

**METHYL ESTER PRODUCTION FROM
VEGETABLE OILS ON HETEREGENEOUS BASIC
CATALYSTS**

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ABSTRACT

METHYL ESTER PRODUCTION FROM VEGETABLE OILS ON HETEROGENEOUS BASIC CATALYSTS

In this study, the activities of heterogeneous mixed oxide catalysts; magnesium and calcium oxide on alumina and silica supports were investigated for transesterification of vegetable oils; canola and sunflower, to methyl esters. The primary objective of this study is to understand whether basicity of the solid catalysts and/or its crystallite size affect the biodiesel yield during the reaction. The mixed oxide catalysts were prepared by a single step sol-gel method. Magnesium oxide (MgO) and calcium oxide (CaO) were chosen because of their basic property.

This study shows that the crystallite size does not have any direct effect on the transesterification activity. Yet, the interaction of the crystallites with the support material may change the number of the active sites and/or the creation of new “basic” sites. In fact, the basicity was found as the critical factor for the choice of the suitable mixed oxide for the transesterification reaction. The addition of CaO to alumina creates synergetic effect. But this is not observed with the catalysts: CaO/SiO₂ and also the MgO/Al₂O₃ and MgO/SiO₂. CaO/Al₂O₃ differs from the others in such a way that it contains the basic sites with the mild basic strength. Not only the crystallite size but also the type of the oxide is important to obtain the heterogeneous catalysts as active as the homogeneous catalyst. CaO/Al₂O₃ has the same activity as that of NaOH for the transesterification of canola and sunflower oils at 50 °C. It was also found that the activity of CaO/Al₂O₃ was truly heterogeneous.

ÖZET

BİTKİSEL YAĞLARDAN HETOROJEN BAZİK KATALİZÖRLER ÜZERİNDE METİL ESTER ÜRETİMİ

Bu çalışmada katı karışık oksit katalizörlerin; alüminyum ve silika destek üzerinde magnezyum ve kalsiyum oksit, bitkisel yağların; kanola ve ayçiçek, metil esterlere transesterifikasyon aktivitesi çalışılmıştır. Bu çalışmanın temel amacı katı katalizörlerin bazikliği ve/veya bunların kristalit büyüklüklerinin reaksiyon sırasında biyodizel verimine etkilerini anlamaktır. Karışık oksit katalizörler tek basamaklı bir sol-jel yöntemi ile hazırlanmıştır. Magnezyum oksit (MgO) ve kalsiyum oksit (CaO) trigliseritlerin transesterifikasyonunda önemli role sahip bazik özellikleri nedeniyle seçilmişlerdir.

Bu çalışma kristalit büyüklüğünün transesterifikasyon aktivitesi üzerinde doğrudan bir etkisi olmadığını göstermiştir. Yinede, kristalitler ile destek malzemesi etkileşimi aktif bölgelerin sayısını değiştirmiş ve/veya yeni aktif bölgelerin oluşumunu sağlamış olabilir. Gerçekte bazikliğin transesterifikasyon reaksiyonu için uygun karışık oksit seçiminde kritik faktör olduğu bulunmuştur. Alüminaya CaO eklenmesi sinerjik etki yaratmaktadır. Ancak bu SiO₂ üzerinde CaO ve bunun yanında SiO₂ ve Al₂O₃ üzerinde MgO katalizörlerde bu gözlenmemiştir. Sadece kristalit büyüklüğü değil ayrıca oksidin tipide homojen katalizörler ile aynı reaksiyon koşullarında aynı aktiviteye sahip katı katalizör elde etmek için önemlidir. Al₂O₃ üzerinde CaO 50 °C sıcaklıkta kanola ve ayçiçek yağlarının transesterifikasyonunda NaOH ile aynı aktiviteye sahiptir.

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CHAPTER 1

INTRODUCTION

In the last century, industrialization and fast growth of the world population have resulted in energy consumption 10 times larger than the rest of the history, which corresponds to 471.8 quadrillion Btu in 2006 (International Energy Outlook 2007). In fact, major part of the energy was consumed in transportation activities resulted in by travel and trade activities and the main fuel used in transportation is gasoline and diesel; both are petroleum derivatives. A similar increase observed for Turkey as seen in figure 1.1 and energy consumption is expected to have reached 21,722 tons of oil equivalents constituting 18% of total consumption by 2010 (Karaosmanoğlu 1999). Consequently, it is predicted that the rapid increase in demand will result in price surge in petroleum to \$157 per barrel in 2030 from ~ \$68 per barrel in 2006. Although fossil fuels seem to be the primary source of energy for the next several decades, such price increase makes them insufficient for sustainable economical growth of countries (developed and developing) in the long term (Zachariadis 2003).

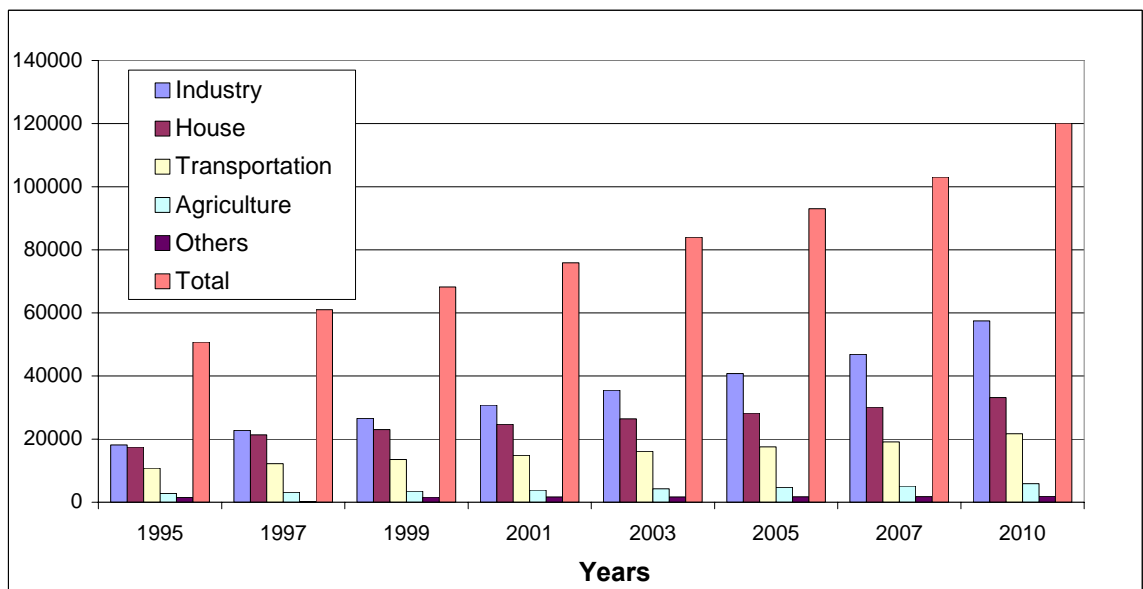


Figure 1.1. General Energy Demand in Turkey (as thousand tons of oil equivalent)
(Source: Karaosmanoğlu 1999)

In addition to petroleum price increases, another important effect of using petroleum derivatives is environmental pollution, such as air, water and soil. Among them, air pollution is major concern due to densely populated urban areas and that transportation is responsible for 28% of total CO₂ emission; in fact, the road transport alone currently is responsible for 84% of all transport related CO₂ emissions (Zachariadis 2003). To reduce the toxic exhaust gases and also evaporative emissions from vehicles, reformulated gasoline is considered to be an alternative solution by focusing on high energy content and low toxic gases, such as NO_x and SO_x emission but it is not very much effective in directly reducing CO₂ emission (Heather 2003). Another fossil fuel alternative is liquefied petroleum gas (LPG), which results in low CO₂ emission but its storage and bulk transportation make the use of LPG potentially hazardous (Heather 2003). With the Kyoto Protocol agreement submitted to the United Nations Framework Convention on Climate Change (UNFCCC), the use of renewable energy sources is encouraged and supported throughout the world. In this regard, renewable energy sources are considered to be much more effective solution to reduce CO₂ emission and to achieve a sustainable economic growth than fossil fuels.

Electricity and hydrogen are energy carriers. Since they are not freely available in nature, they need to be produced from a energy source, such as thermal, nuclear or renewable energy sources. When they are produced from a carbon-free energy source, they eliminate the net carbon dioxide emission to the atmosphere. However, technical and economical problems limit the usage of renewable sources to produce electricity and hydrogen in a large scale, such as power plant. For instance, the lower heating value of hydrogen is ~1.32 kWh/L when stored at 680 atm and also the commercial batteries are capable of storing less than 175 Wh/(kg of battery) of the current energy density whereas gasoline's energy density is ~8.88 kWh/L. Hence, the lack of economically feasible technology to manufacture storage devices and to produce hydrogen from renewable energy sources delays the application of energy conversion systems based on hydrogen. Furthermore, the current infrastructure for fuel delivery is not suitable for hydrogen (Agrawal 2007).

For the transient period between hydrogen and petroleum based economies, the use of renewable feedstock to produce renewable fuels, such as biodiesel and bio-alcohols, seems to be promising to support sustainable economic growth and also to reduce the carbon dioxide and related toxic gases emissions. For example, the alcohols, especially ethanol and methanol, produced from biological sources could be used as fuel

or fuel additives. When ethanol is used in a higher compression ratio, shorter burn time and lean burn internal combustion engine, much better fuel usage efficiency than gasoline could be achieved. In contrast to these advantages, the drawback of ethanol is its low energy content. Methanol has more limitations than ethanol because it is corrosive, highly toxic, colourless, odourless, and its flame when burned is almost invisible in daylight. Similar to ethanol, its energy density is lower than that of gasoline. Although alcohols seem to be inefficient as fuel sources, their usage as fuel additives are considered to be better approach to decrease pollutant emissions (Heather 2003).

Alternatively, vegetable oils are estimated to be promising renewable fuels. They could be used directly or indirectly. Direct usage of them in the internal combustion engines leads to the lubricating problems, coke formation, high viscosity and low volatility. Therefore, when they are converted into better fuels, such as methyl esters, known as biodiesel, the drawbacks related to the direct usage could be eliminated. In addition to vegetable oils, animal fats and waste cooking oils could be used to produce biodiesel.

In general, diesel fuels have high-energy density and biodiesel has further advantage because its usage lowers green house gases (GHG) emission (Heather 2003). Also, it contributes much less to global warming than fossil fuels since carbon in the biodiesel are reused by the plants; hence resulting in a near net zero carbon dioxide (CO₂) emission. Biodiesel has high cetane number, better lubricating properties and safer handling. Although there are many advantages of biodiesel, it is reported that the NO_x emission from the vehicle using biodiesel is slightly higher than that of using petro-diesel.

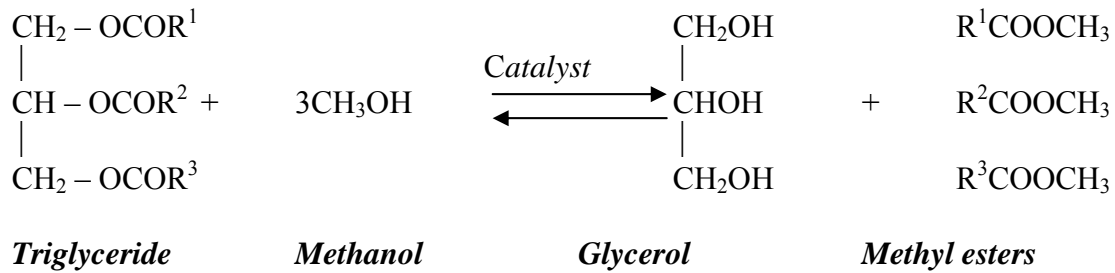
Biodiesel is the mixture of monoalkyl esters formed by a catalyzed reaction of the triglycerides found in the vegetable oils or animal fats with a simple monohydric alcohol. According to reaction stoichiometry, three moles of alcohol are needed for one mole of triacylglycerol to produce methyl esters. In practice, at least 1.6 times more alcohol is needed for a complete reaction because of that transesterification is a reversible reaction. Methanol and NaOH are commonly used in biodiesel production because of their low cost and high reactivity. The transesterification reaction requires approximately 1 hour at 60 °C. Typically, refined vegetables are used as feedstock for this reaction because excess free fatty acids result in soap formation by reacting with the catalyst (NaOH) and also, transesterification of free fatty acids is very slow. In fact, crude oils, fats or fryer grease has high free fatty acid content. Therefore, this types of

acidic feedstock needs to be pre-treated with alkali soaps or acids to remove excess free fatty acids. Similarly, water has the same effect as free fatty acids since it reacts with triacylglycerol to form fatty acids. Although vegetable oils are used mainly for biodiesel production, type of oil varies with the location. Rapeseed or sunflower oils are common in Europe while animal fats and corn oil is common in USA and palm oil is common in tropical climates. Coconut, rice bran, safflower, palm kernel, *Jatropha curcas*, beef tallow or many other lipid feedstock can be used in the production of biodiesel. Type of feedstock is not the only important factor affecting the quality of the biodiesel and the chemical process but also the determining factor on the biodiesel price. In fact, lipid feedstock constitutes 70 to 85% of the overall production costs.

