

**BIODIESEL PRODUCTION FROM SAFFLOWER  
USING HETEROGENEOUS CAO  
BASED CATALYSTS**

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**by  
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## ABSTRACT

### BIODIESEL PRODUCTION FROM SAFFLOWER USING HETEROGENEOUS CAO BASED CATALYSTS

In this study, the activities of heterogeneous mixed oxide catalyst; calcium oxide on alumina was investigated in the transesterification of canola and safflower vegetable oils to produce biodiesel, i.e. methyl esters. The primary goal of this study is to understand the effect of calcination temperature and calcium oxide (CaO) loading on the conversion activity of calcium oxide on alumina in the transesterification of canola and safflower vegetable oils. The mixed oxide catalyst was prepared by a modified single step sol-gel method. Calcium oxide was chosen because of its well known basic property.

This study shows that calcium oxide on alumina catalysts having high CaO dispersion, calcined at high temperature, gave high biodiesel yields even under the reaction conditions, such as low reaction temperature, 50 °C, 9 of methanol/Oil molar ratio, 6 wt. % of catalyst/oil, and also short biodiesel reaction time, such as 4 – 10 minutes in the transesterification of safflower and canola oils. Also, it was observed that 70% CaO/Al<sub>2</sub>O<sub>3</sub> catalyst when calcined at 700 °C was the most active catalyst among all the catalysts prepared in this study. Moreover, the reusability of CaO/Al<sub>2</sub>O<sub>3</sub> demonstrated that ~20 – 250 ppm of Ca was lost during the reaction and the amount of Ca cation leaching depended on the reaction time, CaO loading and the calcination temperature. Also, it was found that Ca cation loss occurred during the reaction did not hinder the activity of the catalysts, which was found by the reusing the catalysts for couple times. Besides, when the biodiesel yield was higher than 70%, the system was influenced by external mass transfer limitation.

## ÖZET

### ASPIR YAĞINDAN HETEROJEN CAO BAZLI KATALİZÖRLER KULLANILARAK BİYODİZEL ÜRETİMİ

Bu çalışmada katı karışık oksit katalizör olan alüminyum destek üzerinde kalsiyum oksitin kanola ve aspir bitkisel yağlarının metil esterlere transesterifikasyon aktivitesi çalışılmıştır. Bu çalışmanın esas amacı, kalsinasyon sıcaklığının ve kalsiyum oksit (CaO) eklenmesinin alümina ( $Al_2O_3$ ) üzerinde kalsiyum oksite etkilerinin, kanola ve aspir bitkisel yağlarının transesterifikasyonu üzerindeki dönüştürme aktivitesini araştırmaktır. Karışık oksit katalizör tek basamaklı bir sol-jel yöntemi ile hazırlanmıştır.  $Al_2O_3$  üzerinde CaO trigliseritlerin transesterifikasyonunda önemli role sahip bazik özelliği nedeniyle seçilmiştir.

Bu çalışma, yüksek CaO dağılımına sahip ve yüksek sıcaklıkta kalsine olmuş  $Al_2O_3$  üzerinde CaO katalizörlerin düşük reaksiyon şartlarında dahi (50 °C düşük reaksiyon sıcaklığı, 9 metanol/yağ molar oranı, kütlece %6 katalizör/yağ oranı ve 4 – 10 dakika kısa biyodizel reaksiyon zamanlarında) kanola ve aspir yağlarının transesterifikasyonlarından yüksek biyodizel verimi verdiklerini göstermiştir. Ayrıca, %70'lik  $Al_2O_3$  üzerinde CaO katalizörü 700 °C'de kalsine edildiğinde, bu çalışmada hazırlanmış tüm katalizörler arasında en aktif katalizör olduğu gözlenmiştir. Dahası,  $Al_2O_3$  üzerinde kalsiyum oksitin tekrar kullanılabilirlik sonuçları, 20-250 ppm'lik Ca iyonunun kaybolduğunu ve Ca iyon kaybı miktarı reaksiyon zamanına, CaO miktarına ve kalsinasyon sıcaklığına bağlı olduğunu gösterdi. Ayrıca, reaksiyon sırasında kaybolan kalsiyum (Ca) iyonunun katalizörün aktivitesine engel olmadığı katalizörlerin bir kaç defa kullanılması ile bulundu. Bununla birlikte, sistem, harici kütle transfer limitasyonundan biyodizel verimi %70'den daha fazla olduğunda etkilenmektedir.

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# CHAPTER 1

## INTRODUCTION

Energy has been the most important issue for humankind for centuries because of its short and long term impact on human life and global/local economy. As it can be seen in Figure 1.1, primary energy production in the world has been built on fossil resources (88%) as oil 35%, coal 29%, natural gas 24%, nuclear energy 5% and hydroelectricity 6% (Lin et al., 2011). Similarly, in Turkey, primary energy consumption is based on petroleum (39%), natural gas (21%), coal (26%), hydroelectricity (6%) and others (7%) (Koyun, 2007).

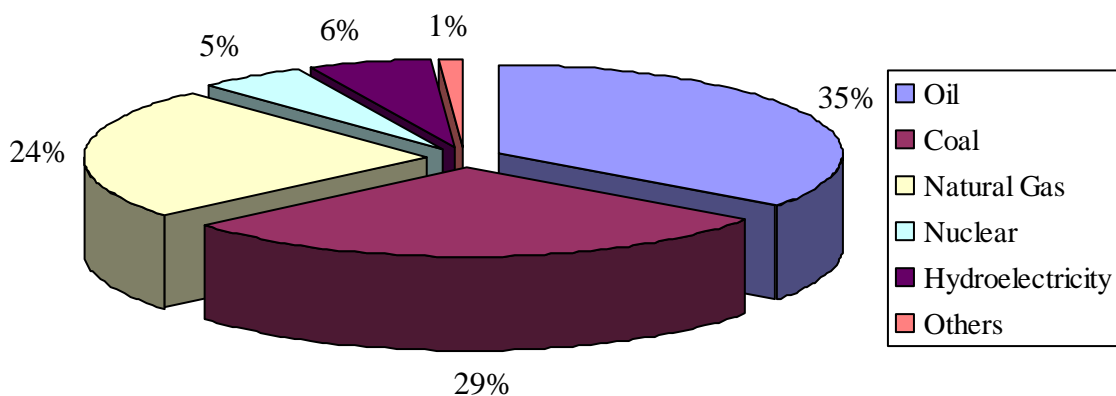


Figure 1.1. World primary energy production in 2009  
(Source: Lin et al., 2011).

Unfortunately, crude oil prices have uncontrollably been fluctuated. Especially over the last decades, these are due to the fast increased primary energy resource consumption in the world, international conflicts and also, the speculative manipulations in crude oil market. From 1970 to 1985, petroleum price increased due to international crises but after 1985, it seemed to stay constant but after year 2000

financial crises, it has started increasing and is estimated that it will keep increasing every year due to declining of oil resources in the world.

In addition to petroleum price increases, the fossil fuels usage result in environmental pollutions, such as air, water and soil pollution. The most importantly, the usage of petroleum derivatives, such as gasoline and diesel, have increased the concentration of CO<sub>2</sub> in Earth's atmosphere to ~392 ppm by volume as of 2011 from 250 ppm measured at beginning of 1900's as seen in Figure 1.2 (Esrl.noaa, 2011). This increased CO<sub>2</sub> concentration causes greenhouse effect; hence resulting in global warming.

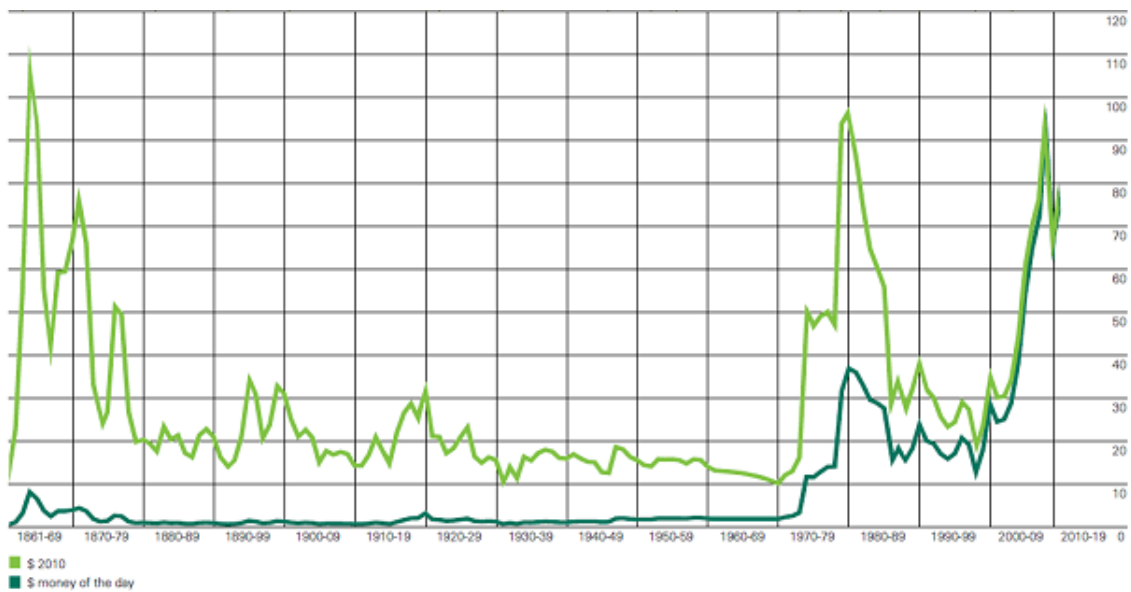


Figure 1.2. Crude oil prices for 1861 to 2010 in terms of US dollars per barrel (Source: BP, 2011).

Also, the main components of the air pollution are sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>) and carbon monoxide (CO). These pollutants come from power and heat generation and residential, industrial, transportation and other sectors, such as agriculture, services, energy industry etc. Especially, transportation, is responsible for 23% of total CO<sub>2</sub> emission; separately, the road transport causes 84% of all transport concerning CO<sub>2</sub> emission, and industry, is responsible for 20% of total CO<sub>2</sub> emission in the world (IEA Statistics, 2011). Similarly, CO<sub>2</sub> emissions by sector in Turkey is given as industry and transport accounting for 24% and 18% of all emissions, respectively

(International Energy Agency, 2010). Industry and transport sectors mostly use fossil fuel resources.

Due to limited resources of fossil energy, over the last decades crude oil price fluctuations and also the greenhouse effect; scientists all over the world have been researching alternative resources which are environmentally friendly, cheap and provides economic benefits without endangering nature. Thus, the renewable feedstock, such as vegetable oils, alcohols, biodiesel etc., has gained significant importance in the recent years.

Vegetable oils have many disadvantages with regards to directly using as a fuel. Firstly, they have much more viscous than petroleum diesel fuel and low volatility. Also, they produce coke formation and result in incomplete combustion problems when using directly in internal combustion engines. Finally, direct usage of them leads to lubricating problems. For this reason, the direct usage could be eliminated when they are converted into the fuels having similar chemical/physical properties of the petroleum based fuels, like biodiesel (methyl esters). Waste cooking oils and animal fats could be used in order to produce biodiesel in addition to producing biodiesel from vegetable oils.

