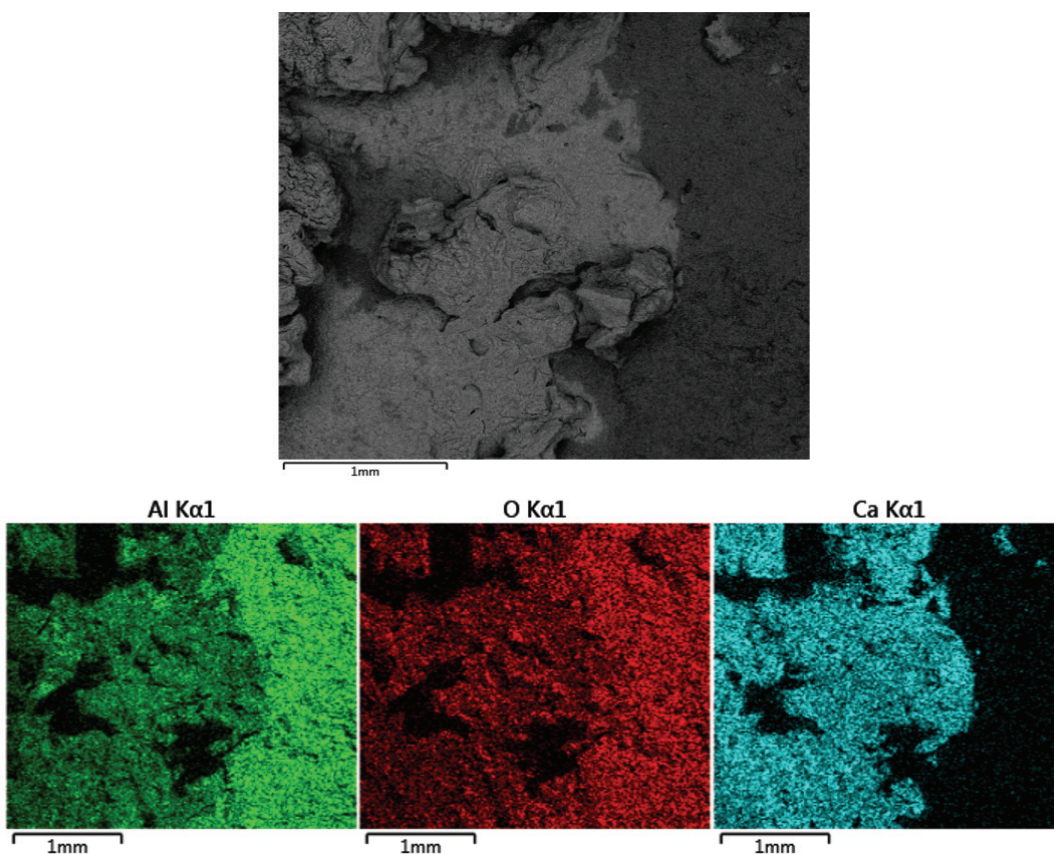


Figure 18. SEM view and EDX mapping of structured catalyst.

Elemental analysis has conducted for 8 different catalyst covered sites and elemental distribution for all the different sites were nearly similar. Average values for elemental distribution in terms of weight and atomic percentages were given in Table 7.

Table 7. Elemental distribution on structured catalyst.

Element	Wt%	Atomic %
C	2.91	5.14
O	46.31	60.75
Al	29.59	22.84
Ca	21.09	11.17
Total:	99.90	99.90

4.2. Catalyst Activity

Butyl esters yields are compared as a function of butanol:lipid ratios, the reaction time and the catalyst amount at 50°C. As seen in Table 8 where the powder catalysts were used, catalyst amount did not show a significant effect on the butyl ester yield. Except the samples CB_9_6_30 and CB_9_9_30, increasing catalyst amount has led to yield increments within the error whereas it slightly improved butyl ester yields for the samples with 30 minutes of reaction time from 28% to 34%, which indicates that all the samples were at or close to equilibrium at the end of 1 hour.