Oils and fats are basically a mixture of lipids; ~95% triacylglycerols and the rest being diacylglycerols, monoacylglycerols, free fatty acids and sometimes phospholipids or other types of minor compounds. Since the beginning of 1900s, potential applications of vegetable oils have been studied. Rudolf Diesel was the first person who tested vegetable oils in his first compression type internal combustion engine (later known as diesel engine). Later it has been found that there are many problems for direct application of oils in diesel engines. First, the injection and atomization of this type of fuel could not be achieved successfully because of high viscosity of oils and especially fats as compared to conventional diesel fuel and second, high molecular weight of triacylglycerols and other compounds results in incomplete combustion because of low volatility. Third, carbon deposits formed during incomplete combustion and thickening of the lubricating oil as a result of contamination by oils cause major engine problems. In addition, the polymerization of unsaturated fatty acids is possible. Therefore, to eliminate polymerization, free fatty acid level should be lowered since crude oils mostly have considerable fatty acid concentrations and they require refining processes for direct applications. Similarly, recycled greases cannot directly be used as fuel in combustion engines, since they already contains polymerized compounds and large amounts of free fatty acids.

To overcome the problems related to direct usage, four methods have been investigated: blending with petrodiesel, pyrolysis, microemulsification, and transesterification. Transesterification is the most common approach among these methods. For this reaction, methanol and NaOH (used as the alcohol and the homogeneous catalyst, respectively) are common choice in the practice.

This reaction is represented as;

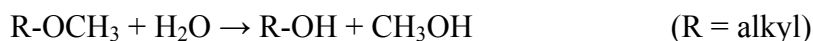


where R1, R2, and R3 are long hydrocarbon chains. This reaction is reversible and hence, to shift the equilibrium towards right (i.e. the formation of methyl esters), excess alcohol is used (Naik 2006). Transesterification can be catalyzed by both acidic and basic catalysts. Acid catalyzed transesterification is slow and needs temperatures higher than 100 °C whereas base catalyzed reaction is known to be fast even at room temperature but highly sensitive to the presence of free fatty acid content.

Free fatty acid and moisture adversely affect the transesterification reaction. For example, the production of methyl esters using base catalysts decreases in the presence of as low as 3% free fatty acid content. In fact, free fatty acids and alkali catalysts forms alkali soaps; hence decreasing the catalyst amount is needed for transesterification reaction. Furthermore, soap could cause emulsion, and this result in difficulties in the downstream recovery and biodiesel purification steps (McLean 2003). Basically, soap formation occurs through the following reaction;



If there is some water, hydrolysis of alkyl esters happen and free fatty acids produced with the following reaction path;



Water can also react with triacylglycerols to form free fatty esters. Higher alcohols are particularly sensitive to water contamination. Thus, for a complete reaction, alcohol must be free of water and free fatty acid content in the oil must be lower than 0.5% (International Energy Outlook 2007). Thus, free fatty acids in feedstock like beef tallow or fryer grease needs to be treated to eliminate the possible side reactions listed above.

In Figure 2, the typical flow diagram for a large scale industrial production of biodiesel is shown. To achieve a high yield of biodiesel, the alcohol and catalyst are added stepwise manner at the start of each step, and the glycerol is removed at the end of each step. Small manufacturing plants use mostly batch reactors. Glycerol is removed following the reaction using a settling tank or centrifuge since it has very low solubility in the esters. Methanol increases contact between oil and NaOH because NaOH dissolves in methanol but separation of methanol from esters and glycerol is an additional step to recover the unreacted excess methanol.

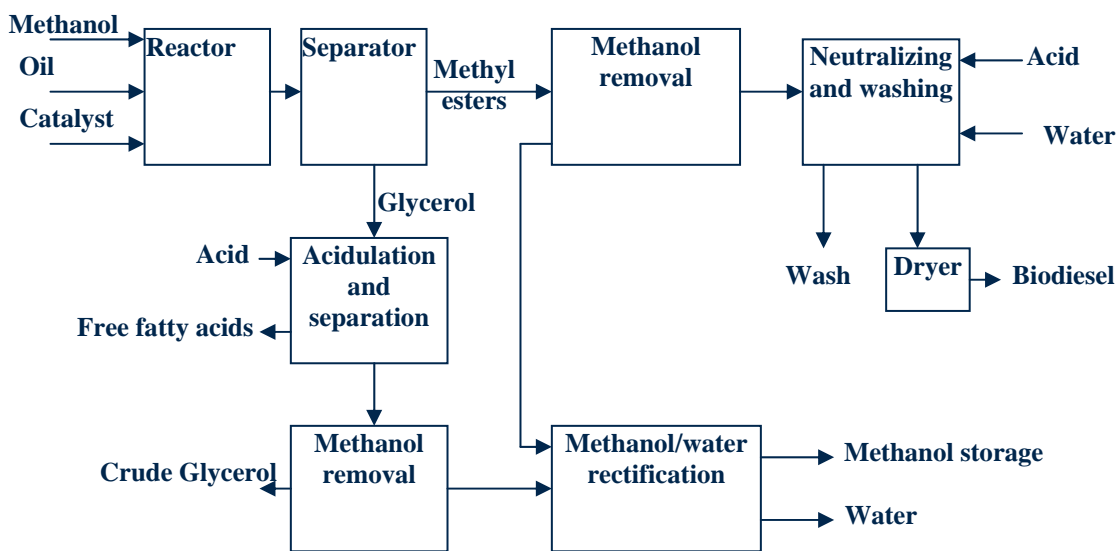


Figure 1.2. Process flow schematic for alkali catalyzed biodiesel production
(Source: Van Gerpen 2005).

The use of acid catalysts, most commonly sulfuric acid, can be applied for the biodiesel production since it has an advantage of insensitivity to free acids in the feed. This is known as esterification reaction. But there are no industrial applications using acid catalyzed reaction path (i.e. esterification) because of long reaction time and high temperature requirements (Dube 2006). Yet, for high free fatty acids levels, the neutralization of acidic oils by esterification is proved to be a useful pretreatment before carrying out the transesterification reaction. But acid catalysts must be neutralized before the transesterification reaction, because it results in increase of ash content (Bondioli 2004). In contrast, it is possible to react oil and methanol without any catalyst. Hence, most of the separation processes in biodiesel production would be eliminated since there is no excess catalyst or soap formed during the reaction. But this reaction

requires high pressures and temperatures. For fats, the reaction takes place at 90 bars and 240 °C. The advantage of this reaction condition is that free fatty acids are also esterified so no pre-treatment steps are needed. Unfortunately, the process is not feasible because of increased operating and equipment cost compared to common industrial processes conducted at mild reaction conditions. The removal of NaOH catalyst from ester or glycerol is difficult and increases the complexity and operational costs of the process. The current biodiesel production processes using homogeneous catalysts cannot compete with petroleum diesel because of the high cost of feedstock; high capital and operational costs and also the difficult and complex separation processes. In contrast, the use of heterogeneous catalyst would eliminate many problems, such as soap formation and some unit operation steps, faced with the homogeneous catalysts.

Primary objective of this study is to understand whether basicity (amount of the basic sites) of the solid catalysts and/or its crystallite size is affecting the biodiesel yield during the transesterification of canola and sunflower vegetable oils. For this purpose, calcium oxide (CaO) and magnesium oxide (MgO) on alumina (Al₂O₃) and silica (SiO₂) were used as the solid catalysts. CaO and MgO are chosen because they are basic catalysts; thus being suitable for transesterification. Preparation of CaO and MgO with controlled crystallite size using conventional preparation techniques, such as precipitation, is very difficult. But indirect approach is to use inert support oxide to disperse CaO and MgO to obtain a controlled variation of their crystallite size. For this purpose, a modified sol-gel method was used to synthesize alumina and silica supported CaO and MgO catalysts because it was possible to control the crystallite size of the CaO and MgO in the alumina and silica by adjusting the preparation conditions; hence resulting in varying crystallite size. Then, it is possible to determine the effect of crystallite size and also the basic amounts of CaO and MgO on the biodiesel yield. To find the optimum reaction conditions, such as methanol/oil ratio and the catalyst amount, the homogeneous transesterification (using with methanol and NaOH) was also performed by using the design of the experiment for both vegetable oils. After that, heterogeneous transesterification was carried out for the solid catalysts made with the modified sol-gel method under the optimum reaction conditions.

This thesis contains five chapters. In chapter one, a general introduction for renewable fuels, the significance of renewable, the production of biodiesel and also the aim of this thesis are introduced. In chapter two, a literature survey on the properties of

oils and the biodiesel production from vegetable oil using both homogeneous and heterogeneous catalysts are presented. In chapter three, the specifications and pretreatment procedures (if any) of the chemicals used in this study and also the single step sol-gel method to synthesize the heterogeneous catalysts is explained in details. Also in this chapter, the material characterization methods, such as X-Ray diffraction and the surface area measurement using N₂ adsorption are given. In chapter four, the catalysts activity, and the material properties, such as crystallite size, are presented and discussed to shed light on the relationship between the catalyst activity and the textural and chemical properties of the catalysts studied in this thesis. Finally, the conclusions and some recommendations are listed in chapter five.

CHAPTER 2

LITERATURE SURVEY

2.1. Oils and fats

Basically oils and fats are a mixture of lipids mainly composed of triacylglycerols and the composition of the most common vegetable oils are given in Table 2.1. In this table numbers in the second row denotes different major fatty acids in the oil; the first number represents number of carbon atoms and second number represents number of unsaturated bonds in the chain. Currently, the choice of the production of vegetable oil is mostly determined by its nutritional value. However, another use of vegetable oils is fuel derivative and also replacement of petroleum based conventional fuels with the fuels based on vegetable oils is starting to gain importance. In the case of biodiesel, the replacement could be done without major adjustments. Physical and chemical properties of the oils and fats vary greatly depending on their source. And such differences directly affect the properties of biodiesel. Free fatty acid value and water content are the most important characteristics to achieve high biodiesel production yield. Water is especially a problem for the conversion of the fats to biodiesel. Although some of these vegetable oils have better characteristics for biodiesel production, they are not widely used as raw materials because of their market share and the special requirements for plantation location.

Table 2.1. Fatty acid composition of common vegetable oils
(Marchetti 2007)

Vegetable oil	Fatty acid composition % by weight									Acid value	Phos (ppm)	Peroxide value
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	1.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11	7	18.4
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07	8	64.8
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36	12	26.5
Peanut	1.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20	9	82.7
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23	1.14	18	30.2
Soybean	1.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20	32	44.5
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15	15	10.7

2.2. Transesterification reaction

The most important factor for transesterification reaction is the catalyst type and its concentration. Basic and acid catalysts (homogeneous and heterogeneous) as well as enzymatic catalysts can be applied. Homogeneous alkali catalysts like NaOH or KOH are conventionally preferred because they are more efficient than other catalysts and also less corrosive than acidic catalysts. But, this process is highly sensitive to the presence of free fatty acids and the moisture. Under such conditions, the soap formation decreases the ester yield and makes downstream recovery more difficult and expensive. Acidic catalysts (most commonly used is sulphuric acid) are insensitive to free fatty acids but they require high temperatures or long reaction time. For example, 99% oil conversion using 1% mol of sulphuric acid is achieved in 50 hours under a reaction of a molar ratio of alcohol to oil 30:1 and 65 °C (Marchetti 2005). They are highly efficient when dealing with high fatty acid containing oils; thus, they are used in pre-treatment of such feed stocks in industrial applications.

Enzymatic catalysts, especially lipase, have gained a considerable interest for the transesterification reaction. They have the advantages of working at room temperatures without producing spend catalysts and this makes the separation of products easier and also it is possible to recycle when immobilized onto a substrate and they have high selectivity since they are highly specific for the reaction under consideration. But, the immobilization can cause the reduction of enzyme activity. And in the case of other enzymes, alcohols can be inhibitory; thus alcohol needed to be in 1:1 mole ratio. Since the reactions are very slow, 4 to 40 hours is required for each step. In addition, they are more expensive than other catalysts (Van Gerpen 2004, Marchetti 2005).

Basically, amount of catalyst increases ester yield for a limited time as expected. In the case of basic catalysts, transesterification of soybean oil was carried out with methanol in the presence of THF at different concentrations of sodium hydroxide for example 1.1, 1.3, 1.4 and 2.0% and the corresponding biodiesel yield were found to be 82.5, 85, 87 and 96.2%, respectively (Naik 2006). The results for acid catalyzed processes are similar to those of base catalyzed ones.

Alcohol type is also another important parameter for achieving high conversions since oils and fats are immiscible in alcohol – sodium hydroxide solution. Theoretically any alcohol can be used for biodiesel production and there is no chemical difference in

the reaction products (Van Gerpen 2005). But mostly ethanol and methanol is used for transesterification of vegetable oils (Naik 2006). Applications of other alcohols such as propanol, butanol or octanol were also reported (Van Gerpen 2004). In conventional processes, methanol is preferred rather than ethanol since more stable emulsions are formed (Naik 2006). For any alcohol, excess amount of the alcohol (at least 1.6 times the stoichiometric amount; which is 1:3 oil/alcohol ratio) is required for complete conversion (Van Gerpen 2005). The excess of alcohol is needed to shift the reversible reaction to the right side (i.e. more biodiesel formation), but recovering glycerol becomes more difficult because of the increased alcohol ratios. For transesterification of soybean oil with methanol in the presence of 1% H₂SO₄ catalyst and 30:1 alcohol/oil molar ratio at a reaction temperature of 65 °C, the complete conversion was observed in 20 h. Under the same reaction conditions and alcohol amounts, the complete conversion was achieved in 3h for butanol at 117 °C and 18h for ethanol at 78 °C (Naik 2006).