Besides, another renewable feedstock is alcohol. Since the cost competitive production of alcohols is not currently feasible, it is more suitable to use as fuel additives. In fact, biological source based ethanol and methanol productions have acceptable application areas as fuel and fuel additives. Due to the undesired properties of methanol, such as high toxicity, colourless, odourless and nearly invisible flame in daylight, it is less preferable than ethanol. In spite of the low energy content of ethanol, it has still more advantages than gasoline under shorter burn time, high compression ratio and lean burn internal combustion engine (MacLean and Lave, 2003).

The researches have reached at the same conclusion: biodiesel that has more technical and environmental advantages than other renewable feedstock. For instance, biodiesel is non-toxic and oxygenated fuel which results in cleaner burning and also, biodiesel has no greenhouse effects since CO<sub>2</sub> amounts emitted by internal combustion engine and absorbed by plants used to produce vegetable oil are equal to each other. Sulfur content of the plant's oil is very low and comply with the future European regulations and also, has lower toxicity and reactive hydrocarbon species than other diesel fuels; thus, being a domestic and renewable energy source. Furthermore, due to high flash point, storage and transportation can easily be achieved and also no further

modifications are needed for compression ignition engines that use biodiesel. Besides, when biodiesel is blended with diesel fuel, engine performance improves. Moreover, biodiesel degradation in water is about 85 – 88%; being four times faster degradation rate than petro-diesel. Emission rates of PAH (Polycyclic aromatic hydrocarbons, such as Benzo(a)anthracene, Chrysene, Benzo(a)pyrene) and nitro PAH (Nitrofluorene, Nitropyrene, Nitrobenz(a)anthracene, etc.), when using biodiesel are lower than using conventional petro-diesel fuel (Murugesan et al., 2009).

The biodiesel has some disadvantages even though it has many advantages in terms of environmental and technical perspectives. Some disadvantages of biodiesel are as follows:

- High freezing point than diesel fuel makes it hard to use in cold weathers but it may be blended with petro-diesel or freezing point lowering chemicals to eliminate high freezing point problem.
- Currently more expensive, owing to less production of vegetable oil.
- Slightly increased NO<sub>x</sub> emission, but automotive catalytic converters reduce the emission to comply with the regulations.

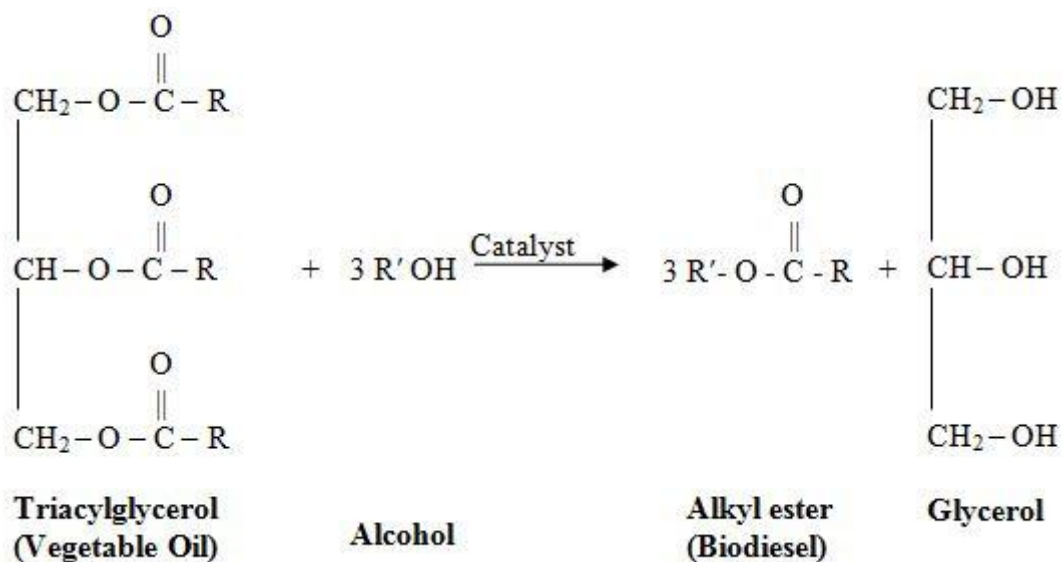


Figure 1.3. The Transesterification reaction. R is various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R' = CH<sub>3</sub>) (Source: Knothe et al., 2005).

Biodiesel, which is known as fatty acid methyl ester (FAME), is the mixture of monoalkyl esters produced from catalyzed reaction of the triglycerides, the major components of vegetable oils and animal fats, with a simple monohydric alcohol as shown in Figure 1.3. Methanol is mostly used as alcohol in the transesterification reaction; so methyl esters are created at the end of the reaction. Also, ethanol (creating ethyl esters) and other alcohols can be used but different processes are required (Vertes et al., 2010). In Figure 1.3, R represents long hydrocarbon chains. Three moles of alcohol react with one mole of triacylglycerol (vegetable oil) in order to produce three moles of alkyl ester (biodiesel) and also, as a result of this reaction one mole of glycerol is produced. Transesterification reaction is a reversible reaction. Moreover, both acidic and basic catalysts can be used to catalyze the transesterification reaction. Acid catalyzed transesterification needs higher than 100 °C and also, is a slow reaction. However, it is known that base catalyzed reaction is fast even at room temperature, but it is highly sensitive to the existence of free fatty acid content (Umdu, 2008). Furthermore, the direct use of all the vegetable oils in compression-ignition (CI) engine cause vehicle operation and durability problems because of high viscosity, low volatility and polyunsaturated characteristics of vegetable oils. The transesterification reaction is an effective and the most common method among others, such as pyrolysis and micro-emulsification, to reduce vegetable oil viscosity and eliminate the operation and durability problems (Ilkılıc et al., 2011).

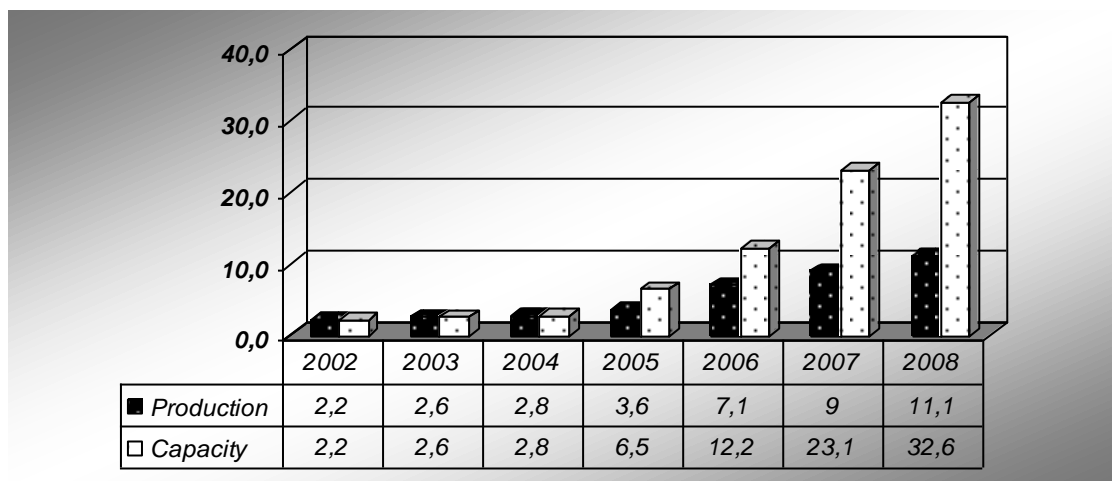


Figure 1.4. World biodiesel production and capacity  
(Source: Emerging-markets, 2011).

World biodiesel production and capacity between 2002 and 2008 are given in Figure 1.4. Looking at the world's demand, biodiesel is the most favorable renewable energy source for the automotive industry according to the International Energy Agency (IEA) which has reported that biodiesel production in 21 leading biofuel producing countries, from 2000 to 2008, increased tenfold and it is possible to double to 21.8 bnl (billion litres) by 2012 (Lin et al., 2011). Moreover, according to 2007 research values, global production of biofuels adds up to 62 bnl per year in 2007 and 10.2 ggaliters, which is equivalent to 2.7 billion gallons, of this production belongs to global biodiesel production. More than 60% of this is produced in Europe, of which approximately 33% belongs to Germany and one-seventh to the USA (Vertes et al., 2010). Biodiesel is the fastest growing biofuel but lower than ethanol because fuel ethanol is reported for most of the world's biofuels, with a production of 49.6 bnl in 2007. However, global biodiesel production has arisen quickly and dramatically in recent years; for instance, global market growth was 43% in 2007, in fact, it was 75% increase in Germany, France, Italy, and Poland and tripling in the United States. The global production increased from 2.1 bnl in 2004 to 3.9 bnl in 2005. Assuming that the development of synthetic biofuel production technologies will accelerate, the potential market for biodiesel is estimated to be in the order of 20 EJ ( $10^{18}$  J) by 2050 (IEA, 2011).

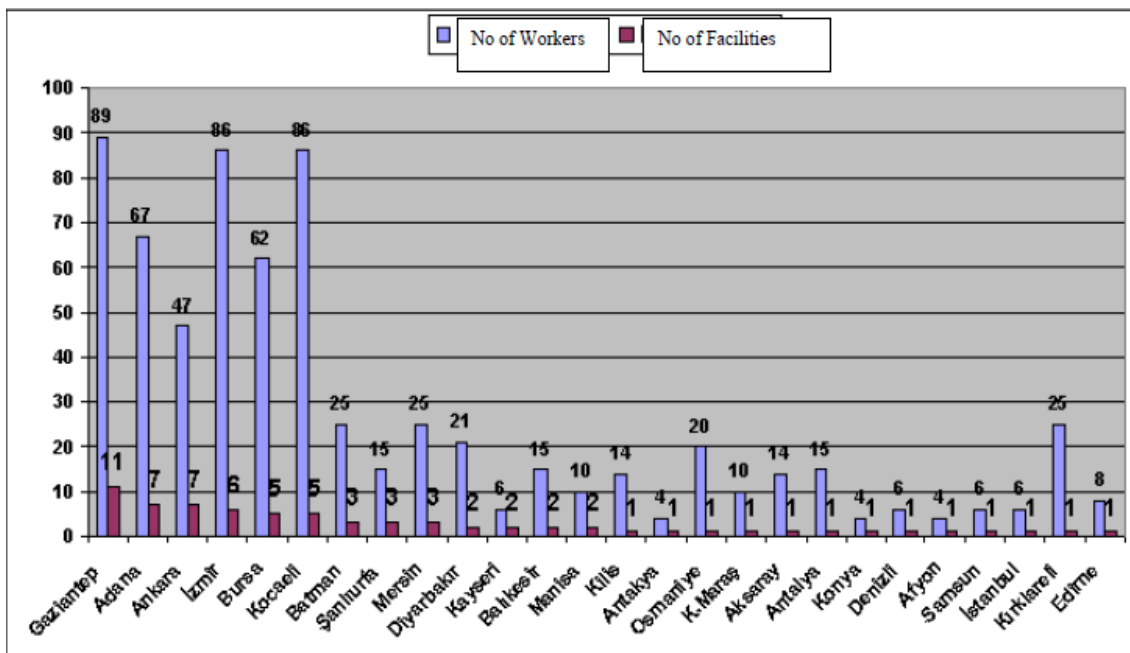


Figure 1.5. Number of biodiesel facilities and employment at various locations in Turkey (Source: Kleindorfer and Öktem, 2007).