Effect of reaction time on butyl ester yields on different butanol:lipid ratios are shown on Figure 19 which demonstrates that butyl esters yield did not show a significant change after 1 hour for the butanol:lipid molar ratios of 9,24 and 60 since the reactions might have reached to equilibrium. On the other hand, at 48 of butanol:lipd molar ratio, biodiesel yield had improved from 72% to 89% when the reaction time was increased from 1 hour to 4 hours which indicates it did not reach equilibrium in 1 hour, unlike others. For instance, at 48 of butanol:lipid molar ratio, it was expected to observe an increase in butyl esters yield when the catalyst amount has increased from 6 to 12. Yet it only increased from %69 to %74 which is in the error bar of 6.64%. Nevertheless, at the butanol:lipid molar ratios of 9,24 and 48, yields were significantly increased from 28%, 36% and 56% to 32%, 45% and 72% respectively, when the reaction time has increased

from 30 minutes to 1 hour. At the butanol:lipid molar ratio of 60, Figure 19 shows that reaction time had not a significant effect on the butyl ester yield after first 30 minutes since it only improved butyl ester yield from 61% to 68%, which is in the range of error bar, between the reaction times of 30 minutes and 1 hour. Even though the further increase in reaction time to 4 hours yielded 73% of butyl ester, which could be considered as an improvement when it is compared with the yield at the first 30 minutes, that increment is still in the range of the error bar when it is compared with the yield obtained at the end of the first 1 hour of the reaction. This is due to the high butanol:lipid molar ratio of 60 might turned reaction medium too dilute in triglyceride when the oil conversion reaches 61%.

Table 8. Butyl ester yields as a function of catalyst amount for powder catalysts.

Sample Name	Butanol:Lipid Ratio	Catalyst Amount (%wt)	Reaction Time	Butyl Ester Yield (%)
CB_9_6_30	9:1	6	30 min	28±1.86
CB_9_9_30	9:1	9	30 min	34±2.26
CB_9_6_60	9:1	6	1h	32±2.12
CB_9_9_60	9:1	9	1h	35±2.324
CB_48_6_60	48:1	6	1h	72±4.78
CB_48_12_60	48:1	12	1h	74±4.91
CB_60_6_60	60:1	6	1h	68±4.51
CB_60_12_60	60:1	12	1h	76±5.04

Previous study of Turkkul (Turkkul, Deliismail, and Seker 2020) has shown that higher alcohol:lipid molar ratio promotes forward transesterification reaction rate and gives higher biodiesel yield. In fact, one way to increase equilibrium conversion is using higher butanol:lipid molar ratio than the stoichiometric butanol:lipid molar ratio of 3. In this study, even the lowest butanol:lipid molar ratio was 3 times higher than the stoichiometric ratio while the highest butanol:lipid molar ratio was 20 times higher. Theoretically, it could have been possible to reach 100% equilibrium conversion at butanol:lipid molar ratios of 48 and 60 and it was expected to obtain higher butyl esters

yields as the butanol:lipid molar ratio increases. Figure 20. demonstrates the effect of butanol:lipid molar ratio on butyl esters yield for the catalyst amount of 6 wt%. It is shown that, increasing butanol:lipid molar ratio from 9 to 48 resulted in higher butyl esters yield yet further increase in butanol:lipid molar ratio led to small decrease in butyl ester yield. For instance, for 1 hour of reaction time, biodiesel yield has decreased from 72% to 68% when butanol:lipid molar ratio was increased from 48 to 60. Decrease in butyl esters yield has become more significant when the reaction has lasted for 240 minutes where it was decreased from 89% to 73%. Thus, it can be claimed that even though high butanol:lipid molar ratio promotes the forward transesterification reaction and increases the equilibrium conversion, after butanol:lipid molar ratio of 48; dilution effect starts to become dominant and decreases the reaction rate. Moreover, at high butanol:lipid molar ratios of 48 and 60, it was observed that biodiesel yields has reached to 70% and 73% in first 10 minutes of reaction respectively, then they were decreased to 56% and 61% when the reaction time increased to 30 minutes as shown in Figure 19. This could be happened due to the glycerolysis reaction, shown in equations (1)-(3) below, occurring in series with transesterification reaction shown in equations (4)-(6).