Alkoxides can directly be used rather than first reacting the alcohols with NaOH. The use of alkoxides also increases glycerol purity (biodiesel handbook). In fact, alcohols react with the basic catalysts to form methoxides which will react with the triacylglycerols. But water forms during the reaction as seen below;



To surpass mass transfer limitations because of the miscibility problems more intense mixing can also be applied. Conversion is insignificant without mixing, and when the threshold mixing required is achieved and two phases mixed reaction starts and there will be no need for stirring. But it should be considered that because of miscibility problems reaction do not follow characteristics of homogeneous reactions and reaction time for complete conversion can be longer if the droplets are not sufficiently small. It is reported that for transesterification at ambient temperature and pressure with NaOH or KOH 99.7% conversion achieved in 10 minutes under vigorous stirring (Van Gerpen 2004, Naik 2006).

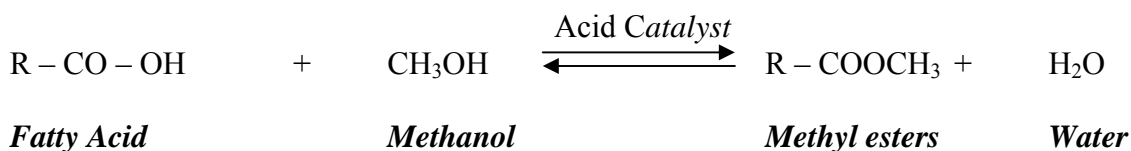
Another way to reduce miscibility problems rather than vigorous stirring is application of co-solvents like tetrahydrofuran,1,4-dioxan (THF) to reduce the formation of emulsions. When THF is applied for soybean oil reacted with MeOH for 1.1% NaOH 82.5% conversion is achieved in 1 minute. Similarly for coconut oil for 1%

NaOH catalyst with THF/MeOH ratio 0.87, 99.9% conversion is achieved in 1 minute (Naik 2006).

Process temperature is mostly limited with the boiling point of alcohol; in the case of methanol close to 60 °C, (Xei 2007). A lower process temperature can be applied if co-solvents as tetrahydrofuran are used (Van Gerpen 2004). Mostly reactions take place at atmospheric pressure (Bondioli 2004), but it is also reported that under supercritical conditions with temperature between 350 to 400 °C and pressures over 80 atm a non-catalytic reaction with complete conversion can be achieved, but high capital and operational costs limits industrial applications (Naik 2006). For the same reaction conditions other than temperature for refined oil with methanol for 6:1 MeOH/oil ratio and 1% NaOH concentration ester yields were 94, 87 and 64% for reaction temperatures of 60, 45 and 32 °C in 6 minutes. But after 1 hour all conversions become slightly the same (Naik 2006).

2.3. Esterification

Esterification is a slow, acid catalyzed reaction and mostly applied when free fatty acids concentrations are higher than 1% as a pretreatment rather than saponification of free fatty acids by alkali catalyst (Solomon 2000).



2.4. Process comparison with heterogeneously catalyzed processes

Application of heterogeneous catalysts improves biodiesel production by eliminating these separation steps. Literature survey shows that acidic and basic heterogeneous catalysts show more promising results than other catalysts. High conversions could be achieved at temperatures ranging from 40 to 65 °C in a few hours by using heterogeneous catalysts. Acidic, basic, enzymatic catalysts or ion-exchanged resins can be considered. Solid acids require higher temperatures and reaction time compared to basic catalysts as in homogeneous catalysis for high conversions. But

conversions higher than 90% are reported. Although enzymatic catalysts, for instance lipases are environmentally more acceptable, they do not provide the degree of reaction completion required to meet the ASTM fuel specification, they are expensive and have various activity problems when immobilized (Van Gerpen 2005).

As stated before water has a negative effect on the reaction, but also it is needed to a degree for ion-exchanged resins since dissociation of sulfonic groups is impossible for a completely dried resin to have any catalytic activity for acidic resins. Strongly basic ion-exchange resins are instable when heated at temperatures higher than 40 °C, while even at low concentrations free fatty acids can neutralize the catalyst. In addition, high viscosity of fatty materials and diffusion within the resin are other problems for resin-catalyzed systems (Bondioli 2004). Despite all these problems ion-exchanged resins has promising capability for trans-esterification processes. Conversions as high as 98.8% for triolein at 50 °C for 60 minute residence time and 10:1 methanol oil ratio is reported for PA306s resin catalysts (Yonemoto 2007).

Solid super acids promote the trans-esterification of vegetable oils as well as the esterification of free fatty acids and by-products (Furuta 2004). But solid acid catalysts may contain various acid sites and their non-ideality can lead often to phase segregation and catalyst degradation (Zhongmin 2007). Further, reaction needs higher temperature when solid acids used as catalysts rather than solid bases. Solid acids of mixed metal oxide; sulphated zirconia, can achieve slightly complete conversions but only at a high temperatures up to 200 °C (Furuta 2004). Despite heterogeneous catalysts can have some drawbacks like mass transfer limitations or ratio of active sites compared to homogeneous counterparts, some of them shows promising results. Studies on a commercial catalyst for the hydration of olefins, heteropolyacid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, has been used as a heterogeneous catalyst exhibits higher activity than H_2SO_4 when it is pretreated at 300 – 400 °C for the production of biodiesel at lower temperatures. As other acid catalysts it is nearly unaffected by high free fatty acid levels or moisture. Heteropolyacid gives high yields of 99% in 45 minutes with a catalyst concentration of 1.85×10^{-3} by weight and methanol/oil ratio of 5.3:1 in the presence of THF for *Eruca sativa* Gars oil. Produced biodiesel also meets ASTM standards and shows significant storage stability (Zhongmin 2007). Zeolites, mixed metal oxides and carbon based solid acids require water tolerance and resistance for the temperatures of up to 200 °C needed for acid catalyzed transesterification (Rothenberg 2006), and they require more reaction times than other basic catalysts. Zeolites do not change conversion significantly, yet

aluminium, silicon and oxygen atoms in the structure of zeolites help to control both acidity and hydrophobicity of catalyst by changing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

Bases are used as catalysts more commonly than acids in biodiesel production because of less energy requirement. Basic strength is one of the most important characteristics for such catalysts. Mostly, catalytic activity increases with basic strength to high conversions; up to 93.5% for solid base catalysts were reported (Zongbin 2006). Base heterogeneous catalysts, potassium and sodium compounds or similar basic sites on various supports like Al_2O_3 are reported as promising catalysts (Lee 2004, Xie 2006, Huang 2006). In some studies ZnO was used as a support material rather than Al_2O_3 (Xie 2006) Another basic catalyst is ion-exchanged zeolites, which has high conversions of 80%, but unfortunately requires long reaction times of 24 h at 60 °C (Suppes 2003). Shorter reaction times are achieved at high temperatures of greater than 100 °C.

Since transesterification of oils is a reversible reaction, which is highly affected by reaction conditions, increasing alcohol amount up to an alcohol/oil ratio to shift the reaction to products side has a great impact on increasing conversion. KI on Al_2O_3 support with 2 wt% catalyst amounts at methanol reflux temperature for 6 hours of reaction time for various methanol ratios showed that maximum conversion are achieved at 15:1 methanol/oil ratio. Further increase of methanol does not affect conversion significantly. At the same reaction conditions (15:1 methanol/oil) increasing catalyst amount positively affected achieved conversions to a maximum conversion of 96% by increasing catalyst concentration up to 2.5 wt% (Xie 2006). Increasing reaction temperature is limited to the alcohol boiling point. Up to 65 °C temperature greatly affects the conversion, increasing the temperature affects the conversion with a lesser degree, yet maximum conversion were achieved at methanol boiling point (Zongbin 2006).

Increasing catalyst load has a positive effect up to a point to achieve high conversions; for potassium iodide (KI), it is reported that the conversion was increased up to 35 wt% catalyst load with the highest conversion of 87.4%. At higher catalyst loads, catalytic activity are lowered since excess KI covers the basic sites on the surface of the composites (Xie 2006).

Solid base catalysts for biodiesel production in literature are most commonly prepared in two different ways: precipitation (Zongbin 2006), impregnation (Xie 2006, Lee 2004). During calcination, temperature may cause transformation of the crystal structure of catalyst and the coordination number of ions on the catalyst surface. Thus,

the number of basic sites and their strength will be changed (Zongbin 2006). Further, homogeneity of the calcined mixture is important for the catalysts activity. BET results of two different studies on CaO catalyst show that pretreatment of the catalyst with ammonium carbonate solution leads to decrease of surface area, e.g. 6 m²/g (Zongbin 2006) as compared to 32 m²/g (Granados 2007). It is stated that mainly two properties are important for highly active heterogeneous catalysts; basicity and crystallinity (Tanabe 1989).

Basicity of catalysts determined by various methods like temperature programmed desorption (TPD), titration or adsorption microcalorimetry (Suppe 2003). The most common technique in the literature for determining basic strength of heterogeneous catalysts for biodiesel is using Hammet indicators. To determine basic strength of catalyst with Hammet indicators required amount of sample was shaken with appropriate volume of a methanol solution of Hammett indicator and left to equilibrate for 2 h after which no further colour changes were observed. Then, base strength is determined by colour change since weaker indicator produces no change. Bromthymol Blue ($H^- = 7.2$), phenolphthalein ($H^- = 9.8$), 2,4-dinitroaniline ($H^- = 15.0$) and 4-nitroaniline ($H^- = 18.4$) are used for determining different basic strengths (Xie 2006). By temperature programmed desorption (TPD) method, the amount of basic sites in different solid samples can be studied to understand whether strong or weak acidic and basic or both are present on the catalyst surface. The distribution of basic site strength of the surface is determined by CO₂ adsorption, and the distribution of acidic sites can be determined with NH₃ used as probe adsorption gas. Samples charged into TPD apparatus and pretreated at high temperatures about 200 – 400 °C for several hours under helium flow to remove any physisorbed organic molecules. After pretreatment, CO₂ was then pulsed into the chamber with regular intervals at room temperature under helium flow, until the basic sites were saturated with CO₂. The physisorbed CO₂ was removed by evacuating the sample at mild temperatures 50 – 80 °C for 1 – 2 hours. The furnace temperature was increased from room temperature to the high temperatures of 500 – 600 °C at a rate of 5 °C per min under a flow of helium. The desorbed CO₂ can be detected by using either a GC-MS or titration (Song 2007, Azzouz 2006). Basic strength, the reaction parameters and conversions of various basic catalysts are listed in Table 2. As seen in Table 2, the high conversions are achieved with highly basic catalysts (Zongbin 2006, MacLeoda 2008, Xie 2006).

Table 2.2. Reaction conditions and conversions for various basic heterogeneous catalysts.

Catalyst	Basic strength	Catalyst Amount	Catalyst Load	Molar Methanol/ Vegetable Oil ratio	Oil	T (°C)	Yield %	Reaction time	
Na/ γ -Al ₂ O ₃	-	1g/80mL	20 wt%.	6:1	Soy bean	60	70	2 h	(Kim 2004)
Na/NaOH/ γ -Al ₂ O ₃	-	1g/80mL	20 wt%	6:1	Soy bean	60	77	2 h	(Kim 2004)
NaOH/ γ -Al ₂ O ₃	-	1g/80mL	20% wt.	6:1	Soy bean	60	69	2 h	(Kim 2004)
Al ₂ O ₃	<7.2	2 wt%	pure	15:1	Soy bean	Reflux	0	8 h	(Xie 2006)
KF/Al ₂ O ₃	15.0–18.4	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	85.8	8 h	(Xie 2006)
KCl/Al ₂ O ₃	<7.2	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	0	8 h	(Xie 2006)
KBr/Al ₂ O ₃	9.3–15.0	2% wt.	2.1 mmol/g	15:1	Soy bean	Reflux	16.7	8 h	(Xie 2006)
KI/Al ₂ O ₃	15.0–18.4	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	87.4	8 h	(Xie 2006)
KI/ZrO ₂	15.0 – 18.4	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	78.2	8 h	(Xie 2006)
KI/ZnO	9.3 – 15.0	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	72.6	8 h	(Xie 2006)
KI/NaX	9.3 – 15.0	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	12.9	8 h	(Xie 2006)
KI/KL	9.3 – 15.0	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	28.3	8 h	(Xie 2006)
K ₂ CO ₃ /Al ₂ O ₃	9.3–15.0	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	48.0	8 h	(Xie 2006)
KNO ₃ /Al ₂ O ₃	15.0–18.4	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	67.4	8 h	(Xie 2006)
KOH/Al ₂ O ₃	15.0 – 18.4	2 wt%	2.1 mmol/g	15:1	Soy bean	Reflux	80.2	8 h	(Xie 2006)
KF/ZnO	15.0 – 18.4	3 wt%	15 wt%	10:1	Soy bean	Reflux	87	9 h	(Huang 2006)
KOH/ZnO	15.0 – 18.4	3 wt%	15 wt%	10:1	Soy bean	Reflux	82	9 h	(Huang 2006)
K ₂ CO ₃ /ZnO	15.0 – 18.4	3 wt%	15 wt%	10:1	Soy bean	Reflux	74	9 h	(Huang 2006)
CaO	26.5 – 33.0	1.5 wt%	pure	9:1	jatropha curcas	70	93.5	2.5 h	(Zongbin 2006)
KOH/NaX zeolite	15.0 – 18.4	3 wt%	10 wt%	10:1	Soy bean	65	85.6	8 h	(Xie 2007)
KNO ₃ /Al ₂ O ₃	15.0 – 18.4	6.5 wt%	35 wt%	15:1	Soy bean	Reflux	87.4	7 h	(Xie 2006)
MgO	-	1.5 wt%	pure	4:1	Rapeseed	70	93	2 h	(Parvulescu 2008)
MgO	-	0.1 wt%	pure	4.5:1	Rapeseed	Reflux	0	2.5 h	(Santacesaria 2007)
CaO	-	0.1 wt%	pure	4.5:1	Rapeseed	Reflux	0	2.5 h	(Santacesaria 2007)
NaNO ₃ /CaO	11.0 – 15.0	5 wt %	5 wt%	6:1	Rapeseed	60	100	3 h	(MacLeod 2008)
KNO ₃ /CaO	11.0 – 15.0	5 wt%	5 wt%	6:1	Rapeseed	60	100	3 h	(MacLeod 2008)
NaNO ₃ /MgO	10.1 – 11.0	5 wt%	5 wt%	6:1	Rapeseed	60	100	3 h	(MacLeod 2008)
KNO ₃ /MgO	10.1 – 11.0	5 wt%	5 wt%	6:1	Rapeseed	60	4	3 h	(MacLeod 2008)
Ca ₂ Fe ₂ O ₅	7.2 – 9.3	10	pure	10:1	Rapeseed	60	92	10 h	(Kawashima 2008)
CaO	-	8	pure	12:1	Soybean	65	97	0.5 h	(Wang 2008)
CaO	-	1	pure	12:1	Sunflower	60	92	10	(Granados 2007)