Biodiesel production in the Turkey was 10,000 tons in 2003. This indicates the importance of preparing a sound regulation policy for the future of biodiesel growth in Turkey (Arslan, 2007). Moreover, according to Prof. Adnan Akyarlı, biodiesel production potential of Turkey may reach to 1,500,000 ton/yr by effective farming potential of the GAP (southeast) region. Mehmet Çağlar forecasted that Turkey had suitable and unused land, which are totally 1,900,000 hectares in various parts of Turkey; thus, a total annual potential of 1,250,000 tons of biodiesel production. Also he noted that total biodiesel production exceeded 50,000 tons in different regions of Turkey, such as Gebze, Adana, İzmir, Bursa, Polatlı, Urfa, Tarsus, Kırıkkale, Ankara with 87 producers in November 2005 as seen in Figure 1.5. These progressions encouraged the biodiesel producers in the Turkey and total biodiesel production capacity of Turkey rose to 450,000 ton/yr at the end of 2005. Another contribution of the biodiesel production is that it creates jobs. Hereof, Dr. Acaroğlu guessed that biodiesel firms in Turkey employed about 700 people distributed in regions as seen in Figure 1.5 (Kleindorfer and Öktem, 2007). Additionally, these firms produced biodiesel used in transport sector, which consumes ~15 kton in 2008 (International Energy Agency, 2010).

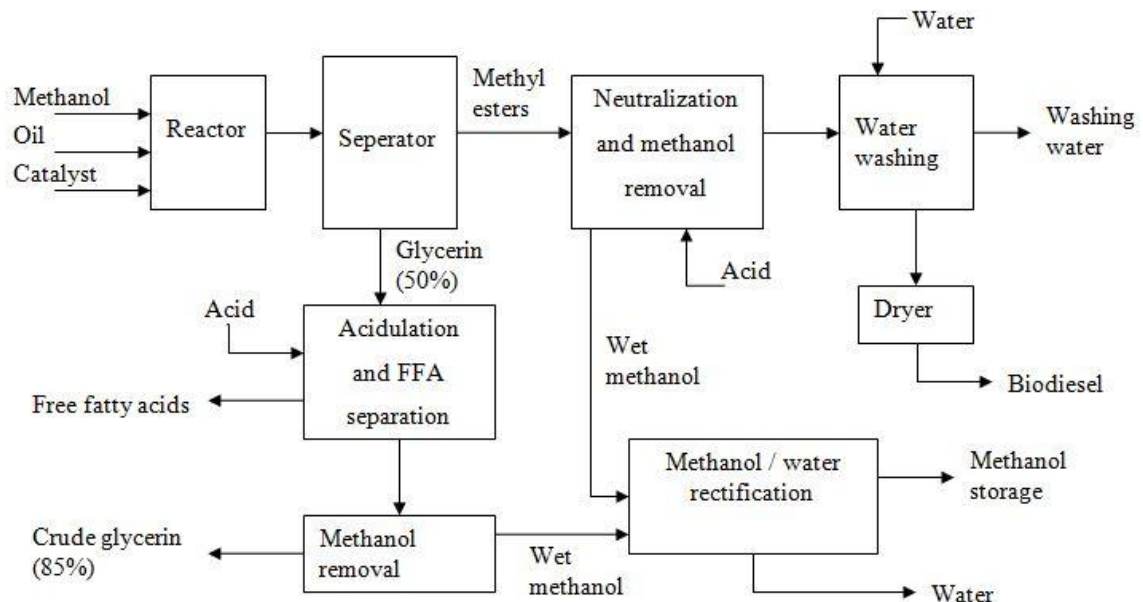


Figure 1.6. Process flow scheme of biodiesel production plant (Source: Knothe et al., 2005).

Figure 1.6 shows the flow diagram of biodiesel production for a large scale industrial process. The alcohol, oil and catalyst react in a reactor but in small scale plants, usually batch reactors are used. After the reaction, products are divided into two streams in the separator. First stream is methyl ester stream and second is glycerin stream. Most producers add between 60% to 200% excess alcohol to drive the chemical reaction to obtain high biodiesel yield. The low solubility of methanol in the oil could restrict the reaction rate. Immediately after the reaction, because of low solubility of glycerol in the esters, glycerol is removed from biodiesel using a settling tank or a disk centrifuge and also, coalescence membrane technology could be used to separate them (Vertes et al., 2010). The excess methanol can slow the separation process whereas it is mostly not subtracted from the reaction stream until after separation of glycerol and methyl esters because of reverse transesterification reaction. After transesterification reaction, due to improving the glycerol separation, water may be added to the reaction mixture (Knothe et al., 2005). In acidification process, the excess catalyst is neutralized and the formed soap is removed by washing and then, FFAs can be removed from the mixture. Finally, in methanol removal unit, the methanol can be evaporated from the glycerin and residue methanol is recovered from water. Besides, the oil and methanol without a catalyst may react; therefore, water washing step is applied to eliminate this situation and also, this reaction needs excess of methanol and high temperatures. In addition to this, lower temperatures, approximately atmospheric pressure and longer reaction times are used in the most biodiesel plants because of equipment cost reduction (Knothe et al., 2005).

For centuries, safflower (*Charthamus tinctorius* L.) has been grown as vegetable oil and preparing textile dye and also, for its colorful petals, which is used as a food coloring and flavoring agent. With respect to growth conditions, it is not selective and adore more arduous weathers, like drought and low temperatures than other oil crops. It can also be planted in fallow areas especially in arid conditions. For this reason, due to adaptability of safflower to various environmental conditions, it is cultivated in many different parts of the world. It has a great potential for arid areas of Turkey, which are mainly in Central and South Eastern Anatolia (Akınerdem and Öztürk, 2008). In addition, it is believed that its origin is in Euroasia, including Turkey and the neighboring countries (Şensöz and Angın, 2008). Nowadays, it has gained a lot of attention worldwide since its seed oil has a significant food-value on account of high linoleic acid content (Bäumler et al., 2006). Safflower oil contains 75 to 80% linoleic



acid. Therefore, its oil can be used as a raw material for producing fatty acid methyl esters in transesterification. The existence of unsaturated and long chain fatty acid is useful in improving the low temperature properties, which are cloud point, pour point and cold filter plugging point, of finally produced biodiesel fuel (Meka et al., 2007). In parallel with this issue, the properties of some vegetable oils are presented in Table 1.1. According to Table 1.1, the heating value and cetane number of safflower is close to heating value and cetane number of diesel and also the safflower provides an advantage over diesel because of higher flash point.

Table 1.1. Properties of some vegetable oils  
(Source: Branwal and Sharma, 2005).

Vegetable oil	Kinematic viscosity at 38°C (mm <sup>2</sup> /s)	Cetane no. (°C)	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Com	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	-	31.0	-	267	0.9180
Diesel	3.06	50	43.8	-	-16	76	0.855

Furthermore, one of the best examples of crops is safflower in the sense of variability for fatty acid composition in seed oil because standard safflower oil comprises about 6 – 8% palmitic acid, 2 – 3% stearic acid, 16 – 20% oleic acid, and 71 – 75% linoleic acid as seen in Table 2.1. However, some kind of safflowers have very high levels of linoleic acid and very low levels of oleic acid, such as 87 – 89% and 3 – 7%, respectively. Also, it has been reported that some safflowers have very high oleic acid content, such as higher than 85% (Gecgel et al., 2007). The best oil seeds are

safflower for biodiesel production in Turkey because their cultivation is much easier and the cost of production is lower than canola and sunflower oil in Turkey (Kleindorfer and Öktem, 2007). Besides, in 1976, the total production of safflower was 1600 tones; however, it had decreased to 20 tons by 2000's in Turkey. Then, safflower seed production reported as 150 metric tonnes in 2005 (Şensöz and Angın, 2008) and its cultivated area varies between nearly 1,000 to 7,000 hectares in Turkey (Kleindorfer and Öktem, 2007).

The objective of this study is to investigate the effect of calcination temperature and active phase loading of single step sol-gel made ( $\text{CaO}/\text{Al}_2\text{O}_3$ ) heterogeneous base catalysts on the biodiesel yield in the transesterification of canola and safflower vegetable oils. For this purpose, calcium oxide ( $\text{CaO}$ ) on alumina ( $\text{Al}_2\text{O}_3$ ) was used as the heterogeneous basic solid catalyst. Using conventional preparation techniques (e.g. precipitation) are very difficult for preparation of  $\text{CaO}$  with controlled crystallite size whereas indirect approach can be used for highly dispersed  $\text{CaO}$  on a support oxide; hence a modified single step sol-gel method was applied to synthesize  $\text{CaO}/\text{alumina}$  catalyst. The effect of  $\text{CaO}/\text{alumina}$  basicity and  $\text{CaO}$  crystallite size on the biodiesel yield was determined at a fixed methanol/oil and a catalyst/oil ratio.

This thesis consists of five chapters. Renewable energy, biodiesel and its production, advantages and disadvantages of biodiesel, its demand in the world and Turkey, and also, the aim of this thesis are mentioned in chapter one. The literature studies on properties of oils and fats, transesterification reaction of vegetable oils and the investigations of solid base catalysts with respect to basicity and basic strength are summarized in in chapter two. In chapter three, pretreatment procedures of the chemicals, the single step sol-gel method to synthesize the heterogeneous catalyst ( $\text{CaO}/\text{Al}_2\text{O}_3$ ) and also catalyst characterization methods, such as X-Ray diffraction, are explained. In chapter four, the conversion activity of the catalysts are introduced and discussed to shed light on the relationship between the active phase loading and the calcination temperature of the catalysts studied in this thesis. Finally, the conclusions are listed in chapter five.