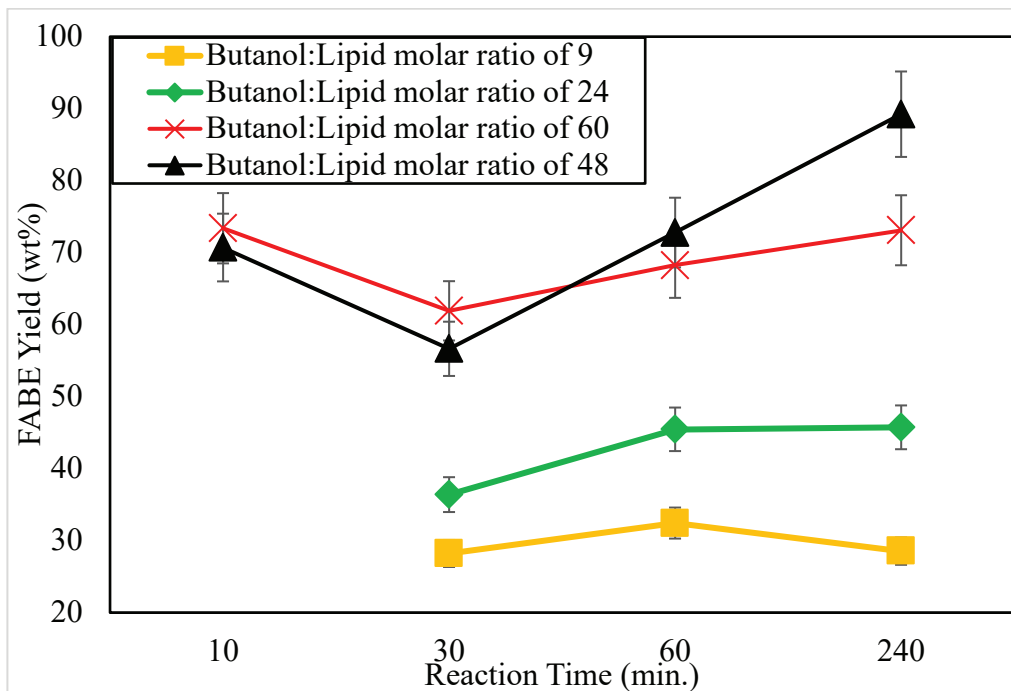
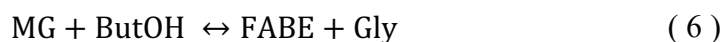


Figure 19. Effect of reaction time on different butanol:lipid molar ratios with the powder catalyst amount of 6 wt%.

Glycerolysis reaction:



Transesterification reaction:



TG is referring triglyceride; DG is diglyceride; MG is monoglyceride; Gly is glycerol; FABE is fatty acid butyl ester and ButOH is butanol. In literature (Zhong et al. 2013), it was stated that glycerolysis reactions are favored by base catalyst and high solvent amount is necessary for glycerolysis reaction at relatively low temperatures. At butanol:lipid molar ratios of 48 and 60, the conversion was already reached to 70% and 73% in the first ten minutes, and enough glycerol was generated through the transesterification reactions (4-6) to allow glycerolysis reaction to take place (1-3) when the reaction time has increased to 30 minutes. Consequently, the increasing amount of DG and MG in the reaction medium due to the glycerolysis reaction led reverse transesterification reaction to occur and consumed FABE to form TG, which has resulted in a decrease in butyl esters yield. At relatively lower butanol:lipid molar ratios such as 9 and 24, no butyl esters formation have observed in the first ten minutes, and further increase in reaction did not lead to any decrease in FABE yield, which indicates that glycerolysis reactions only occurred at high alcohol:lipid molar ratios under the presence of enough amount of glycerol which is a similar trend that has been observed in the study of Turkkul (Turkkul, Deliismail, and Seker 2020).

Table 9 shows the dissolved Ca cation amount in FABE for different reaction times. At butanol: lipid molar ratio of 48 with catalyst amount of 6 wt% and 1 hour of reaction time, dissolved Ca cation amount in butyl ester biodiesel was found less than 2

ppm which is a much lower amount than that found in our previous studies where methanol and ethanol were used as alcohol (Turkkul, Deliismail, and Seker 2020, Umdu 2008). However, it was found that as the reaction time was increased from 1 hour to 4 hours, dissolved Ca cation amount in biodiesel increased drastically. Even so, it was checked that if dissolved Ca cations caused homogenously catalyzed transesterification reaction and no butyl ester formation has been observed. Thus, it was concluded that, all the reactions conducted in this study were heterogeneously catalyzed by 60 wt.% CaO/Al₂O₃ catalyst.