These various studies show that catalyst activity is increased with basicity. The basicity is increased with the ionic radii of the active material for alkaline–earth materials since their electronegativity decreases (Gryglewicz 1999). When catalyst preparation parameters effecting basicity for KNO₃/Al₂O₃ catalysts is inspected it is seen that basic strength was increased up to 35for 20 wt%. catalyst load then started

decreasing, and results in loss of catalyst activity. But high basicity of catalyst does not the only parameter effecting catalyst biodiesel yield. Catalyst preparation and pre-treatment also affect the activity of the catalyst. CaO is known for its basicity which has basic sites stronger than $H_- = 26.5$ (Wang 2008), and it is the most common heterogeneous catalyst studied for transesterification of oils. Two different researchers; Santacesaria (Santacesaria 2007) and Zongbin (Zongbin 2006) states totally different results for pure CaO. Zongbin reported a high yield as 93.5% where Santacesaria states there were no observed conversion. The main difference between these two studies is calcination temperatures which are 850 and 500 °C for Zongbin and Santacesaria respectively. Other two studies on CaO also shows that for similar temperature and same MeOH/oil ratio biodiesel yields over 97% (Wang 2008) and 92% (Granados 2007) was achieved in 0.5 and 10 hours respectively. The reason of this great variation between these two results is the catalyst amount. By increasing catalyst amount 8 times the required reaction time is decreased nearly 20 times. Similarly increasing calcination temperature results in increasing basicity for KNO_3/Al_2O_3 catalyst. But with increased catalyst load potassium becomes more soluble in MeOH and catalyst becomes less stable especially at high calcination temperatures. When KNO_3/Al_2O_3 catalyst is compared with K_2O formed after decomposition it is seen that basic sites are not only associated with potassium species only. A wide range of various basic sites are available on the surface of the catalysts (Xie 2006). And when CaO is used as support for alkali metals calcination is not needed to achieve high basic strength. Formation of O^- centers through the substitution of M^+ ions into the alkaline earth oxide lattice might increase in base strength on alkali promotion. Similarly the same is true for MgO used as support and K and Na are active phases, but basic strength is lower compared to CaO. And for Al_2O_3 supported alkali oxide catalysts calcination is required for high basicity. This increase might be caused by decomposition of salt anions to form an O^- anion (MacLeod 2008).

Basicity is also affected by the ionic facet exposed at the surface of the catalyst. Studies on pure MgO nano film show that catalysts with (111) surface shows the highest basicity by comparison of the amount of CO_2 absorbed. But catalyst activity changes only slightly 75 to 85% methylester yield for MgO prepared by three totally different preparation technique which are nanosheets, conventional and aerogel (Parvulescu 2008). Further it is reported that pure MgO catalyst may be subject to leaching effect in the presence of FFAs and forms Mg-soaps (Santacesaria 2007).

Although basicity was inspected in most of these studies, these studies were focused on catalyst screening and total basicity was inspected. Effect of basic strength of the active sites on transesterification activity was not studied, to the best of our knowledge. But only McLeod et. al. reported that only catalyst with basic strength (pK_{BH^+}) higher than 11 were shows activity (McLeod 2008). Base strength must be high in order to form methoxide, which attacks the carbonyl group on the triglyceride as in homogeneous catalysts. This result is also consisted with the other studies in the literature (Xie 2007, Huang 2006). But there was no clear correlation between basic strength and catalyst activity reported until now (Rudolph 2008).

Other important properties of a catalyst; crystallographic structure, chemical composition, and physical properties of materials are determined by different X-ray diffraction (XRD) techniques. Powder XRD results show that for KI/ Al_2O_3 catalyst, it is observed that amorphous structure of alumina does not change even though KI was in the crystalline form at higher loading of KI and a good dispersion of KI as a monolayer on Al_2O_3 is also observed by SEM pictures. Further spontaneous dispersion capacity of KI on the Al_2O_3 is found between 35 – 40% and high activity is reported to be a result of carbonate groups formed on the surface (Xie 2006). And also effects of residual chemicals during catalyst preparation can be easily observed by crystalline defects (Zongbin 2006). For KNO_3/Al_2O_3 catalysts with catalyst loads less than 15% there are no peaks observed in XRD pattern, which indicates that a fine dispersion was achieved (Xie 2006). Further spontaneous dispersion of KNO_3 over Al_2O_3 for catalyst loads of 15 to 20 wt% results in monolayer dispersion on Al_2O_3 . Another important fact is that at 35 wt% catalyst load KO_2 peaks starts to emerge, and this might be the result of increased basicity and activity. Although effect of different sites formed on the surface by interaction of support and active materials were considered as a factor for catalyst activity, the effect of crystallite size on this mechanism had not been considered.

CHAPTER 3

MATERIALS and METHOD

3.1. Materials

In this study, four mixed oxide catalysts were synthesized; CaO/Al₂O₃, CaO/SiO₂, MgOAl₂O₃ and MgO/SiO₂ with the loadings of 5, 20, 50 and 80 wt%. In the synthesis of the catalysts, magnesium nitrate hexahydrate (Fluka) was used as a precursor for magnesium oxide and calcium nitrate tetrahydrate (Fluka) as precursor for calcium oxide. Aluminum isopropoxide (AIP) and tetraethyl orthosilicate (TEOS) (Fluka) were used as precursors for alumina and silica support oxides, respectively. Ethanol (EtOH) and deionised water (DIW) were used as solvents and hydrochloric acid (HCl), nitric acid (HNO₃) and ammonium hydroxide (NH₄OH) were used as peptizer in the sol-gel method. Used chemicals are summarized in the Table 3.1.

Table 3.1. Properties of materials used in mixed oxide catalyst synthesis.

	Chemical formula	Molecular Weight (g/mol)	Purity (%)
Aluminum isopropoxide	Al(OCH(CH ₃) ₂) ₃	204.24	98
Tetraethyl orthosilicate	Si(OC ₂ H ₅) ₄	208.33	98
Calcium nitrate tetrahydrate	Ca(NO ₃) ₂ ·4H ₂ O	236.15	99.3
Magnesium nitrate hexahydrate	Mg(NO ₃) ₂ ·6H ₂ O	256.41	98

Homogeneous transesterification reaction was carried out using sodium hydroxide (NaOH) and methanol (MeOH). Commercially available canola (from Yonca Inc.) and sunflower (from Tansaş Inc.) oils were used as the lipid feedstock. Acetic acid was used to remove the unreacted NaOH from the biodiesel.

3.2. Methods

In this study experiments can be categorized into four groups;

- Homogeneous transesterification of the oils
- Catalyst preparation
- Solid oxide catalyst testing in transesterification of the oils
- Catalyst Characterization

3.2.1. Homogeneous transesterification of the oils

Commercially available sunflower and canola oils were used and transesterification was carried out under reflux condenser to avoid methanol losses. The temperature was kept constant by a thermostatic bath during the reactions. First, NaOH was added to methanol at room temperature and stirred at 1100 rpm for 10 min to form methoxide. After methoxide formation, temperature was increased to 50 °C and then oil was added. The reaction medium was stirred at the same speed and the temperature for 4 h to achieve the complete conversion for the oil. After reaction stopped, the settling of glycerol was observed. Then, methyl esters were analyzed using a GC equipped with FID detector and DB-WAX 122-7032 capillary column with a 30 m column length, 0.25mm column thickness and 0.25 µm film thicknesses.

In order to find the optimum process conditions, star experimental design was applied (Montgomery 2005). Process conditions, such as 50 °C temperature, 1100 rpm stirring speed and 1 h of reaction time were kept constant but NaOH amount and methanol/oil ratio were varied according to the star design analysis. There were 5 replicates at the central point and star distance was chosen as 1.414. Total of 13 experiments were evaluated for the stated reaction conditions. Methanol/oil molar ratio was changed from 3 to 13, and NaOH amount was accordingly varied from 0.59 to 3.00 g/kg. For all the experiments, 20 mL of the vegetable oil was used.

3.2.2. Catalyst preparation

MgO and CaO on Al₂O₃ and SiO₂ catalysts were synthesized using a modified single step sol-gel method. To prepare alumina supported catalysts; first, necessary amounts of alumina isopropoxide (AIP), water and HNO₃ were mixed at 85 °C under total reflux for 1 h. Then, calcium nitrate was added. Finally, excess water was removed with slow evaporation to obtain the mixed oxide gel. For silica supported catalysts first needed amounts of 1.00 M HCl, DIW, TEOS and ethanol were mixed at 80 °C and stirred for 2 h at the same temperature. Then, the catalyst precursor was added and mixture was stirred for 10 min. After that 0.05 M of HN₄OH was added and waited for the gel to occur. All the gels were dried at 120 °C for 18 h. The catalysts were calcined at 500 °C for 6 h prior to the transesterification reaction. The catalysts were ground and sieved for less than 325 mesh and stored in the desiccators. Pure MgO was obtained by pH controlled precipitation of magnesium nitrate precursor in DIW with NH₃OH. The same calcination and sieving procedures were applied for pure CaO and MgO catalysts. The schematic diagram for both sol-gel procedures are given in Figure 3.1 and 3.2.

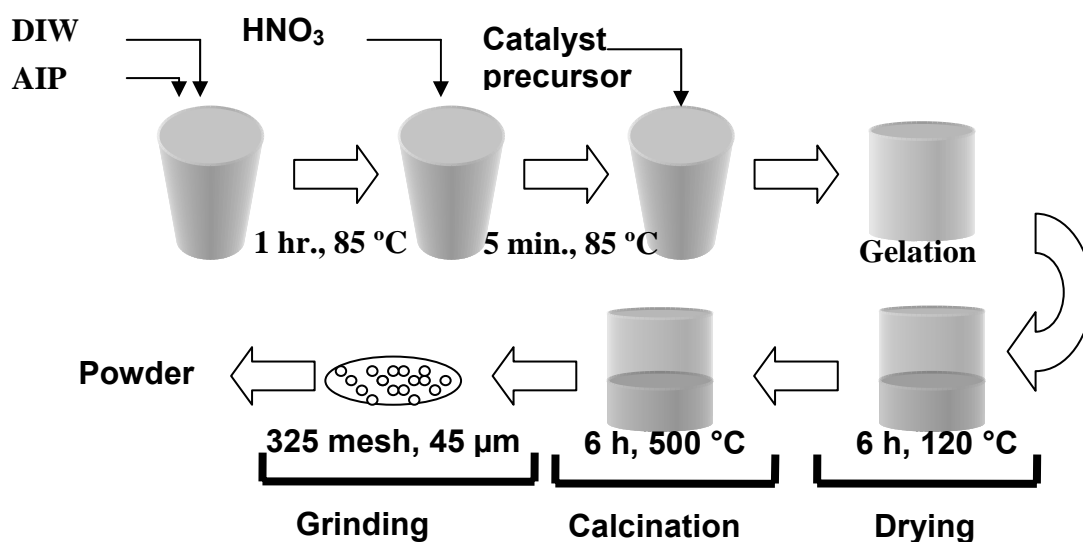


Figure 3.1. Experimental procedure for the preparation of alumina supported catalysts

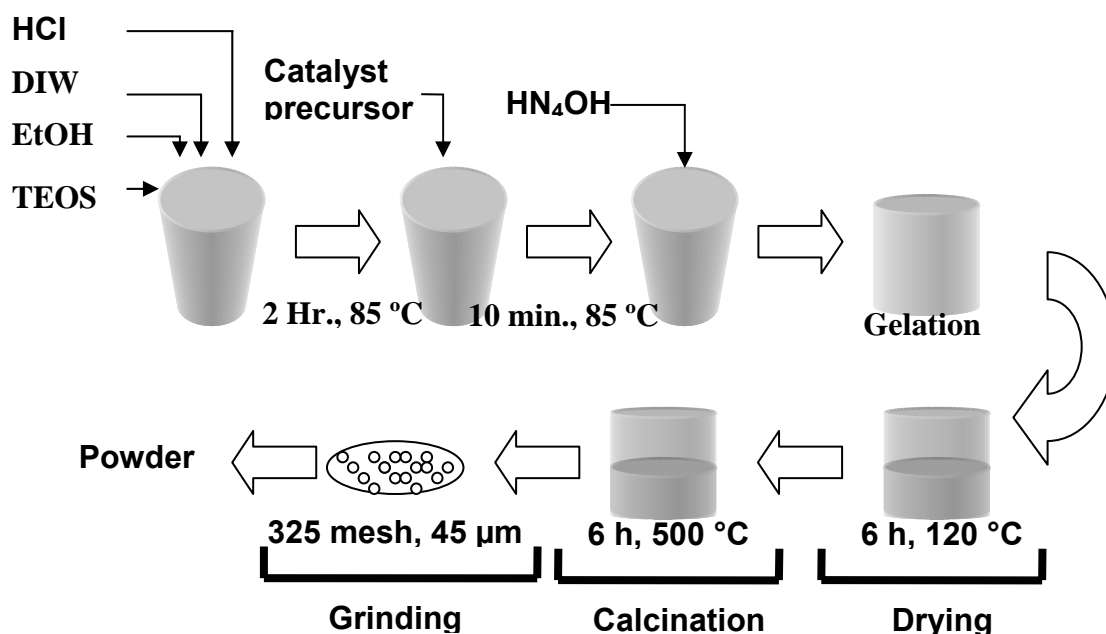


Figure 3.2. Experimental procedure for the preparation of silica supported catalysts

3.2.3. Solid oxide catalyst testing in transesterification of the oils

Methanol/oil ratio was fixed at 3.6 found from the experimental design study and also the catalyst amount (defined as the catalyst weight in total weight of the oil, methanol and catalyst) was 6 wt%. The reaction was carried out for 4 h. 3 replicates were done for each catalyst during catalyst activity evaluation. All the catalysts were tested under these conditions.