## CHAPTER 2

### LITERATURE SURVEY

#### 2.1. Properties of Oils and Fats

Vegetable fats and oils are lipids extracted from plants and both of them composed of triglycerides (triacylglycerols) which are a mixture of fatty acids with carbon chains of different lengths as well as different degrees of unsaturated carbon-carbon bonds. Some of the fatty acids commonly found in vegetable oil are as follows: lauric (12:0), myristic (14:0), palmitic (16:0), palmitoleic (16:1), stearic (18:0), oleic (18:1), linoleic (18:2), linolenic (18:3), etc. The two most common saturated fatty acids found in vegetable oils are palmitic (16:0) and stearic (18:0) (Connectworld, 2011). Moreover, vegetable oils usually contain free fatty acids (FFA), water, sterols, phospholipids, odorants and other impurities and one of the most significant features of vegetable oils is fatty acid composition. Table 2.1 shows fatty acid compositions of the most common vegetable oils. In this table, fatty acid types are described as xx:y where xx denotes the number of carbon atoms and y the number of double bonds in the fatty acid chain; for example, 18:1 indicates 18 carbon atoms and one carbon-carbon double bond. Furthermore, the parameters to classify the properties of final biodiesel, such as cetane number, oxidative stability and cold-flow properties, are determined by the ratio of saturated fatty acids to unsaturated fatty acids. Unlike double bonds of unsaturated fatty acid chains, saturated alkyl esters having also high cetane number are not reactive to the oxidative attack; hence, elimination of long term storage problems resulting in due to polymerization and cross linking . In contrast to long term storage benefit of saturated fatty acids, solidification of saturated fatty acids occurs below cloud point temperature. In fact, the cloud point temperature of methyl esters is the highest as compared with higher alcohol esters (Vertes et al., 2010).

Table 2.1. Fatty acid compositions of vegetable oils or animal fats  
(Source: Knothe et al., 2005; Connectworld, 2011).

Oil or fat	Fatty acid compositions % by weight						Iodine value	Saponification value
	16:0	16:1	18:0	18:1	18:2	18:3		
Canola	3 - 6	-	1 - 4	55 - 75	15 - 25	8 - 22	110 - 126	188 - 193
Olive	0.5 - 5.0	-	55 - 84.5	3.5 - 21	-	-	75 - 94	184 - 196
Palm	3.5 - 6.3	<1.0	36 - 53	6 - 12	-	-	35 - 61	186 - 209
Peanut	6 - 14	<1.0	1.9 - 6	36.4 - 67.1	13 - 43	-	80 - 106	187 - 196
Rapeseed	1 - 6	-	0.5 - 3.5	8 - 60	9.5 - 23	1 - 13	94 - 120	168 - 187
Safflower	5.3 - 8	-	1.9 - 2.9	8.4 - 23.1	67.8 - 83.2	-	126 - 152	175 - 198
Soybean	2.3 - 13.3	<1.0	2.4 - 6	17.7 - 30.8	49 - 57.1	2 - 10.5	117 - 143	189 - 195
Sunflower	3.5 - 7.6	<1.0	1.3 - 6.5	14 - 43	44 - 74	-	110 - 143	186 - 194

Besides, the two most significant factors affecting biodiesel production yield are free fatty acid and water contents of used vegetable oil. Some vegetable oils, such as palm oil, are not substantially used in biodiesel production plants as raw materials due to their market share and special requirements for improving of their properties even though they have better characteristics than current using raw materials (Umdu, 2008).

## 2.2. Transesterification Reaction

Transesterification reaction or alcoholysis can be described as the transformation of an ester into another through interchange of the alkoxy component when the original ester is reacted with an alcohol. General equation of transesterification reaction can be given below;



(Source: Schuchardt et al., 1997)

It is an equilibrium reaction and the proper mixing of the reactants substantially affect the transformation of the oil to biodiesel (Schuchardt et al., 1997). However, a catalyst, which is possibly a basic or an enzymatic catalyst, affects the rates of forward and reverse reactions given above. In fact, the most important factor affecting the rates is the catalyst type and its amount in the transesterification reaction. Brønsted acids, such as favorably sulfonic and sulfuric acids, giving very high yields of alkyl esters, catalyze the transesterification of free fatty acids at temperatures above 100 °C and long reaction time, such as 3 hours, in order to achieve high conversions. For instance, higher than 99% conversion of soybean oil was obtained using 1% mol of sulfuric acid with an alcohol/oil ratio of 30:1 at 65 °C in 50 hours of reaction time (Schuchardt et al., 1997; Marchetti et al., 2007).

The transesterification reaction on base catalysts progresses faster than the acid catalyzed transesterification of vegetable oils. Therefore, homogeneous base catalysts, such as alkaline metal alkoxides, hydroxides and sodium or potassium carbonates, are preferred in industrial processes. It has been proved that higher than 98% oil conversion using 0.5% mol  $\text{CH}_3\text{ONa}$  is achieved in 30 minutes (Schuchardt et al., 1997). Unfortunately, the base catalyzed transesterification reaction is highly sensitive to the presence of free fatty acids and water content; in fact, the ester yield decreases through the soap formation if excess free fatty acid and water present in the vegetable oils.

Enzymatic catalysts have some advantages as compared with other catalysts because they are insensitive to high levels of free fatty acids. The enzymatic transesterification reaction needs mild reaction conditions, such as low reaction temperature (for lipase between 30 °C and 55 °C) in order to prevent loss of lipase activity (Gog et al., 2012). This situation results in easy product separation. Also, enzymatic catalysts can be reused when immobilized onto a substrate but, the degradation of enzymatic activity is reported for the immobilization of enzyme. Lipase is commonly used for transesterification since in non-aqueous media, it shows high catalytic activity and stability (Gog et al., 2012) but, they are more expensive than homogeneous acid and base catalysts. Moreover, alcohols, especially methanol, becomes inhibitor for lipase when the alcohol/fatty acid molar ratio is greater than 0.5 (Marchetti et al., 2007).

The molar ratio of alcohol to vegetable oil is another variable affecting the ester yield. High alcohol/vegetable oil molar ratio makes the glycerin separation although high biodiesel yields are obtained. Acid, peroxide, saponification and iodine value of methyl esters are not affected by the molar ratio of alcohol to vegetable oil. Moreover,

for any alcohol, alcohol/vegetable oil molar ratio must be at least 6:1 in order to achieve maximum conversion. For instance, the complete conversion was observed at 9:1 alcohol/vegetable oil molar ratio for the transesterification of Cyrena oil with ethanol whereas very low conversion was obtained when molar ratio was less than 6:1 (Meher et al., 2006). In fact, 6:1 molar ratio is normally used in industrial processes in order to achieve higher than 98% conversion (Branwal and Sharma, 2005). Another variable for the transesterification process is the usage of organic co-solvent to reduce the formation of emulsion. Using co-solvents, like tetrahydrofuran (THF) or methyl tert-butyl ether (MTBE), drives the methanolysis of vegetable oils to completion because solubility of methanol in the oil is enhanced through butanolysis reaction. Also, co-solvent addition in biodiesel production affects the alcohol/vegetable oil molar ratio and other parameters (Knothe et al., 2005). After 1 min, for transesterification of soybean oil with methanol, the ester contents are obtained as 82.5, 85, 87 and 96.2% for different sodium hydroxide concentrations, such as 1.1, 1.3, 1.4 and 2.0%. In a similar way, the conversion of 99% was reported for coconut oil in 1 min by using 1% NaOH catalyst and 0.87 THF/methanol volume ratio (Meher et al., 2006).

The reaction time increases the conversion of the transesterification reaction. When 0.5% sodium methoxide catalyst and 6:1 methanol/oil molar ratio were used, after 1 min, the conversion was approximately 80% at 60°C for soybean and sunflower oils and after 1 h, the conversion increased to 93 – 98% (Freedman et al., 1984).

The reaction temperature strongly influences the rate of reaction and yield of ester but the maximum reaction temperature is limited to the boiling point of methanol (60 – 70 °C) at atmospheric temperature. In general, the maximum yield is achieved at 6:1 alcohol/oil molar ratio and temperatures varying between 60 and 80 °C for transesterification process (Branwal and Sharma, 2005). Similarly, for 1% NaOH catalyst and 6:1 methanol to refined oil molar ratio, ester formations were reported to be observed for three different temperatures; hence, after 0.1 h, for 60, 45 and 32 °C, the ester yields of 94, 87 and 64% were obtained, respectively (Freedman et al., 1984).

Another important parameter in the transesterification reaction is the speed of mixing since oils and fats are not miscible with sodium hydroxide and methanol solution. No reaction is observed without stirring in a reasonable time (Meher et al., 2006). In 10 minutes, 99.7% conversion was observed by using NaOH or KOH at ambient pressure and temperature when vigorous stirring was applied (Knothe et al., 2005; Meher et al., 2006).

In addition, for soybean oil transesterification with methanol in the presence of the THF, different biodiesel yields were achieved as 82.5, 85, 87 and 96.2% at various concentration of sodium hydroxide such as 1.1, 1.3, 1.4 and 2.0%, respectively and also the same results are obtained for acid catalyzed processes (Meher et al., 2006).

It has been reported that after 3h, for soybean oil in alkaline-catalyzed transesterification, the biodiesel yield, 80%, was obtained using 8% of oil used as CaO, 6:1 methanol to oil molar ratio and 65 °C reaction conditions. When water content was increased to 2.03%, the yield of biodiesel reached 95% because the transesterification reaction was claimed to be accelerated by generating OH groups, which occurred upon the dissociative adsorption of water molecules on the CaO surfaces. Whereas, larger than 2.8% excess water was found to increase the soap formation (Liu et al., 2008).

### **2.3. Basicity and Basic Strength in Solid Base Catalysts**

As stated previously in transesterification reaction part, in the biodiesel production, base catalysts are commonly preferred since base catalysts require low temperature reaction condition. For catalytic activity, basicity, i.e. the number of basic sites, is found to be related to transesterification activity. Also, solid surface basic strength of the basic sites, i.e. the ability of the surface to donate an electron pair or proton to an adsorbed acid, determines the activity of the catalysts. Gaseous acid adsorption and benzoic acid titration methods are the most common methods in order to determine the strength and amount of basic sites (Tanabe et al., 1989).

For benzoic acid titration method using indicators, it has been claimed that results for CaO calcined in air, basicity measurements at different temperatures and base strengths are obtained and the various basic strengths of CaO was found to increase with raising calcination temperatures until reaching optimum calcination temperature (Tanabe et al., 1989).

Acidic molecules, such as carbon dioxide, nitric oxide and phenol, can be used as adsorbents for determining basicity and basic strength. Temperature programmed desorption (TPD) is widely used method to measure the basic site amount by analyzing irreversibly absorbed carbon dioxide amount on solid surfaces. Depending on the adsorption time and temperature, the alkaline earth oxides, such as MgO, CaO, SrO,





above the optimum calcination temperature, the basicity was found to decrease with increasing temperature.

Thermal treatment and its duration affect surface area and pore diameter of catalysts. For instance, bulk CaO catalyst preparation at higher calcination temperature and longer treatment time resulted in surface area decrease and pore diameter increase. However, for transesterification of vegetable oils, the basicity of CaO catalyst increases with calcination temperature (Huaping et al., 2006). Also, in the study of Endalew et al. (2011), longer calcination time and high temperature treatment resulted in surface area loss, hence giving 2 m<sup>2</sup>/g of total surface area. But high surface basicity was observed (Endalew et al., 2011). Moreover, catalyst crystalline structure and the coordination number of ions on the catalyst surface may change due to calcination temperature. Hence, this transformation will result in change of basic site number and their strengths (Huaping et al., 2006). Besides, the catalyst activity is affected by homogeneity of the calcined mixture. It was reported that the pretreatment of CaO catalyst with ammonium carbonate solution reduced the surface area such as 6 m<sup>2</sup>/g (Huaping et al., 2006) and 32 m<sup>2</sup>/g (Granados et al., 2007).