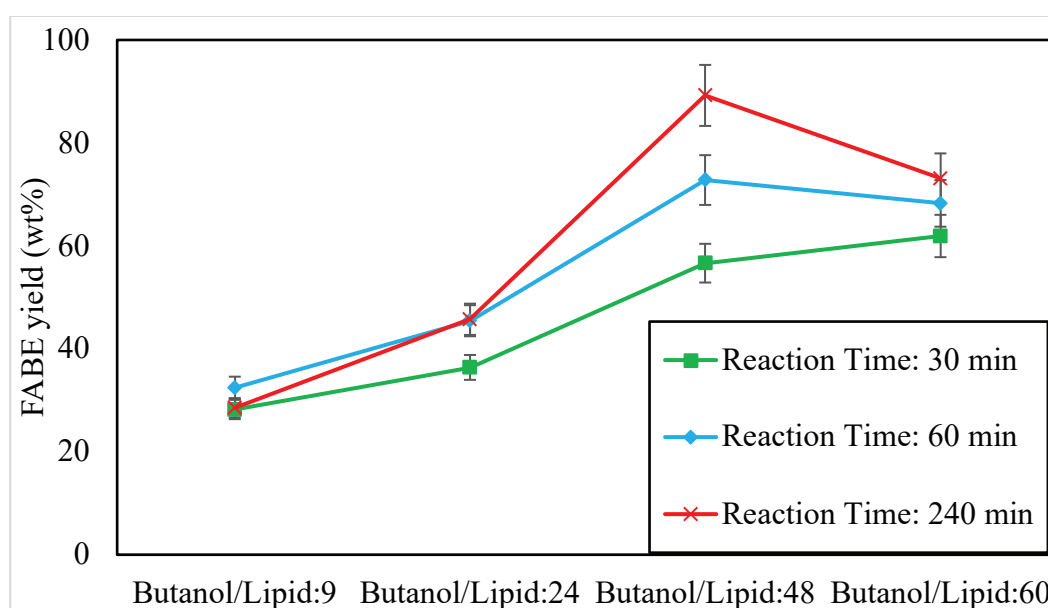


Figure 20. FAME yield as a function of butanol:lipid molar ratio and reaction time for the powder catalyst amount of 6 wt%.

Activity of structured catalysts was tested for butanol:lipid molar ratio of 48:1 and the reaction times of 1 hour and 4 hours, as they have given the highest butyl esters yield for powdered catalysts cases. They are also tested for 4 runs to investigate the reusability. For the case of 1 hour of reaction time, yields were determined as 67%, 56%, 57% and 55% for each consecutive run as it is shown in Figure 21. Figure clearly shows that activity of the catalysts decreased after the first run and then stayed constant for the further runs. It was an expected behavior considering the ICP results of the leaching test. However, ICP tests showed that leaching was occurring even in the 4th hour of the reaction yet in the structured catalyst case, there was no activity loss after the 1st run. This could be indicating that all the weakly bounded Ca ions on the catalyst surface were leached

out in the 1st hour of the reaction. Compared to the powdered catalyst, structured catalyst has given lower yields for all the executed runs, which is also expected since the available catalyst surface area was decreased in the structured case.

Table 9. Amount of dissolved Ca cation in FABE at butanol:lipid molar ratio of 48 and powder catalyst amount of 6 wt%.

Reaction Time	Ca (mg/L)
1 hour	1.405
4 hours	232.761

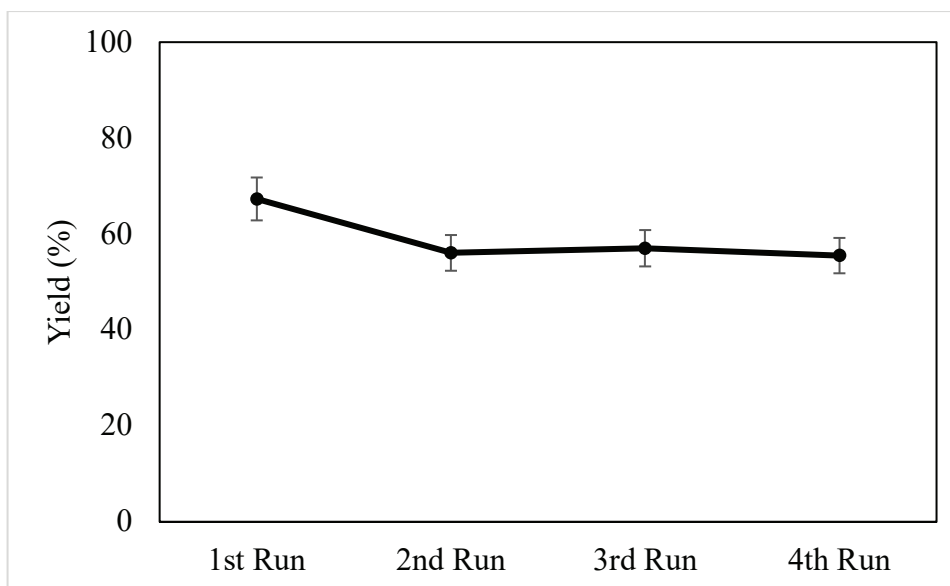


Figure 21. Activity of structured catalyst for the butanol:lipid molar ratio of 48:1 with 1 hour of reaction time.