Biodiesel content was measured by using a Shimadzu GC-17A gas chromatograph equipped with a FID detector. The separation was achieved using an isothermal analysis method: the column was at 225 °C and for the injection port and detector, 250 °C was used and helium flow was set to 32 cm/s and the split ratio was 150. The sample injection size was 0.1 μL (using 1 μL of liquid syringe). For calibration, pure biodiesel was obtained for both sunflower and canola oil by transesterification using homogeneous catalyst under the same reaction conditions but 4 h of reaction time was used to ensure complete conversion and the purification step was applied. In the purification step, first, the medium was washed with 5% acetic acid and a volume ratio (acetic acid to reaction medium) was 1/3 and then this solution was stirred at 500 rpm for 1 h at 50 °C and the wash water was separated from methyl ester. The pH of wash water was measured with a Selecta pH2001 pH meter and checked.

Washing with 5% acetic acid was repeated for several times until the pH of the wash water reached the same pH of unused 5% acetic acid. Then, methyl ester was centrifuged in a Hettich Rotina 38 centrifuge at 5000 rpm for 10 minute to remove any remaining suspensions. After that drying was performed in a BÜCHI R205 rotary evaporator at 40 °C under 100 mbar vacuum for 2 h. Finally, calibration samples containing the known amounts of purified biodiesel were prepared by dissolving the known amount of purified biodiesel in 5 ml methanol. Then, the amount of biodiesel in each sample was measured with GC and used to prepare the calibration curve.

In addition, homogeneous transesterification studies obtained with the GC analysis were confirmed with Near Infrared analysis (NIR). FTS-3000 Near Infrared spectrometer (Bio-Rad, Excalibur, Cambridge, MA) equipped with Tungsten-Halogen lamp as a source, calcium fluoride (CaF₂) as a beam splitter, lead selenide (PbSe) as a detector and 2 mm quartz cell as a sample container was used. The instrument parameters were 16 cm⁻¹ as a resolution with 128 scan number. The gathered data was evaluated with a genetic algorithm based on least square method coded by MATLAB 5.3 software (Özdemir 2004).

3.2.4. Characterization

In the characterization of the samples, X-ray diffraction (XRD), BET and TPD were used. XRD pattern of the samples were determined using a Philips Xpert XRA-480 Model X-ray diffractometer. XRD patterns were analyzed to find out the crystallite phase and also the average crystallite sizes using the Scherrer equation given below:

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

Where T is crystal thickness, K is Scherrer constant (~0.9-1), λ is wavelength of the X-ray, B is the broadening of a diffracted peak found using the full width at half maximum in terms of radian and θ is diffraction angle in degrees (Patterson 1939).

BET analysis was used to calculate the porosity and the specific surface area of the oxide samples. The measurements were performed by Micrometrix Gemini V at scan mode at 77.35 K in the presence of N₂ for six chosen catalysts; pure CaO, 50% CaO/Al₂O₃, 80% CaO/Al₂O₃, pure MgO, 50% MgO/Al₂O₃ and %80 MgO/Al₂O₃. All

samples kept in a desiccator after calcination and de-gassed at 400 °C for three hours before analysis.

Thermal programmed desorption (TPD) is used to determine number and base or acid strength of sites on a solid surface with an adsorbed gas. Then this gas is desorbed with increasing temperature. Amount of desorbed gas is monitored with gas chromatographic techniques. Carbon dioxide (CO₂) is used as adsorbed gas to determine strength of basic sites. Shimadzu GC-17A gas chromatograph equipped with a TCD detector and an external oven were used to carry out TPD analysis. First catalysts are activated by heating up to 500 °C with 10 °C/min heating rate and kept at that temperature for 1 h and cooled to room temperature under helium flow. Then adsorption is carried out for 1 h at room temperature with 30 mL/min CO₂ flow over 100 mg catalyst. Then desorption takes place with 20 mL/min helium gas as carrier gas by increasing temperature up to 500 °C with 10 °C/min increment. After that catalysts were cooled to room temperature and heating program was applied under same conditions without CO₂ adsorption to observe the behaviour of catalyst without any adsorbed species on the catalyst surface. Detected CO₂ peaks are calculated by TCD responses of known amounts of CO₂ gas for quantitative measurements.

CHAPTER 4

RESULTS and DISCUSSION

Catalytic activities of CaO and MgO on alumina and silica oxides for transesterification of canola and sunflower vegetable oils were investigated in a batch reactor. To compare the activities of the catalysts, a test condition was first determined by using the experimental design on homogeneous transesterification (using NaOH as the catalyst) for both canola and sunflower oil. In star experimental design, two factors, 1.414 of a star distance and 5 replicates at centre point were used. The first factor was NaOH amount changed from 0.586 g/kg to 3 g/kg, and the second one was MeOH/oil ratio changed from 3 to 13. Reproducibility was calculated as 99% from the central point using the following reproducibility relation:

$$\text{Repeatability} = 1 - (\text{MS (Pure error)} / \text{MS (total SS corrected)}) \quad (4.1)$$

where SS is the total sum of squares corrected for the mean, and MS is mean squares or variance. A multiple linear regression model is fitted to find the heterogeneous catalyst testing conditions. The details about the model are given in table 4.1. Here R^2 is percent of the variation of the response explained by the model and Q_2 is the percent of the variation of the response predicted by the model according to cross validation. Basically SDY is the standardized residual is the raw residual divided by the residual standard deviation. And SDY is the standard deviation of the response.

Table 4.1. Summary of the statistical analysis of experimental design.

R^2	0,96	RSD	0,09
Q_2	0,74	Model Validity	-0,2
SDY	0,35	Repeatability	0,99

It is seen that methanol/oil ratio of 3.6 is sufficient to achieve the complete conversion for homogeneous transesterification using NaOH. As seen in the response surface plot in Figure 4.1, biodiesel yield decreases with MeOH/Oil ratio rather than one would expect to observe an increase with the methanol/oil ratio because biodiesel yield increases with the high MeOH/Oil molar ratios by pushing the reaction in the

forward direction. But in the experimental design used in this study, the mass of oil was kept constant and only methanol amount was increased. Therefore, the concentrations of oil and the catalyst decreased with the increase of methanol amount; thus resulting in low rate of biodiesel formation. Furthermore, it is seen that at a constant MeOH/oil molar ratio, biodiesel yield increases with the amount of NaOH; especially clearly seen at high MeOH/oil molar ratios. At a constant NaOH amount, biodiesel yield mainly increases with decreasing MeOH/Oil molar ratio because of the increased oil concentration. Interestingly, at low MeOH/Oil ratio, such as ~3.6, increasing the amount of NaOH decreases the biodiesel yield from 80% to 60%. This seems to be due to the direct saponification of the oil with NaOH; hence resulting decreased amount of NaOH for the transesterification reaction. This observation is in parallel with the literature results (Van Gerpen 2004, Aracil 1998). Figure 4.1 also indicates that 1 h of transesterification time is not enough to achieve 100% biodiesel yield. In fact, it was found that 4 h of reaction was sufficient to achieve ~100% biodiesel yield under low MeOH/oil ratio and NaOH amount at 50 °C.

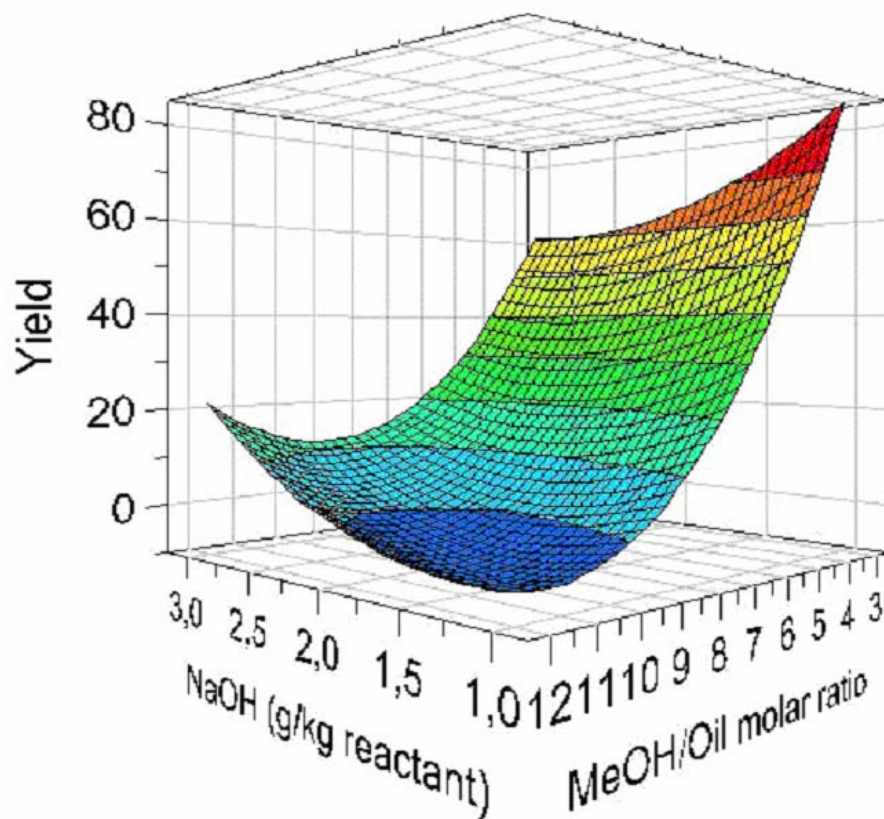


Figure 4.1. Response surface plot of the experimental design results for canola oil reacted in the presence of NaOH as homogeneous reaction.

The experimental design study showed that MeOH/Oil ratio of 3.6 and low NaOH amount resulted in the high biodiesel yield. Hence, for heterogeneous transesterification, MeOH/oil was kept at 3.6 and also the amount of the solid oxide catalyst was 6 wt% of the total amount of the reactants (this was chosen from the literature study and also the previous trial runs conducted in this study). Before testing the solid catalysts, an appropriate pretreatment was applied because water and carbon dioxide must be removed to reveal basic sites and this depends on treatment temperature (Tanabe 1989)). Therefore, the calcination temperature necessary to remove water and carbon dioxide was determined using TGA analysis. TGA for pure CaO is seen in Fig. 4.2. There is almost no weight loss until 400 °C but the decrease observed between 400 °C and 500 °C which is known to be caused by the removal of water and carbon dioxide. Especially, the decrease around 450 °C is caused by evolution of CO₂ due to the decomposition of surface carbonates. The decrease observed above 600 °C is known to be related to the evolution of surface oxygen (Tanabe 1989)). Therefore, 500 °C is chosen as the calcination temperature for this study. Also, the necessary precaution was given to catalyst pretreatment before being used in the transesterification reaction because in atmosphere, water and carbon dioxide are present and it was observed that when the solid oxide catalysts synthesized in this study left open to the atmosphere, they adsorbed water and carbon dioxide from air. Thus, to avoid the exposure to atmospheric water and carbon dioxide, all the catalysts were prepared for the transesterification reaction under nitrogen atmosphere after they were removed from the oven at 500 °C. This step is crucial because the adsorption of carbon dioxide and water on the active basic sites deactivates the catalysts because the transesterification reaction occurs on the basic sites.