Many studies have shown that the catalytic activity of basic catalysts mostly increase with basicity (Huaping et al., 2006; Xie and Li, 2006). However, Huaping et al. (2006) also stated that high conversions up to 93.5% can be achieved on solid base catalysts. In Table 2.2, the reaction conditions, biodiesel yields and the basic strength for various basic catalysts are listed. From Table 2.2, it can be said that highly basic catalysts can give high biodiesel yields.

Table 2.2. Basic strength and biodiesel yield results in terms of various basic heterogeneous catalysts and reaction conditions (Source: Umdu, 2008).

Catalyst	Basic strength	Catalyst Amount	Catalyst Load	Molar Methanol/ Vegetable Oil ratio	Oil	T (°C)	Yield %	Reaction time	Reference
Na/ $\gamma$ - $\text{Al}_2\text{O}_3$	-	1g/80mL	20 wt %	6:1	Soy bean	60	70	2 h	(Kim et al., 2004)
Na/NaOH/ $\gamma$ - $\text{Al}_2\text{O}_3$	-	1g/80mL	20 wt %	6:1	Soy bean	60	77	2 h	(Kim et al., 2004)
NaOH/ $\gamma$ - $\text{Al}_2\text{O}_3$	-	1g/80mL	20 wt %	6:1	Soy bean	60	69	2 h	(Kim et al., 2004)
$\text{Al}_2\text{O}_3$	<7.2	2 wt %	Pure	15:1	Soy bean	Reflux	0	8 h	(Xie and Li, 2006)
KF/ $\text{Al}_2\text{O}_3$	15.0–18.4	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	85.8	8 h	(Xie and Li, 2006)
KCl/ $\text{Al}_2\text{O}_3$	<7.2	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	0	8 h	(Xie and Li, 2006)
KBr/ $\text{Al}_2\text{O}_3$	9.3–15.0	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	16.7	8 h	(Xie and Li, 2006)
KI/ $\text{Al}_2\text{O}_3$	15.0–18.4	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	87.4	8 h	(Xie and Li, 2006)
KI/ZrO <sub>2</sub>	15.0 – 18.4	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	78.2	8 h	(Xie and Li, 2006)
KI/ZnO	9.3 – 15.0	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	72.6	8 h	(Xie and Li, 2006)
KI/NaX	9.3 – 15.0	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	12.9	8 h	(Xie and Li, 2006)
KI/KL	9.3 – 15.0	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	28.3	8 h	(Xie and Li, 2006)
K <sub>2</sub> CO <sub>3</sub> / $\text{Al}_2\text{O}_3$	9.3–15.0	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	48.0	8 h	(Xie and Li, 2006)
KNO <sub>3</sub> / $\text{Al}_2\text{O}_3$	15.0 – 18.4	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	67.4	8 h	(Xie and Li, 2006)
KOH/ $\text{Al}_2\text{O}_3$	15.0 – 18.4	2 wt %	2.1 mmol/g	15:1	Soy bean	Reflux	80.2	8 h	(Xie and Li, 2006)
KF/ZnO	15.0 – 18.4	3 wt %	15 wt %	10:1	Soy bean	Reflux	87	9 h	(Huang et al., 2006)
KOH/ZnO	15.0 – 18.4	3 wt %	15 wt %	10:1	Soy bean	Reflux	82	9 h	(Huang et al., 2006)
K <sub>2</sub> CO <sub>3</sub> /ZnO	15.0 – 18.4	3 wt %	15 wt %	10:1	Soy bean	Reflux	74	9 h	(Huang et al., 2006)
CaO	26.5 – 33.0	1.5 wt %	Pure	9:1	jatropha curcas	70	93.5	2.5 h	(Huaping et al., 2006)

(cont. on next page)

**Table 2.2 (cont.)**

KOH/NaX zeolite	15.0 – 18.4	3 wt %	10 wt %	10:1	Soy bean	65	85.6	8 h	(Xie and Yang, 2007)
KNO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	15.0 – 18.4	6.5 wt %	35 wt %	15:1	Soy bean	Reflux	87.4	7 h	(Xie et al., 2006)
MgO	-	1.5 wt %	pure	4:1	Rapeseed	70	93	2 h	(Parvulescu et al., 2008)
MgO	-	0.1 wt %	pure	4.5:1	Rapeseed	Reflux	0	2.5 h	(Santacesaria et al., 2007)
CaO	-	0.1 wt %	pure	4.5:1	Rapeseed	Reflux	0	2.5 h	(Santacesaria et al., 2007)
NaNO <sub>3</sub> /CaO	11.0 – 15.0	5 wt %	5 wt %	6:1	Rapeseed	60	100	3 h	(MacLeod et al., 2008)
KNO <sub>3</sub> /CaO	11.0 – 15.0	5 wt %	5 wt %	6:1	Rapeseed	60	100	3 h	(MacLeod et al., 2008)
NaNO <sub>3</sub> /MgO	10.1 – 11.0	5 wt %	5 wt %	6:1	Rapeseed	60	100	3 h	(MacLeod et al., 2008)
KNO <sub>3</sub> /MgO	10.1 – 11.0	5 wt %	5 wt %	6:1	Rapeseed	60	4	3 h	(MacLeod et al., 2008)
Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	7.2 – 9.3	10	pure	10:1	Rapeseed	60	92	10 h	(Kawashima et al., 2008)
CaO	-	8	pure	12:1	Soybean	65	97	0.5 h	(Liu et al., 2008)
CaO	-	1	pure	12:1	Sunflower	60	92	10 h	(Granados et al., 2007)
Ba/ZnO	15.0–18.4	6 wt %	2.5 mmol/g	12:1	Soybean	65	95.2	5 h	(Xie and Yang, 2007)

Furthermore, catalyst basic site density as well as their strength has a significant influence on the catalyst activity (Ilgen, 2011). It is also claimed in Xie et al. (2006) that basic site amount plays an efficient role as much as the strength of basic sites on the catalytic activity, and hence; it is not easy to explain catalytic activity with only one parameter. Similarly, transesterification of soybean oil with various solid base catalysts were found to be related to basic sites amount but not directly to the basic strength and also basic site density was effective parameter for refined palm kernel oil transesterification (Ngamcharussrivichai et al., 2008). It was reported that biodiesel synthesis from soybean oil on 35 wt. % KI on Al<sub>2</sub>O<sub>3</sub> calcined at 500 °C for 3 h had the highest catalytic activity which showed a strong relationship to the strength of basic sites and their amount (Xie and Li, 2006).

The amount of ions loading on support material affects basicity and basic strength but BET surface and also pore volumes of the catalysts decreased as loading sodium and sodium hydroxide was increased (Kim et al., 2004). According to Georgogianni et al. (2009) study, under 60 °C reaction temperature and 51.5:1

methanol/oil weight ratio, 0.1 wt. % catalyst amount with respect to oil and 25 h reaction time, the highest catalytic activity (i.e. 97% conversion) was obtained on Mg-Al hydrotalcite, which had the highest content of K as  $K_2O$  and Mg as MgO (total of 25 wt. %) and lowest surface area ( $82 \text{ m}^2/\text{g}$ ). Also, authors reported that the basicity of the catalyst shifted with added amount of cation (K and Mg) content in the solid catalyst. In addition, it was observed that for transesterification of frying oil on  $ZrO_2$ , catalytic activity enhanced with increasing potassium cation because of increased basicity. Although the basicity increased with cation content, the catalytic activity decreased with the Mg/Al molar ratio exceeding 3.0 because of weaker basic sites formation (Georgogianni et al., 2009; Xie et al., 2006). Furthermore, it was shown that basicity was proportional to increasing KF content with a maximum basicity of 2.16 mmol/g for 30% KF/MgO. However, if the loading of KF was more than 30%, the basicity decreased. In fact, 79.3% biodiesel yield was achieved at  $500 \text{ }^\circ\text{C}$  and 35% KF loading in the transesterification of rapeseed oil (Wan et al., 2008). Besides, lithium loaded CaO showed increased catalytic activity and basicity and it was related to the creation of solid solution having lack of structural defects and the decrease of the catalyst surface area (Endalew et al., 2011). Watkins et al. (2004) reported that 4 wt. % Li doping increased the basic strength from  $10 > pK_{BH^+} > 8$  on CaO to  $17.2 > pK_{BH^+} > 15.0$  by using Hammet indicator method, while Kumar and Ali (2010) reported that 28.5 wt. % Li doping increased the basic strength of CaO from  $9.8 < pK_{BH^+} < 10.1$  to  $11.1 < pK_{BH^+} < 15.0$ ; Similarly, it is enough to obtain high basicity on the catalysts prepared at  $550 \text{ }^\circ\text{C}$  calcination temperature, 3 hour of calcination time and Li doping of 6.6% of CaO (Endalew et al., 2011). Besides, the base strength of the catalyst could be increased by incorporation of other materials. For instance, the basic strength of CaO increases with lithium doping. It is known that CaO is the most promising heterogeneous catalyst for the transesterification of oils because it is cheap, the least toxic material, and has low methanol solubility, higher activity, long catalyst life times, and mild reaction conditions (Helwani et al., 2009; Liu et al., 2008). Furthermore, its basic sites had stronger basic strength, such as higher than  $H_- = 26.5$ , (Liu et al., 2008). It was found that in 25 min of the reaction time, CaO showed only 2.5% conversion in the transesterification of triglyceride whereas when  $LiNO_3$  added to CaO, 83 and 100% conversions was obtained for 0.23 and 1.23 wt. % Li loadings, respectively (Helwani et al., 2009).

In general, the catalyst activity also depends on catalyst preparation and pretreatment conditions. According to two different studies on pure CaO; due to calcination temperature differences; Santacesaria et al. (2007) and Huaping et al. (2006) have reached completely different results; 93.5% yield observed on the catalyst calcined at 850 °C by Huaping and no conversion on the catalyst calcined at 500 °C by Santacesaria.

SEM studies on KI/Al<sub>2</sub>O<sub>3</sub> catalysts indicated that in spite of a good dispersion of KI as a monolayer on Al<sub>2</sub>O<sub>3</sub>, KI crystallites formed at high KI loading but amorphous structure of alumina did not change. In addition to this; carbonate groups on the surface was reported to result in high activity for KI on the Al<sub>2</sub>O<sub>3</sub> (Xie and Li, 2006). Mg – Al mixed oxide generated by the decomposition of Mg – Al hydrotalcites, was found to have high surface area and also strong Lewis base sites and the amount of these basic sites was controlled by Mg – Al ratio in the precursor (Helwani et al., 2009).