The activity of the structured catalyst for the butanol:lipid molar ratio of 48:1 with 4 hours of reaction time was shown in Figure 22. Yields were improved since the reaction lasted for 4 hours as 67% was increased to 77% for the initial run and then it stayed constant at around ~65%. Similarly, activity loss was only observed after the 1st run which supports the idea of “all weakly bonded Ca ions leached out in the 1st hour of the reaction”. When it is compared with the powdered catalyst, butyl esters yield decreased from 89% to 67% for the initial run. It can be again explained by the decrease of the

available surface area on the structured catalyst. Corresponding yields for each run of structured catalysts were briefly summarized in Table 10.

Table 10. FABE yields obtained by structured catalysts.

Reaction time: 1 hour		Reaction time: 4 hours	
Run	FABE Yield (%)	Run	FABE Yield (%)
1st	67.32	1st	77.08
2nd	56.07	2nd	63.38
3rd	57.04	3rd	65.09
4th	55.50	4th	63.21

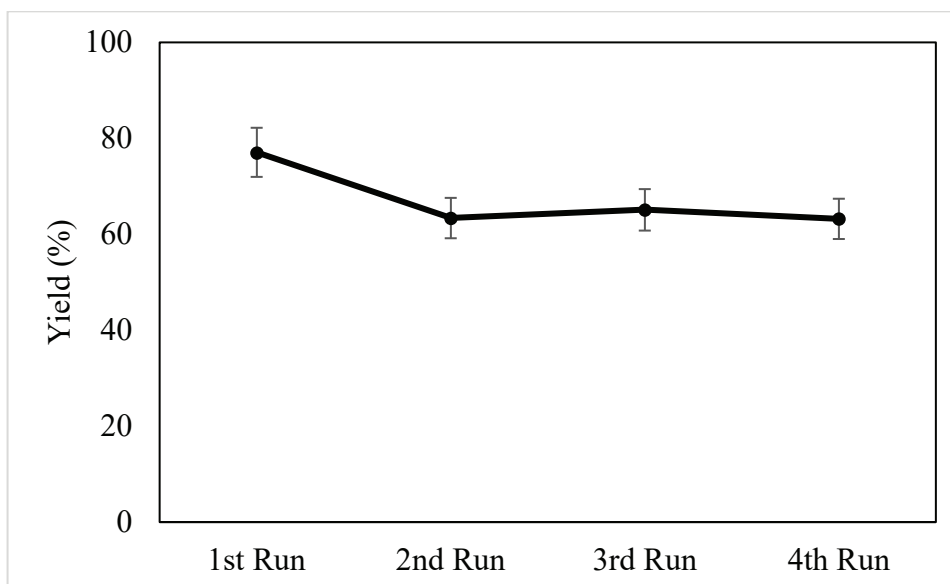


Figure 22. Activity of structured catalyst for the butanol:lipid molar ratio of 48:1 with 4 hour of reaction time.

CHAPTER 5

CONCLUSION

In this study, the transesterification reaction of canola oil with butanol was investigated over powder and structured CaO/Al₂O₃ catalyst. Both powdered and structured catalysts were prepared via single step sol-gel method with the only difference of calcination on the surface of alumina ceramic in the case of structured catalyst.

Regardless of the form of the catalyst, 60 wt% CaO/Al₂O₃ catalysts have shown high activity at high butanol:lipid molar ratios of 48:1 and 60:1. For instance, 70% and 73% FAME yield has been achieved in 10 minutes for transesterification reaction of canola oil with catalyst amount of 6 wt% at butanol:lipid molar ratios of 48 and 60, respectively at 50°C and 1 atm. Higher yields were achieved for longer reaction times. 89% FAME yield was obtained in 4 hours at butanol:lipid molar ratio of 48:1 for the powdered catalyst. Even though FAME yields were decreased for structured catalysts, it still has shown high activity with ~55% and ~65% FAME yields in 1 and 4 hours at butanol:lipid molar ratio of 48:1. Moreover, they were reused 4 times and no activity loss was observed after the 1st run.

FAME production has not been achieved over pure CaO catalyst even though its higher basic site density compared to 60% CaO/Al₂O₃ catalyst. This can be an indication of the importance of basic strength on the catalyst for transesterification reaction. For instance, relatively weaker basic strength of 60% CaO/Al₂O₃ might favor the transesterification reaction of canola oil to FAME.

Glycerolysis reaction did not occur at low butanol:lipid molar ratios. At high butanol:lipid molar ratios of 48:1 and 60:1, and 30 minutes of reaction time; glycerolysis reaction has occurred and promoted reverse transesterification reaction.

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