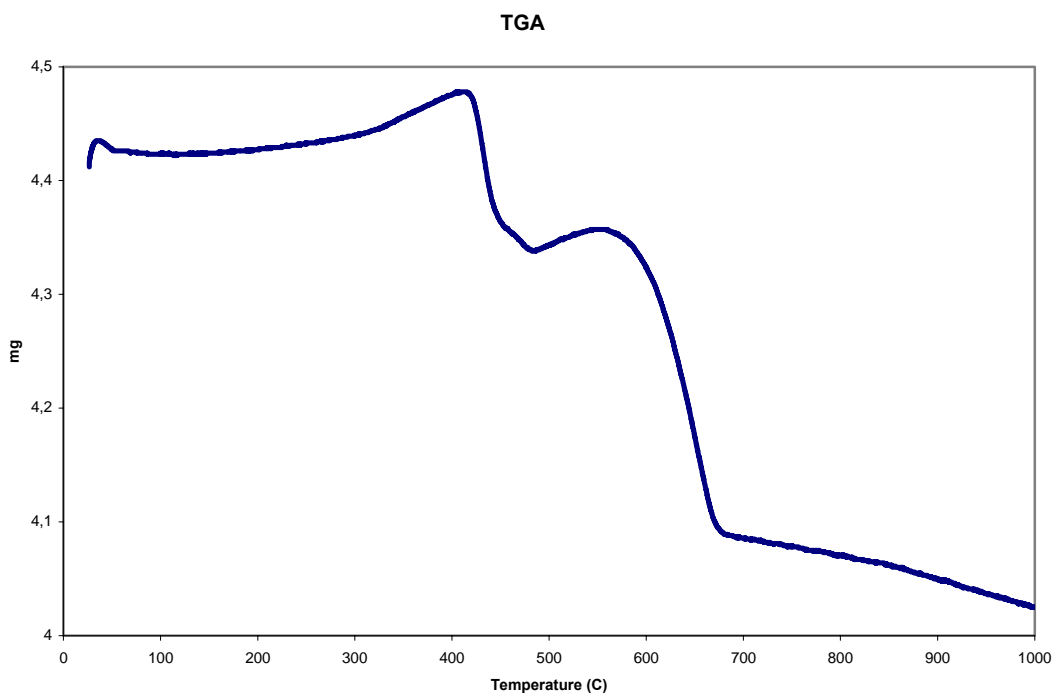


Figure 4.2. Thermal gravimetric analysis of pure calcium oxide.

In this study, percentage yield was used to compare activities of different catalysts. And yield was stated as number of moles methylesters formed over the number of moles of triglycerids. The activity test results for canola and sunflower vegetable oils show that only 80% CaO/Al₂O₃ catalysts have the highest biodiesel yield of 100% whereas other mixed oxide catalysts shows only minor activities as seen in Table 4.2. For instance, for canola, the biodiesel yield over Al₂O₃ supported CaO catalysts changes from 3.5% to 100% when the loading of CaO is increased from 5 to 80 wt%, respectively. Most importantly, pure CaO and pure MgO show biodiesel yield less than 10%. Interestingly, 50% and 80% CaO/Al₂O₃ catalysts are very active even at low MeOH/Oil molar ratio of 3.6 and 50 °C of the reaction temperature as compared to the literature reports; in fact, usually, MeOH/Oil ratio of more than 10 and also temperatures higher than 50 °C were used. Temperature is limited for transesterification reactions up to 68 °C which is MeOH boiling point when reaction is carried at atmospheric pressures. Thus, mostly temperatures about 60 °C were used in most studies (Van Gerpen 2004, Naik 2006). When pure MgO and CaO are compared, the catalyst activity of CaO is higher than that of MgO. This seems to be due to that the ionic radii and alkalities of the alkaline earth metal is increased toward calcium ion and it is suggested that basic strength (i.e. the catalytic activity for transesterification) is

increased (Liang 2008). This is also related to the increased electron donating ability with alkalinity of alkaline earth oxides (Tanabe 1989). But a high temperature pre-treatment is required to obtain a high catalytic activity.

Table 4.2: Heterogeneous catalyst testing results for both canola and sunflower oil at 50 °C, the stirring speed of 1100 rpm, and the catalyst load of 6 wt% for 4 h.

Canola Oil Heterogeneous Catalysts		Sunflower Oil Heterogeneous Catalysts	
Catalyst	Yield %	Catalyst	Yield %
Pure CaO	11.18 ± 1.86	Pure CaO	0.98 ± 0.95
80% CaO/SiO ₂	1.23 ± 0.36	80% CaO/SiO ₂	6.43 ± 0.42
50% CaO/SiO ₂	5.07 ± 0.45	50% CaO/SiO ₂	8.27 ± 1.07
20% CaO/SiO ₂	3.92 ± 1.89	20% CaO/SiO ₂	3.92 ± 1.10
5% CaO/SiO ₂	1.32 ± 1.22	5% CaO/SiO ₂	1.16 ± 0.91
80%CaO/Al ₂ O ₃	100 ± 3.84	80% CaO/Al ₂ O ₃	96.62 ± 3.21
50% CaO/Al ₂ O ₃	86.72 ± 8.66	50% CaO/Al ₂ O ₃	79.96 ± 5.81
20% CaO/Al ₂ O ₃	6.50 ± 1.14	20% CaO/Al ₂ O ₃	2.56 ± 0
5% CaO/Al ₂ O ₃	3.00 ± 0.82	5% CaO/Al ₂ O ₃	2.90 ± 1.74
Pure MgO	1.31 ± 0.19	Pure MgO	3.96 ± 1.45
80% MgO/Al ₂ O ₃	3.50 ± 1.27	80% MgO/Al ₂ O ₃	6.91 ± 5.47
50% MgO/Al ₂ O ₃	1.90 ± 0.21	50% MgO/Al ₂ O ₃	8.21 ± 0.16
20% MgO/Al ₂ O ₃	6.59 ± 1.82	20% MgO/Al ₂ O ₃	4.54 ± 0.69
5% MgO/Al ₂ O ₃	2.72 ± 1.13	5% MgO/Al ₂ O ₃	2.50 ± 0.58
5% MgO/SiO ₂	1.72 ± 1.47	5% MgO/SiO ₂	1.39 ± 0.66
20% MgO/SiO ₂	1.05 ± 0.60	20% MgO/SiO ₂	0.98 ± 0.06
50% MgO/SiO ₂	1.86 ± 1.67	50% MgO/SiO ₂	1.35 ± 0.56
80% MgO/SiO ₂	0.52 ± 0.18	80% MgO/SiO ₂	2.93 ± 1.61

When support effect is considered, the activity of CaO on Al₂O₃ is higher than the corresponding SiO₂ supported catalysts. This could be caused by mixed oxide phase, such as calcium aluminates or calcium silicates, formed during the calcination (Tanabe 1989). These phases could act as basic/acidic sites at the surface.

For heterogeneous catalysis, it is important to find out if the reaction occurs on the solid surfaces rather than that through the dissolution of the ionic species from the solid catalyst into the solution medium; hence resulting in homogeneous catalysis. To test this, 50% CaO on Al₂O₃ catalyst were removed from the reaction medium after 30 minute of the reaction time and the analysis of the reaction medium using GC showed ~20% biodiesel yield. Then, the reaction medium (without catalyst) was kept under the same reaction conditions for 20 minute more. At the end of 20 minute, the reaction medium was again analyzed using GC and the same biodiesel yield was observed; hence indicating that there was no homogeneous transesterification occurring.

Two catalysts showing the maximum yields, 80% CaO/Al₂O₃ and 50% CaO/Al₂O₃, were tested as a function of time using the same reaction conditions for sunflower oil. It was observed that 1 h of the reaction time was enough to reach 100% yield using 80% CaO/Al₂O₃ catalyst whereas 50% CaO/Al₂O₃ catalyst reached only 82% yield at 50 minute.

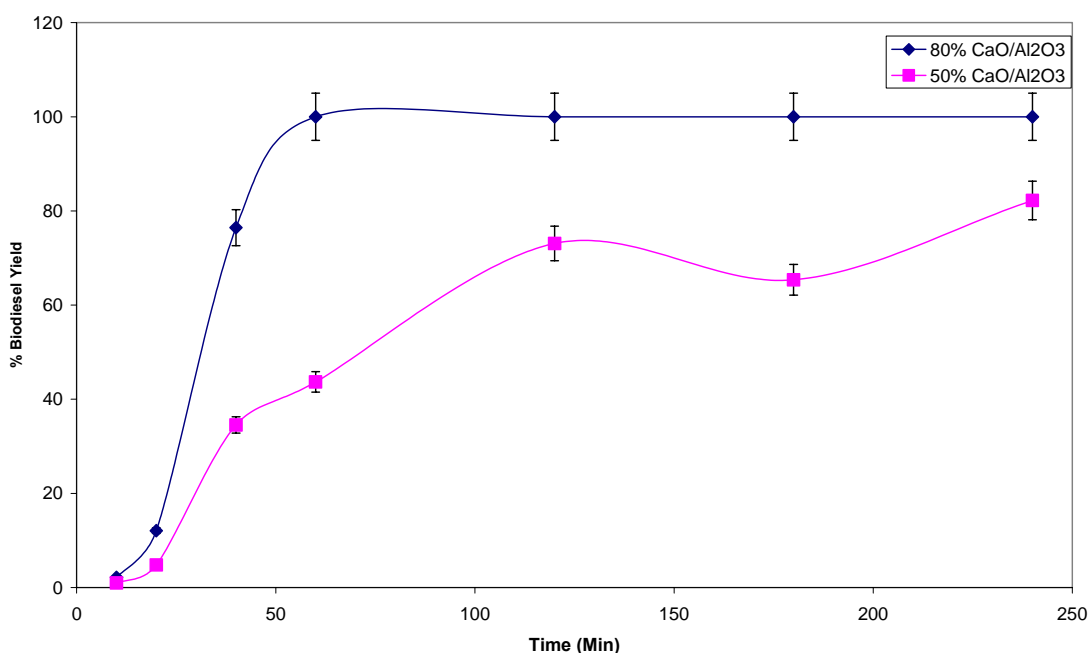


Figure 4.3. Biodiesel yield versus time for 80% CaO/Al₂O₃ and 50% CaO/Al₂O₃ catalysts through 4 hours, 6 wt% catalyst amount, at 50 °C, 3.6 MeOH/oil molar ratio, 1100 rpm stirring speed for sunflower oil.

To better understand the activity variation observed with the catalyst formulations, six catalysts, such as pure CaO and MgO, 50% CaO/Al₂O₃, 80%

CaO/Al₂O₃, 50% MgO/Al₂O₃ and 80% MgO/Al₂O₃, were characterized by N₂ adsorption and also XRD. It is observed that all the catalysts are mesoporous mixed oxides as seen in Table 4.3. The specific surface areas of alumina supported calcium oxide catalysts are lower than pure alumina which has surface of 200 – 300 m²/g (Do 1998). The BET results show that adsorption isotherms are of type 4 and the surface areas of the CaO/Al₂O₃ catalysts slightly changes with the catalyst loading; for example, the BET surface area of 50 and 80 wt% catalysts are 1.58 and 0.99 m²/g, respectively. On the other hand, pure calcium oxide has 2.43 m²/g of BET surface area. Yet, as seen from the table, BET surface area increases when MgO is dispersed in Al₂O₃ as compared to pure MgO synthesized in this study. For instance, BET surface of pure MgO is 3.22 m²/g whereas it is 47.29 for 50 wt% MgO on Al₂O₃ catalyst. But when MgO loading is 80 wt%, the surface drops to 40.42 m²/g. These results shows that the surface area seems not to be critical on the transesterification activity since although the surface area of MgO on Al₂O₃ catalysts are much larger than that of CaO on Al₂O₃ catalysts, MgO on Al₂O₃ catalysts show significantly lower transesterification activity as compared to 50 and 80 wt% CaO on Al₂O₃ catalysts.

Table 4.3. BET results of selected catalysts.

Catalyst	BET Surface area (m ² /g)	BJH Adsorption average pore width (Å)	Pore Volume (cm ³ /g)
Pure CaO	2.43	52.92	0.0043
50% CaO/Al ₂ O ₃	1.58	47.11	0.0031
80% CaO/Al ₂ O ₃	0.99	60.03	0.0011
Pure MgO	3.22	54.57	0.0068
50% MgO/Al ₂ O ₃	47.29	35.96	0.0678
80% MgO/Al ₂ O ₃	40.42	46.65	0.0699

XRD results show that CaO catalysts were highly dispersed on silica support for all the catalyst loadings. As seen in figure 4.5, the crystallite size of pure calcium oxide is ~164 nm, yet the crystallite size of calcium oxide on both silica and alumina supports is less than 5 nm (which is below the detection limit of XRD). Similarly, magnesium oxide catalysts with low catalyst loads 5, 20 and 50 wt% on SiO₂; and 5 and 20 wt% MgO on Al₂O₃ are highly dispersed; thus indicating crystallite sizes below 5 nm as seen

in figure 4.6. However, the crystallite size of 50 wt% MgO on Al₂O₃ is relatively the same as that pure MgO, ~25 nm. Increasing MgO loading to 80% wt. on Al₂O₃ results in a slight decrease in the crystallite size, ~20 nm. Unlike alumina supported magnesium oxide catalysts, the crystallite size of MgO on SiO₂ stays less than 5 nm until 50 wt% MgO but it increases to ~30 nm on 80 wt% MgO on SiO₂. These results show that the type of the support influences the crystallite size of CaO and MgO based catalysts.