## CHAPTER 3

### MATERIALS AND METHOD

#### 3.1. Materials

CaO/Al<sub>2</sub>O<sub>3</sub> with loadings of 60, 70, 80 wt. % were synthesized using a sol-gel method in this study. Calcium nitrate tetrahydrate was used as a precursor for calcium oxide and aluminum isopropoxide (AIP) was used as precursor for alumina. Methanol (MeOH) and deionized water (DIW) were solvents and nitric acid (HNO<sub>3</sub>) was used as peptizer in the sol gel method. Chemicals used in this synthesis are listed in Table 3.1.

Table 3.1. Properties of chemicals used in the synthesis of catalyst.

Chemical Name	Chemical Formula	Molecular Weight (g/mol)	Purity (%)
Aluminum isopropoxide	Al(OCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub>	204.24	98
Calcium nitrate tetrahydrate	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	236.15	99.3
Methanol	CH <sub>3</sub> OH	32.04	99
Nitric acid	HNO <sub>3</sub>	63.01	65

Heterogeneous transesterification reaction was carried out using calcium oxide on alumina (CaO/Al<sub>2</sub>O<sub>3</sub>) and methanol (MeOH). Commercial canola (from Yonca Inc.) oil was used as the lipid feedstock.

#### 3.2. Methods

The work done in this study can be summarized in three steps;

- Catalyst preparation
- CaO/Al<sub>2</sub>O<sub>3</sub> testing in transesterification of the oils
- Catalyst characterization

### 3.2.1. Catalyst Preparation

A modified single step sol-gel method was used to synthesize CaO on Al<sub>2</sub>O<sub>3</sub> catalysts. In the preparation of alumina supported catalyst, first, alumina isopropoxide (AIP), water and HNO<sub>3</sub> were mixed at 85 °C for 1 hour. Then, the necessary amount of calcium nitrate was added to the solution. After gelation, the mixed oxide gel was dried at 120 °C. The dried catalyst was calcined at various calcination temperatures and followed by grinding and sieving to less than 325 mesh. Calcined and sieved powder catalysts were stored in the desiccators.

### 3.2.2. CaO/Al<sub>2</sub>O<sub>3</sub> Testing in Transesterification of the Oils

In this study, transesterification on calcium oxide (CaO)/alumina catalysts were carried out at 50 °C under methanol/oil ratio of 9 and the catalyst amount of 6 wt. % of the oil amount. For all the reactions, 1100 rpm stirring speed and 4 hours of reaction time was used. CaO loading of the catalysts were 60%, 70%, and 80% with regards to weight of total catalyst. Calcination temperatures of the catalysts were 400 °C, 500 °C, 600 °C, and 700 °C.

### 3.2.3. Catalyst Characterization

Philips Xpert XRA-480 Model X-ray diffractometer was used to determine the crystalline phase and crystallite sizes of the catalysts. Scherrer equation, which is given below, was used with line broadening of a diffraction peak to calculate the average crystallite size:

$$T = K \lambda / (B(2\theta) \cos\theta) \quad (3.1)$$

where T shows crystallite thickness, K is Scherrer constant, 0.94 is commonly used,  $\lambda$  is wavelength of the X-ray, B is the full width in radians corresponding to the half maximum intensity width of the diffraction peak at  $2\theta$  angle (Warren, 1990).

In order to calculate the oxide samples' specific surface area and the porosity, BET analysis in the presence of N<sub>2</sub> was performed with Micrometrix Gemini V at scan mode at -195.8 °C for three chosen catalysts; 80% CaO/Al<sub>2</sub>O<sub>3</sub>, 70% CaO/Al<sub>2</sub>O<sub>3</sub>, 60% CaO/Al<sub>2</sub>O<sub>3</sub>. After calcination, all samples kept in a desiccator and before analysis, degassed at 400 °C for 3 hours.

Basic strength and basicity of solid catalysts were determined with an adsorbed gas, such as CO<sub>2</sub>, using a standard Temperature Programmed Desorption (TPD) procedure available on Micromeritics AutoChem 2910 instrument equipped with an inline Balzers Thermostar GS300 quadrupole mass spectrometer.



## CHAPTER 4

### RESULTS AND DISCUSSION

Transesterification of canola and safflower oils on basic CaO on alumina catalysts were studied in a batch reactor. Percentage biodiesel yield which is the ratio of the number of moles of methyl esters formed over the number of moles of triglycerides was determined in order to compare the activities of different catalysts.

#### **4.1. The Effect of CaO Loading and the Calcination Temperatures on Biodiesel Yield**

Biodiesel yields obtained for canola oil at 50 °C, 1100 rpm stirring speed, and 6 wt. % catalyst loading for 4 h of reaction time are listed in Table 4.1 as a function of different catalyst active phase loadings of CaO and calcination temperatures. In this study; as seen in Table 4.1, the highest biodiesel yield, ~95%, was observed at 700 °C of calcination temperature on 70% CaO/Al<sub>2</sub>O<sub>3</sub> and also, the same biodiesel yield was achieved at 500 °C of calcination temperature on 80% CaO/Al<sub>2</sub>O<sub>3</sub>; in fact, it is the same biodiesel yield that was obtained for canola and sunflower vegetable oils on the 80% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 500 °C (Umdu, 2008). In addition to this; Umdu stated that as CaO loading increased from 5% to 80% resulted in increased biodiesel yield from 3.5% to ~96% while pure CaO and MgO gave less than 10% biodiesel yield. Since Umdu's study (Umdu, 2008) showed that high biodiesel yields were obtained on 50% and 80% CaO/alumina catalysts, 60%, 70%, and 80% loadings were used together with higher calcination temperatures in this study. Moreover; the reaction condition parameters were kept constant at MeOH/Oil= 9, Catalyst/Oil =6 wt.%, 50 °C of the reaction temperature, 1100 rpm stirring speed, and 4 h of the reaction time which were the same as that used in Umdu's study (Umdu, 2008).

Table 4.1. Heterogeneous basic catalyst CaO/Al<sub>2</sub>O<sub>3</sub> test results for canola oil at 50 °C, the stirring speed of 1100 rpm, and the catalyst load of 6 wt. % for 4 h.

Active Phase Loading of CaO/Al <sub>2</sub> O <sub>3</sub> (%)	Calcination Temperature (°C)	Biodiesel Yield (%)	Biodiesel Reaction Time (min)
80	400	76.34 ± 2.87	240
80	500	92.85 ± 2.41	240
80	600	83.89 ± 1.22	240
80	700	86.94	240
70	400	70.09 ± 3.97	240
70	500	67.62 ± 3.12	240
70	600	82.67 ± 1.80	240
70	700	94.74	240
60	400	72.91 ± 3.84	240
60	500	71.98 ± 3.86	240
60	600	88.97 ± 0.2	240
60	700	85.22 ± 0.62	240

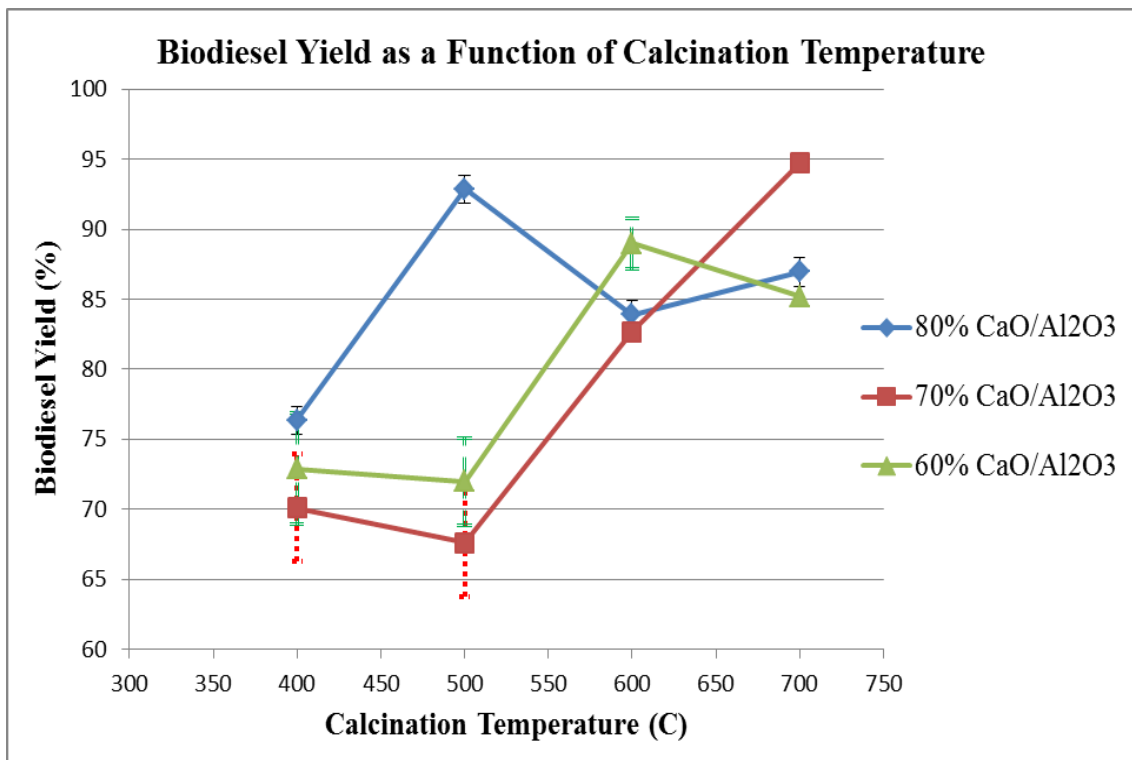


Figure 4.1. Biodiesel yield versus calcination temperature for 60% 80% and 70% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts for 4 h of reaction time.

As seen in Figure 4.1, at 700 °C of calcination temperature, 80% and 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts' biodiesel yields are ~87% and 85% but at 600 °C of calcination temperature, biodiesel yields on 80% , 70% and 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts are 84%, 83% and 89%, respectively. In fact, it seems that biodiesel yields on the catalysts calcined at 600 °C and 700 °C are almost the same within the experimental errors shown as error bars in the Figure. Consequently; for 4 h of the reaction time, high calcination temperatures, such as 600 °C and 700 °C, and CaO loadings of 60 and 80% do not significantly affect biodiesel yield except for 70% CaO and 700 °C of calcination temperature.

## **4.2. The Effect of Reaction Time and the Reusability of the Catalysts**

The biodiesel yields on 80%, 70%, and 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 700 °C were investigated as a function of reaction time as seen in Table 4.2. It was observed that the biodiesel yield on 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 700 °C reached approximately to 75% at 2 min., then increased to 85% at 4 min and finally, decreased to 70% at 30 min and stayed constant at ~75% at 60 min. Interestingly, as seen in Figure 4.1, 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalyst gave 85% biodiesel yield at 4 h of the reaction time; hence, showing slow increase of biodiesel yield in 3 h after 1 h of the reaction time. This may indicate that the effect of external mass transfer limitations caused by the formation of products, such as glycerol and biodiesel, controls after 1 h of the reaction time even though external mass transfer limitation was checked before the reaction and 1100 rpm was found to be adequate to eliminate the external mass transfer limitations. Therefore, a higher stirring speed, ~1300 rpm, was used and found that it improved the biodiesel yield. Unfortunately, there was no stirrer with the capability of more than 2000 rpm available to be used. In contrast, in Umdu's study (Umdu, 2008), 80% CaO/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C was shown to reach 97% biodiesel yield in 1 hour of the reaction time under the same reaction conditions used in this study. However, in this study, 80% CaO/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C was found to give 63% biodiesel yield in 6 min under the same reaction conditions. This also indicates that all the catalysts prepared in this study were highly active; thus giving 60% more biodiesel yield in 1 h of reaction time.