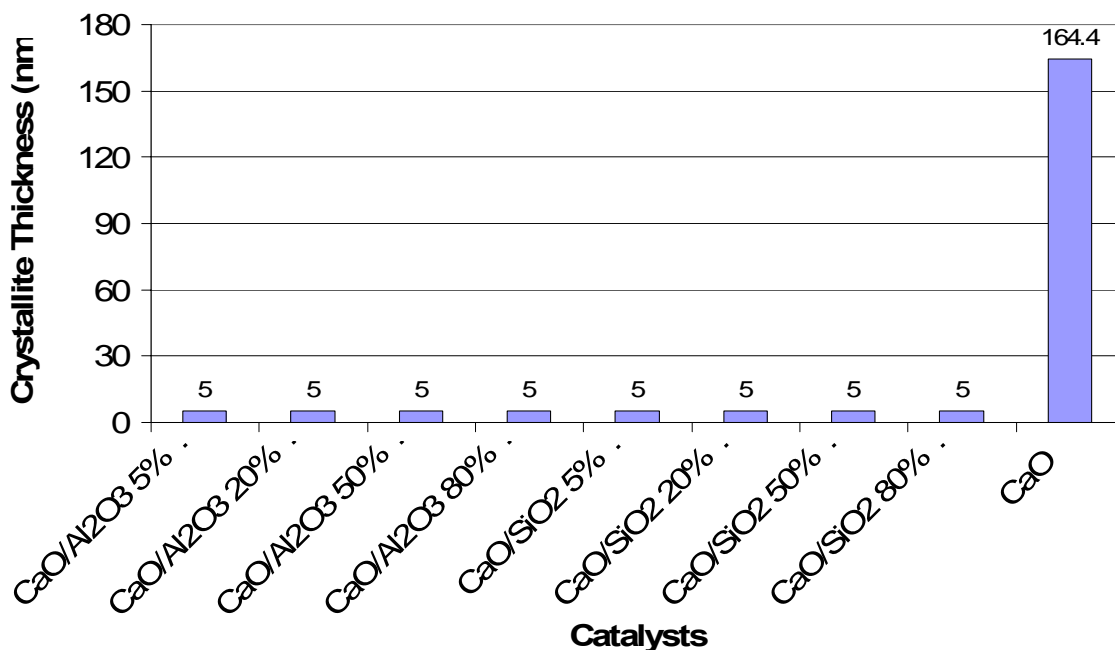


Figure 4.4. Crystal thicknesses of calcium oxide catalysts.

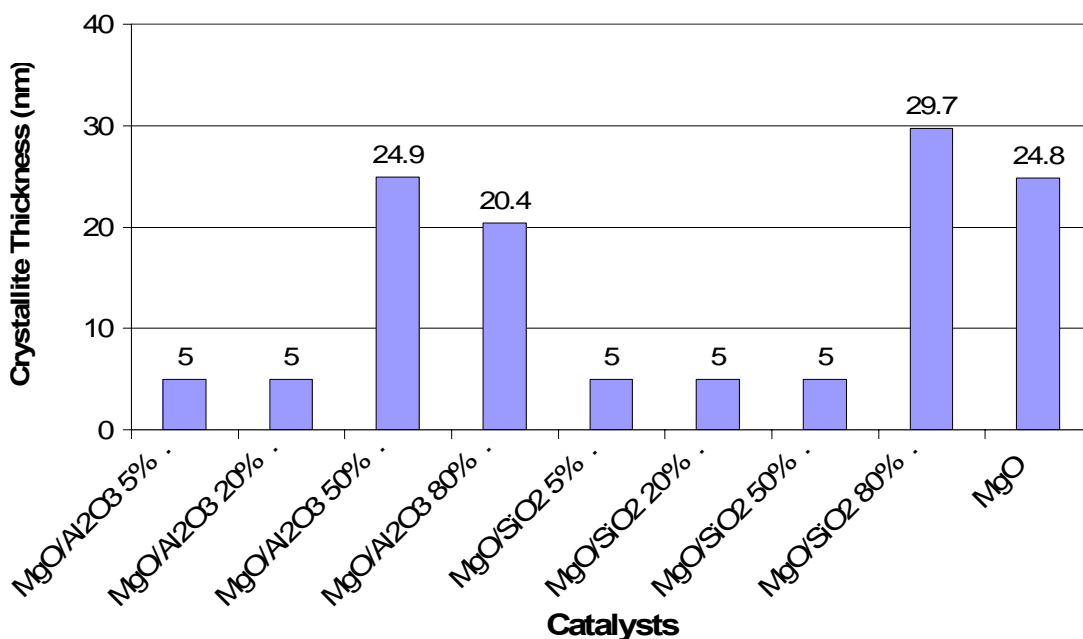


Figure 4.5. Crystal thicknesses of magnesium oxide catalysts.

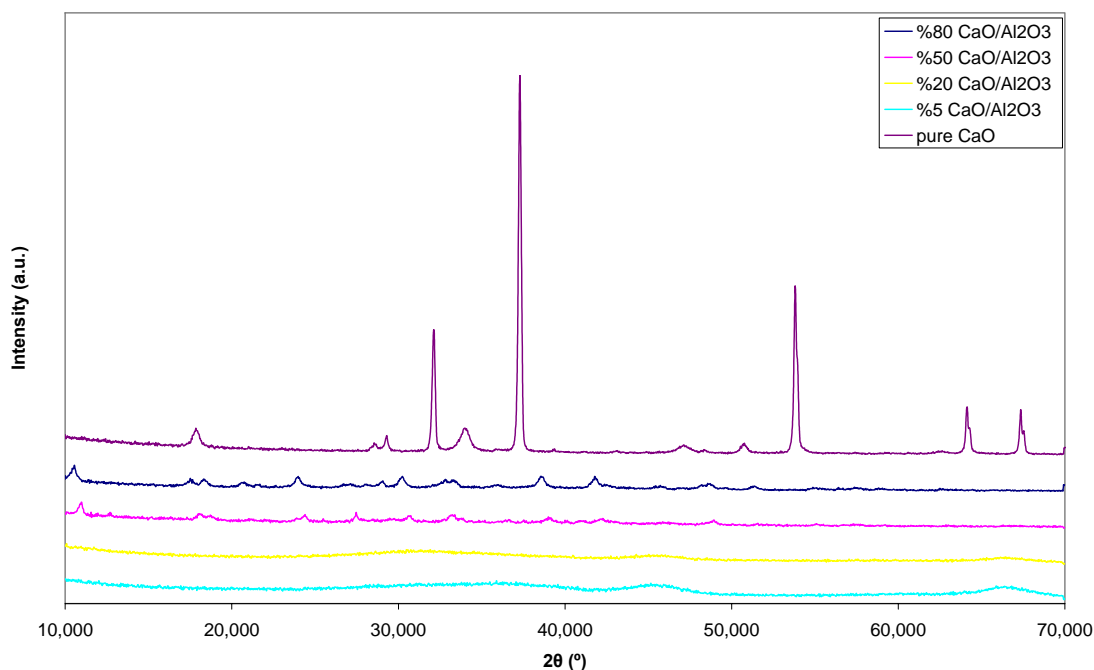


Figure 4.6. Comparison of XRD results for alumina supported calcium oxide catalysts.

Comparison of XRD patterns of alumina supported calcium oxide catalysts shows that pure CaO peaks could not be observed on any of the catalysts since XRD is insensitive to crystallite sizes below 5 nm; hence this shows that the crystallite size is less than 5 nm as seen in figure 4.6. For instance, the major diffraction peak of calcium oxide at 2θ angle of 37.29 was not observed on all the mixed oxide catalysts. Yet, other peaks around 2θ angle of ~ 38 and ~ 42 were observed on the catalysts with the high loadings of 50 and 80 wt%. These observed peaks were identified as CaCO_3 peaks using powder XRD diffraction patterns. Since XRD instrument is open to atmospheric air, it is plausible that CaCO_3 is formed by the adsorption of CO_2 from atmosphere during XRD analysis. In contrast, in Figure 4.7 calcium silicate and hydrogen silicate hydrate peaks located around 2θ angle of ~ 40 are only observed on 80% CaO/SiO_2 . It is known that for SiO_2 supported catalysts made with a single step sol-gel, it is possible to form silicates since silica sol is more active to react with metal ions to form silicates than pure bulk silica.

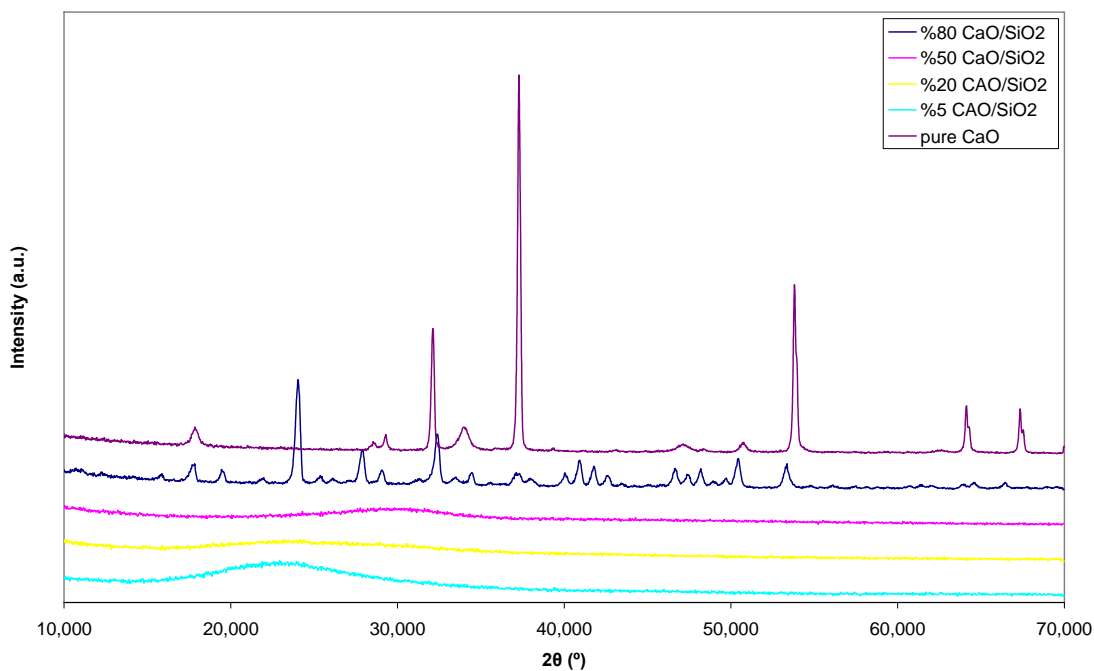


Figure 4.7. Comparison of XRD results for silica supported calcium oxide catalysts.

As seen in Figure 4.8 and 4.9, magnesium oxide on both silica and alumina catalysts shows low dispersion as the MgO loading is increased. All three major diffraction peaks of magnesium oxide are clearly seen at 2θ angles of 36.72, 42.67 and 62.12. As seen in figure 4.9, there are no peaks observed other than MgO on alumina for all MgO loadings. Yet, as seen in silica supported calcium oxide catalysts, silica interacts with magnesium to form silicates, such as forsterite (Mg_2SiO_2), when the MgO loading is 80 wt%. Although there is no peak on MgO on SiO_2 catalysts for MgO less than 80 wt%, there may be small silicate crystallites in addition to MgO crystallites which are less than 5 nm in size. It seems that for MgO based catalysts, the crystallite size does not have any effect on the transesterification activity regardless of the type of the support used. In fact, when compared with CaO based catalysts, it seems that the basicity is the critical factor for the choice of the suitable oxide for the transesterification reaction. But, as seen from the results obtained on CaO based catalysts, the type of support is also important in obtaining the active CaO catalysts. The change in the crystallite size may be responsible for the variation in the biodiesel yield observed through either directly with the changes in the number of the active sites due to the CaO loading and/or the creation of new “basic” sites due to the interaction of the crystallites with the specific support materials, for example, alumina since this type of synergetic effect is not observed on silica supported CaO catalysts.

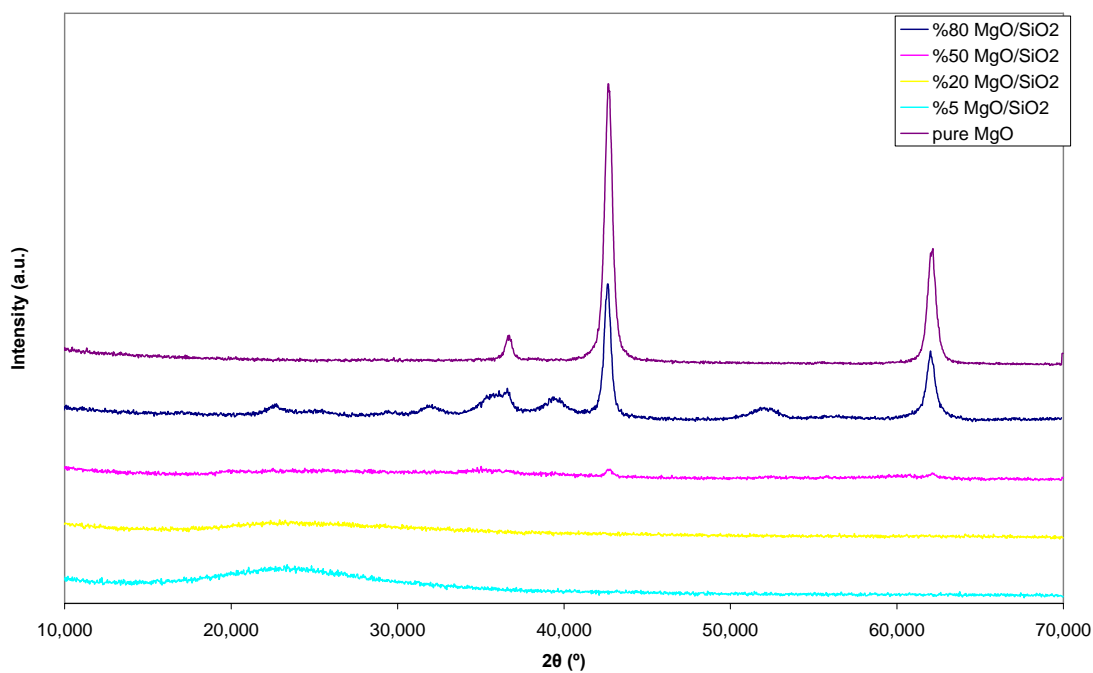


Figure 4.8. Comparison of XRD results for alumina supported magnesium oxide catalysts.