Table 4.2. Biodiesel yield results of various CaO/Al<sub>2</sub>O<sub>3</sub> for canola oil at 50 °C, the stirring speed of 1100 rpm, and the catalyst load of 6 wt. % for 4 h with regard to different reaction times.

Active Phase Loading of CaO/Al <sub>2</sub> O <sub>3</sub> (%)	Calcination Temperature (°C)	Biodiesel Reaction Time (min)	Biodiesel Yield (%)
80	700	2	45.34
70	700	2	72.51
60	700	2	75.64
80	700	4	43.14
70	700	4	66.11
60	700	4	84.34
80	700	6	80.46
70	700	6	77.46
60	700	6	79.60
80	500	6	62.65
70	500	6	67.69
70	700	30	69.67
60	700	30	67.58
70	700	60	72.18
60	700	60	74.04

### 4.3. The Amount of Leaching of Ca Cation from the Catalysts

ICP analyses of the biodiesel phase obtained on 80% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 500 °C showed that Ca ion concentration was 24 ppm at 10 min of the reaction times but increased to ~256 ppm at 30 min. Moreover, using 70% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 700 °C for 10 min of the reaction time resulted in ~40 ppm Ca cations in biodiesel phase. Therefore, the reusability of CaO/Al<sub>2</sub>O<sub>3</sub> was checked to see if the leaching of Ca cation adversely affected the activity of the catalysts. As seen in Table 4.3, 3 times successive use of the catalysts showed that there was no loss of biodiesel yield in 10 min reaction time; hence, indicating that the loss of Ca cation did not hinder the activity of the catalysts. But, the long term use test still must be done to confirm this effect.

Table 4.3. Biodiesel yield results of various CaO/Al<sub>2</sub>O<sub>3</sub> for canola and safflower vegetable oils at 50 °C, 1100 rpm stirring speed, and 6 wt. % catalyst load for 10 min.

Oil type	Use number	Active Phase Loading of CaO/Al <sub>2</sub> O <sub>3</sub> (%)	Calcination Temperature (°C)	Biodiesel Yield (%)	Error
Canola	1	70	700	71.99	± 2.41
Canola	2	70	700	78.26	
Canola	3	70	700	79.93	
Safflower	1	70	700	58.77	± 8.00
Safflower	2	70	700	84.34	
Safflower	3	70	700	80.85	
Safflower	1	60	700	67.22	± 4.26
Safflower	2	60	700	80.95	
Safflower	3	60	700	78.83	

## 4.4. Catalyst Characterizations

### 4.4.1 XRD Analyses of All the Catalysts

XRD analyses showed that there were no diffraction peaks corresponding to CaO crystalline phase (e.g. 2θ angle of 37.29 °) for all the CaO loadings and the calcination temperatures, such as 400, 500, 600 and 700 °C, as seen in Figure 4.2 - 4.5. This indicates that CaO crystallite size in CaO/Al<sub>2</sub>O<sub>3</sub> catalysts for all the CaO loadings and the calcination temperatures is less than 5 nm. This explanation is plausible since XRD analysis is not sensitive to the crystallite sizes less than 5 nm. In other words, CaO was highly dispersed in CaO/Al<sub>2</sub>O<sub>3</sub> catalysts and on all the CaO/Al<sub>2</sub>O<sub>3</sub> catalysts, there were some diffraction peaks located at ~38 and ~42 ° 2θ angles which did not correspond to CaO crystalline phases but they were identified as hydrated calcium aluminate and alumina crystalline phases using the powder XRD diffraction pattern (JCPDS-International Centre for Diffraction Data (ICDD) (2000) Powder Diffraction File (PDF-2 Database), Newtown Square Pennsylvania). The formation of these phases is expected because the adsorption of water and CO<sub>2</sub> from air must have occurred during the XRD analyses; in fact, the samples were open to atmosphere prior to and also during the XRD measurements. It was difficult to clearly distinguish the crystalline phases to calculate the average crystallite sizes of those phases.

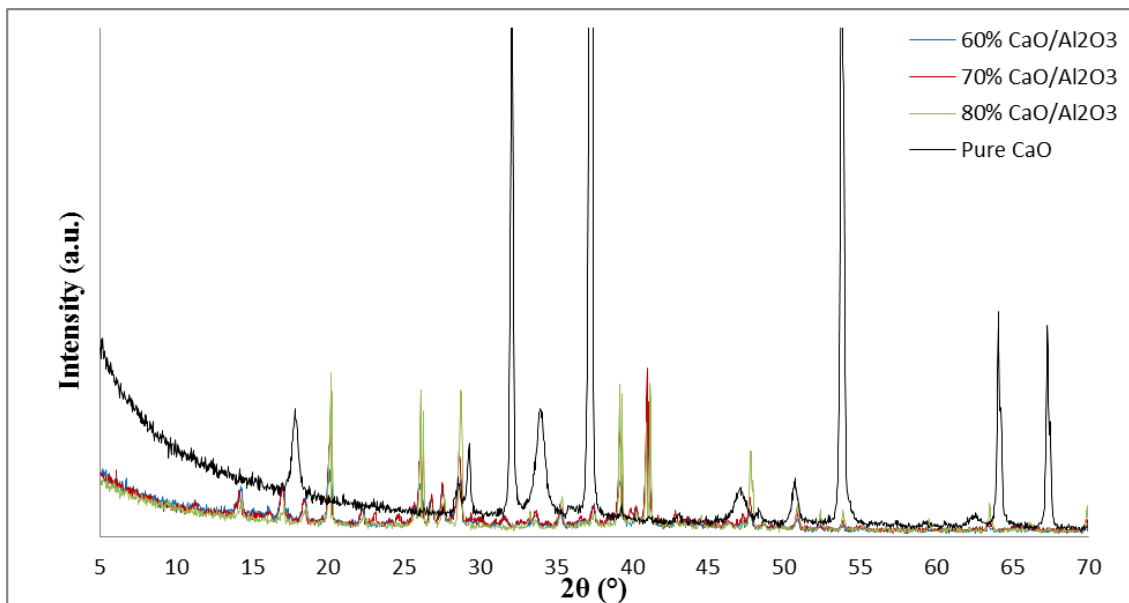


Figure 4.2. Comparison of XRD results at 400 °C calcination temperature for CaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

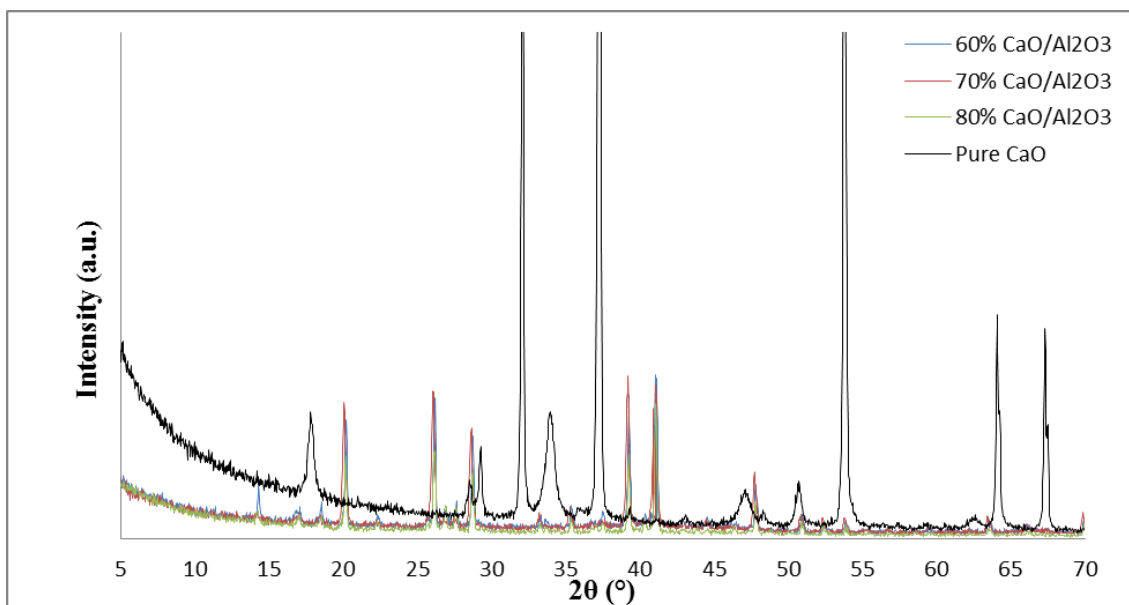


Figure 4.3. Comparison of XRD results at 500 °C calcination temperature for CaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

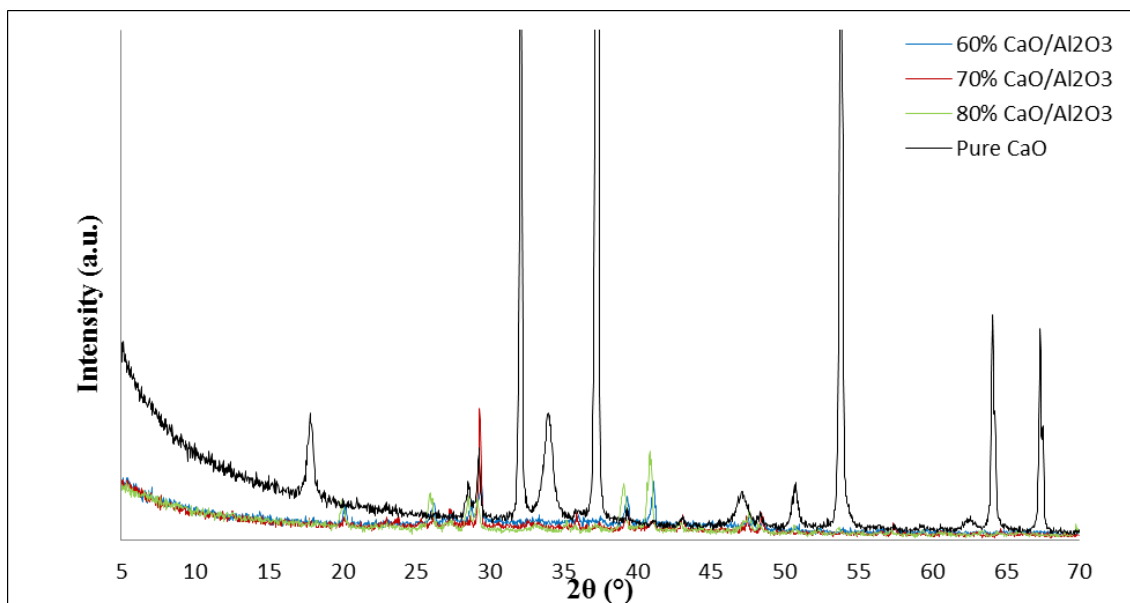


Figure 4.4. Comparison of XRD results at 600 °C calcination temperature for CaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

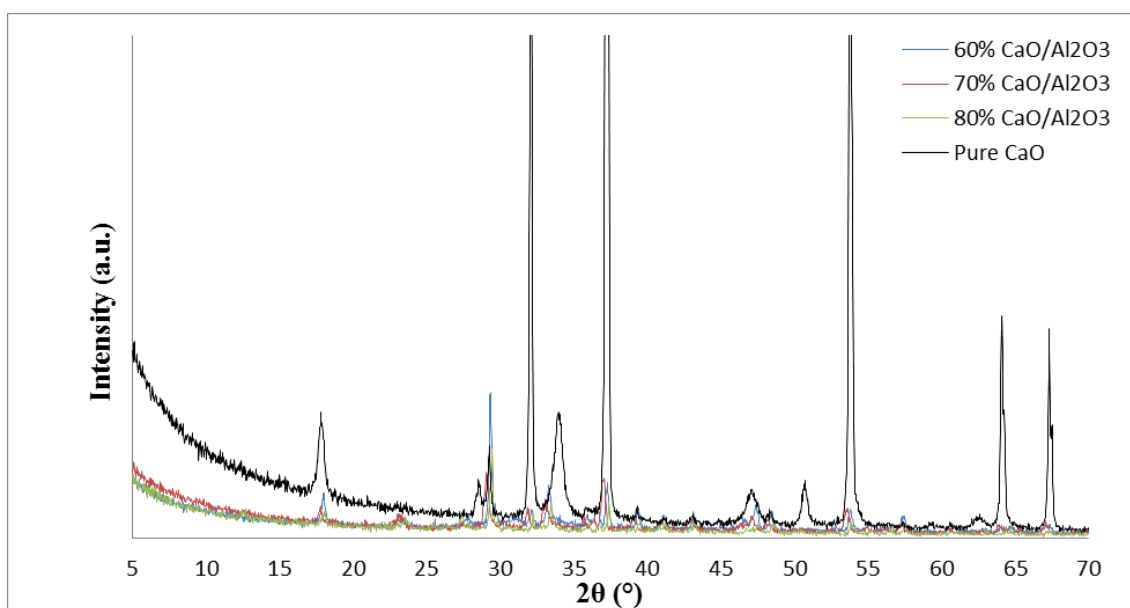


Figure 4.5. Comparison of XRD results at 700 °C calcination temperature for CaO/Al<sub>2</sub>O<sub>3</sub> catalysts.

#### 4.4.2 Basicities and Basic Strengths of the Selected Catalysts

It is known that basic catalysts are very active in the transesterification of vegetable oils at low temperatures. Hence, the basicity and basic strength of the selected catalysts were determined using CO<sub>2</sub> FTIR and also CO<sub>2</sub> Temperature Programmed Desorption technique. The amount of irreversibly adsorbed CO<sub>2</sub> gives the total amount of basic sites ( $\mu\text{mol}/\text{m}^2$ ) on solid surfaces and also, the desorption temperature of CO<sub>2</sub> is the indication of basic strength of the basic site; for instance, the stronger the basic sites, the higher the temperature (Tanabe et al., 1989). Figure 4.6 shows CO<sub>2</sub> FTIR for 70% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 700 °C and also, CO<sub>2</sub> TPDs for 60 and 80% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500 °C are given in Figure 4.7. From the TPDs, the total basicities of 60% and 80% CaO was determined to be 7.15 and 63.23  $\mu\text{mol CO}_2/\text{m}^2$ , respectively. Their basic strengths, i.e. peak desorption temperatures, were located at 146 and 157 °C, respectively. From previous studies conducted in Assoc. Prof. Seker's research group, it is known that pure alumina had similar basicity as 60% CaO/Al<sub>2</sub>O<sub>3</sub> catalysts but its basic strength was 170 °C. Therefore, it seems that although 60% CaO/Al<sub>2</sub>O<sub>3</sub> and pure Al<sub>2</sub>O<sub>3</sub> had almost the same basicity, the biodiesel yield in 4 h of reaction time on 60 wt. % CaO/Al<sub>2</sub>O<sub>3</sub> xerogel was ~72% whereas it was zero over pure Al<sub>2</sub>O<sub>3</sub>. This indicates that the biodiesel yield difference found on 60 wt. % CaO/Al<sub>2</sub>O<sub>3</sub> and pure Al<sub>2</sub>O<sub>3</sub> is not due to the basicity. In fact, these results show that the biodiesel yield is not directly correlated with the basicity. However, both of the basic strengths and the basicity were found to significantly affect the biodiesel yield.



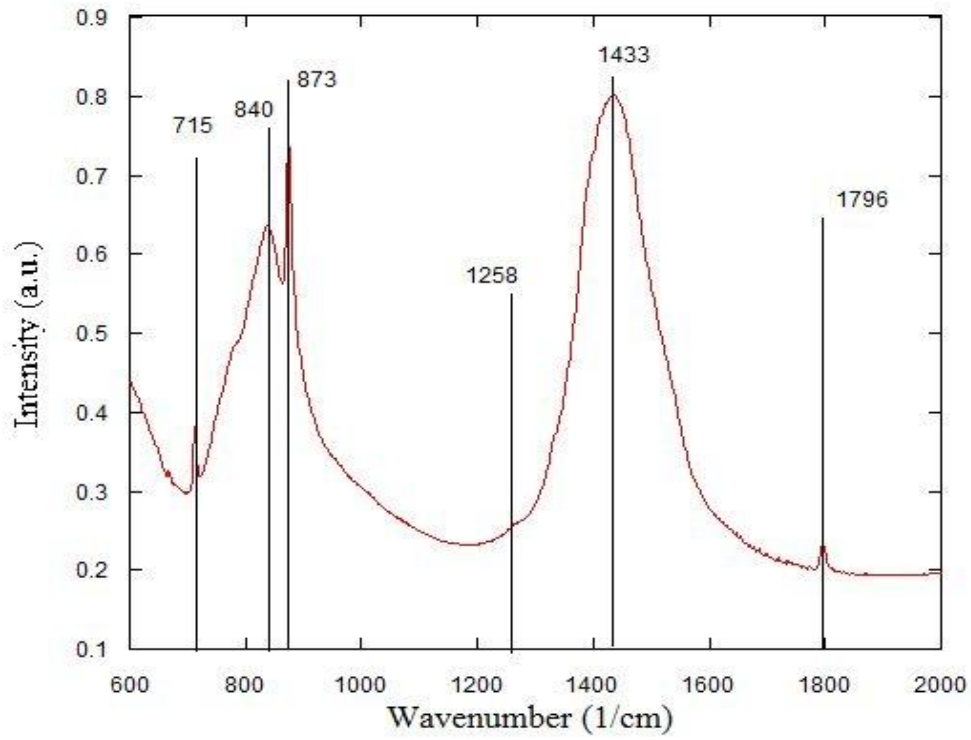


Figure 4.6. CO<sub>2</sub> FTIR of 70% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 700 °C.

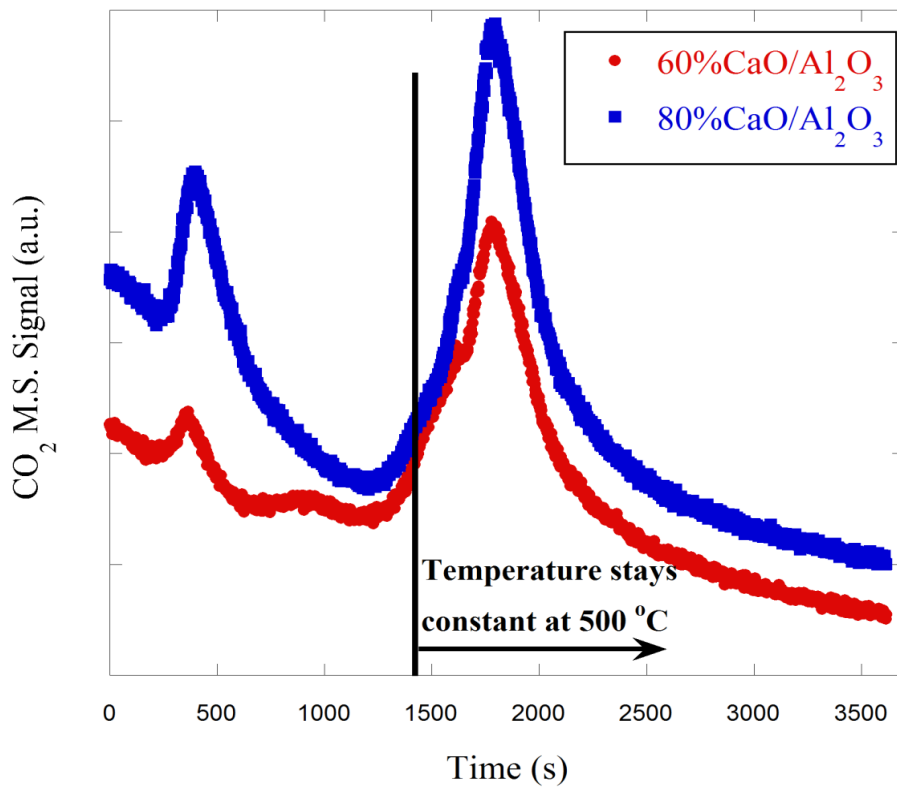


Figure 4.7. CO<sub>2</sub> TPD of 60 and 80% CaO/Al<sub>2</sub>O<sub>3</sub> calcined at 500 °C.

## CHAPTER 5

### CONCLUSIONS

In this study, the effect of calcination temperature and active phase loading of the catalysts on the biodiesel yield during the transesterification of canola and safflower vegetable oils were studied on the heterogeneous basic calcium oxide on alumina catalysts.

The catalysts with high CaO loading, such as 80% and 70%, were prepared using modified single step sol-gel method and also, varying calcination temperatures were employed.

When comparing this study to the reported literature studies, even under the reaction conditions, such as low reaction temperatures, 50 °C, 9 methanol/Oil molar ratio, 6 wt. % of Catalyst/Oil, and also short biodiesel reaction time, such as 4 – 10 minutes, resulted in high activity. It seems that catalyst when calcined at 700 °C and having 70% CaO loading is more active. As indicated in the study; the system was influenced by external mass transfer limitation when the biodiesel yield was higher than 70%. Besides, CaO/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 700 °C showed low Ca<sup>+</sup> ions leaching during the reaction. Consequently, it was shown that highly active catalyst with high CaO dispersion could be prepared using the modified single step sol-gel method together with the high calcination temperature and 60 – 70% CaO loadings.

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