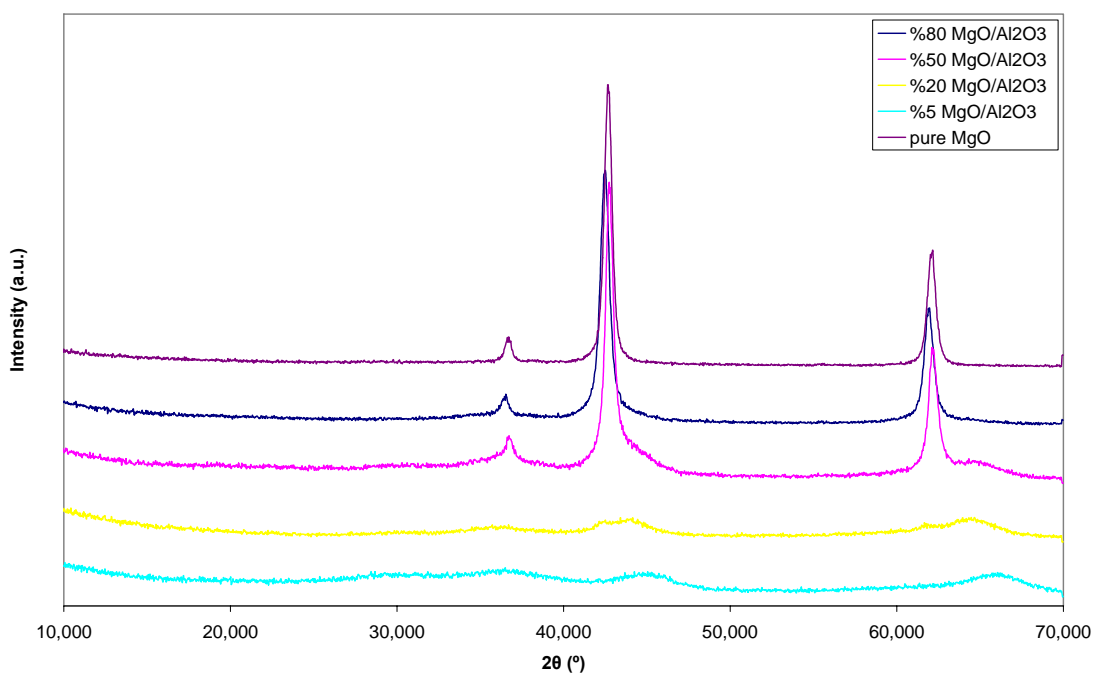


Figure 4.9. Comparison of XRD results for silica supported magnesium oxide catalysts.

In order to clarify the reason behind the variation in the catalytic activities observed on CaO/Al₂O₃ catalysts, the basicity and basic strength of the selected catalysts were determined using a home-made CO₂ adsorption desorption system. It is known that the base catalyzed reactions are initiated by forming anionic intermediates following abstraction of an H⁺ from reactants. The ability of surface to convert an adsorbed neutral acid to its conjugate base or the ability to donate an electron pair to the adsorbed acid is called basic strength of a solid material (Tanabe 1989). To determine the basic sites, CO₂ is used as the probe molecule. Temperature programmed desorption of the adsorbed CO₂ gives the temperatures where the evolution of CO₂ is observed; hence indicating the strength of the basic sites. Higher the desorption temperature, higher the basic strength. The total amount of CO₂ adsorbed gives the number of moles of basic sites which given in Table 4.3. It is known that silanol groups of silica are very weakly acidic in nature. Acidity of silica is reported as 0.001 μmol/g, thus it is mostly considered as inert. Alumina which has an amphoteric nature also reported to have similarly low basic and acidic strengths (Tanabe 1989). It was found that 50 wt% CaO/Al₂O₃ has lower basicity than that 80% wt. CaO on Al₂O₃; thus indicating that the higher basicity, higher the biodiesel yield as obtained on 80 wt% CaO/Al₂O₃. This seems plausible but when the basic strength of the 50 and 80 wt% CaO/Al₂O₃ catalysts are analyzed, it is seen that there are two temperatures where the desorption of CO₂ occurred as seen in Figure 4.10. In fact, the basic strength of the 80 wt%. CaO/Al₂O₃ catalyst is between the temperatures obtained on 50 wt% CaO/Al₂O₃ catalysts. This indicates that not only the basicity but also the sites with mild basic strength which are observed around 400 °C is required to achieve 100% biodiesel yield. TPD profiles of both 50% and 80% CaO/Al₂O₃ can be seen in figures 4.11 and 4.12. In these figures uncovered surfaces were catalyst surfaces desorbed to be ready for CO₂ adsorption, where covered surfaces were CO₂ adsorbed catalyst surfaces.

Tablo 4.4. Basic strength of selected catalysts.

Catalyst	Total Basicity ($\mu\text{mole CO}_2/\text{m}^2$)	Basic strength (Peak Temperature $^{\circ}\text{C}$)	Full width At Half Height ($^{\circ}\text{C}$)
CaO	-	> 500	-
50% CaO/Al ₂ O ₃	78.6	300	50
	35.7	488	61
80% CaO/Al ₂ O ₃	126.0	407	73
50% MgO/Al ₂ O ₃	79.8	147	99
80% MgO/Al ₂ O ₃	34.5	180	85
	1.0	394	7
	30.3	472	39

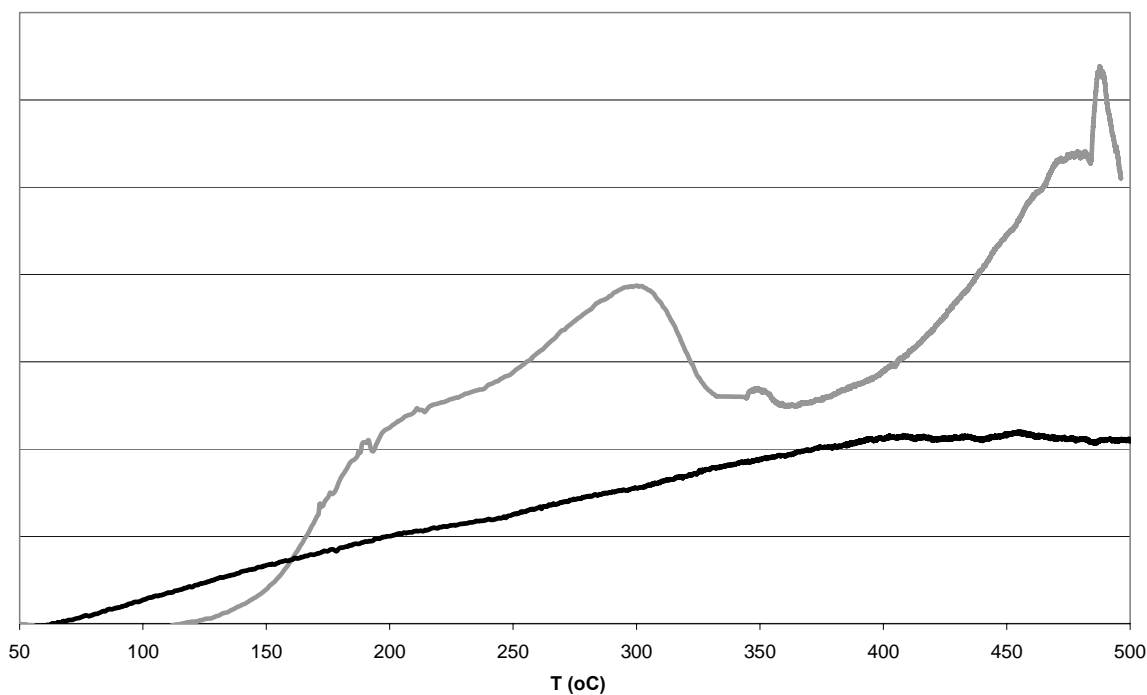


Figure 4.10. TPD profiles 50 wt% CaO/Al₂O₃ catalyst for CO₂ adsorbed on the catalyst (—) and for fresh (without CO₂ adsorption), only helium (---).

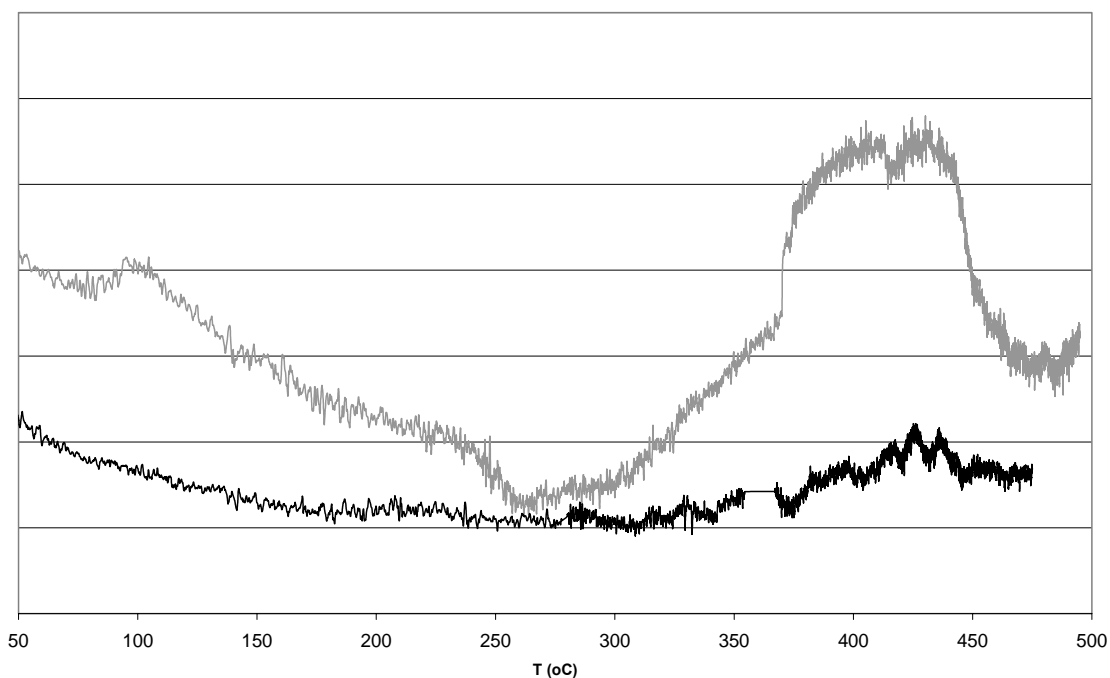


Figure 4.11. TPD profiles 80 wt% CaO/Al₂O₃ catalyst for CO₂ adsorbed on the catalyst (—) and for fresh (without CO₂ adsorption), only helium (- -).

It should be noticed that the reaction conditions, such as the methanol/oil ratio and the reaction temperature, used in this study are not favourable unlike heterogeneous catalysts' conditions reported in the literature. In fact, it is found that the mild basic strength with high basicity is required for the catalysts in order for the heterogeneous catalysts to be as active as the homogeneous catalysts, such as NaOH, under these unfavourable reaction conditions.

CHAPTER 5

CONCLUSION

In this study, the effect of basicity (amount of the basic sites) of the solid catalysts and/or its crystallite size on the biodiesel yield during the transesterification of canola and sunflower vegetable oils were investigated on the heterogeneous mixed oxide catalysts: calcium oxide and magnesium oxide on silica and alumina supports.

Both alumina and silica supported catalysts were prepared via the modified single step sol-gel methods and XRD results showed that the high dispersion of active phases was achieved for CaO based catalysts even with the high CaO loading of 80 wt%. Also, the effect of support material on crystallite size was observed on CaO and MgO based catalysts.

CaO/Al₂O₃ catalysts with the high CaO loadings show the high activity even under the unfavourable reaction conditions, such as low MeOH/Oil molar ratio of 3.6 and the low reaction temperature, 50 °C, as compared to the studies reported in the literature. This study shows that:

- The crystallite size does not have any direct effect on the transesterification activity.
- The change in the crystallite size may be responsible for the variation in the observed biodiesel yield through either directly with the changes in the number of the active sites and/or the creation of new “basic” sites due to the interaction of the crystallites with the specific support materials.
- Basicity is the main factor for the choice of the suitable oxide for the transesterification reaction, since high biodiesel yield is obtained with high basicity but the basic strength is also as critical as the basicity.
- Mild basic strength is required to achieve the high biodiesel yield in the transesterification of canola and sunflower oils.

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