

Norwegian University of Life Sciences  
Faculty of Environmental Science and  
Technology  
Department of Mathematical Sciences and  
Technology

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# The use of heterogeneous catalysts in the production of biodiesel

Aleksander Hykkerud









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## Preface

This thesis is the result of a master project in biodiesel production at the Norwegian University of Life Sciences Department of Mathematical Sciences and Technology.

With this thesis I conclude my master's degree in Environmental Physics and Renewable Energy.

Ås, December 12<sup>th</sup>, 2014

Aleksander Hykkerud





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Aleksander Hykkerud







## Abstract

In this thesis a parameter screening of the esterification of oleic acid with ethanol in the presence of the heterogeneous catalyst Amberlyst 15 wet ion exchange has been conducted with the intent to produce biodiesel. The parameters screened were temperature, catalyst amount and molar ratio. In addition a reuse test was done to test the catalysts recyclability. The catalyst that was tested is an acidic polymer resin with an open pore structure with good thermal, physical and chemical stability [1] which has been shown to work in the esterification of oleic acid in the presence of methanol [2], [3]. Higher temperature and catalyst amounts increased conversion while the molar ratio that gave the highest conversion was one to one.

## Sammendrag

I denne oppgaven ble en parameter screening av esterifikasjon av oljesyre med etanol ved hjelp av den heterogene katalysatoren Amberlyst 15 wet ion exchange utført med hensikt å produsere biodiesel. Parameterne som ble screenet var temperatur, katalysator mengde og mol forhold. I tillegg ble en gjenbrukstest utført for å teste katalysatorens resirkulerbarhet. Katalysatoren som ble testet er en syrlig polymer resin med en åpen porestruktur med god termisk, fysisk og kjemisk stabilitet (1) som har blitt vist å fungere i forestring av oljesyre i nærvær av metanol (2), (3). Høyere temperatur og katalysatormengder ga økt produkt utbytte, mens det molare forholdet som ga den høyeste omdannelse var en til en.





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## Abbreviations and Glossary

DG	Diglyceride
FA	Fatty Acid
FAAE	Fatty Acid Alkyl Ester
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
Feedstock	Alternative name for raw material used for fuels or in industrial processes
FFA	Free Fatty Acid
LD <sub>50</sub>	Median lethal dose 50 is a measurement of how lethal a substance is. It is the dose of a substance needed to kill 50 % of a population
MG	Monoglyceride
TG	Triglyceride



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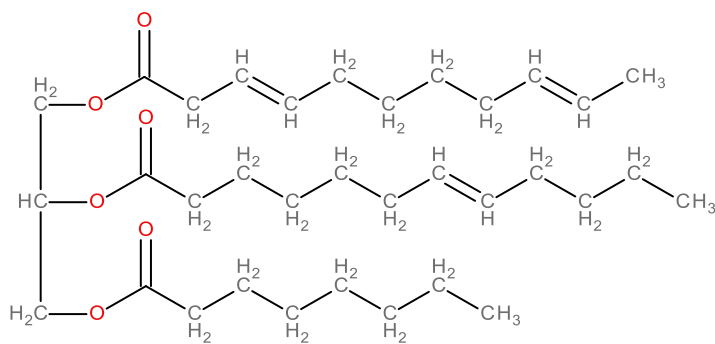
# 1 Introduction

The world is dependent on fossil fuels, but as they are a contributing factor to environmental change and are also finite [4] they are going to have to be replaced with alternative energy sources. Biodiesel shows promise as an alternative fuel as it can directly replace fossil diesel due to similar properties and is also potentially renewable. The use of vegetable oils in diesel engines has been known since the beginning of the twentieth century and the production of biodiesel from these oils has been known since the nineteen thirties and has seen much work since then [5, pp. 1-21]. The current methods that are most often used in the production of biodiesel today require high quality raw materials, which are expensive as they compete with food production. It is therefore important to investigate alternative methods that allow for the use of lower cost raw materials such as non-edible oils, waste oils and animal fats [6].

## 2 Theory

### 2.1 Biodiesel basics

Biodiesel is a fuel comprised of monoalkyl esters of long chain FAs derived from vegetable oils or animal fats. These oils and fats are composed mainly of esters called TG which is shown in Figure 1.



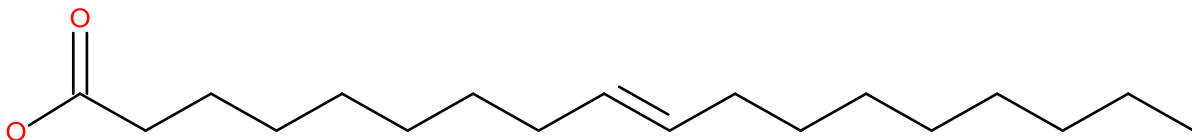
**Figure 1:** Triglyceride with fatty acids of different lengths and number of double bonds.



The TGs are made out of a glycerol backbone where instead of having three hydroxyl groups there are three FAs. FAs or carboxylic acids which they are also known as are hydrocarbon chains with a carboxyl group attached to them. The different FAs are determined by their carbon chain lengths and the amount of double bonds in their structure. The different vegetable oils have different quantities of these FA types and Table 1 shows the FA composition of some oils with oleic acid, a common FA, emphasized in red. Not all FAs are bound in glycerol and these are considered FFAs and appear in forms as the one shown in Figure 2.

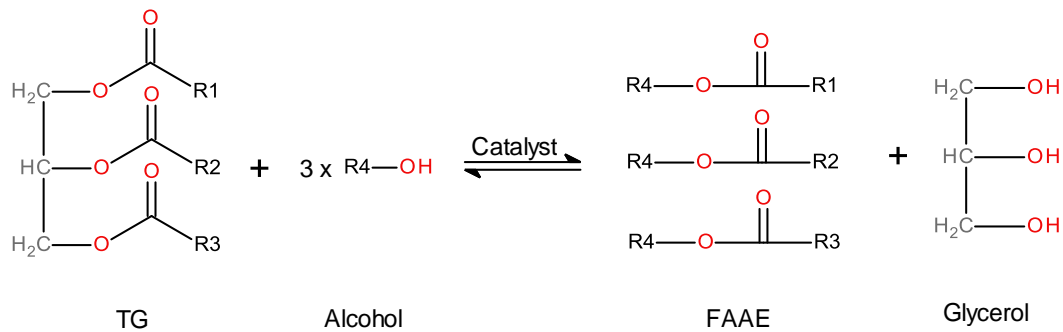
**Table 1:** FA composition of some oils.

Oil/fat	FA composition (Wt. - %)									
	14:0	16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1
Corn [5, p. 462]	0-0.3	11.7-14.5	1.4-2.6	22-32.3	52.2-61.7	0.6-0.9				
Olive [5, p. 462]		10.5	2.6	76.9	7.5					
Peanut [5, p. 462]	0-0.5	10.8-14.2	2.1-3.3	36.4-67.1	13-43		1.6-1.8	1.0-1.1	1.9-2.7	0-0.3
Rapeseed [5, p. 462]		4	1	14.8	14.2	9.1		10		45.1
Tallow [2]	2.8	23.3	19.4	42.4	2.9	0.9				
Mahua [2]		16-28.2	20.0-25.1	41.0-51.0	8.9-13.7	0.8	0.0-3.3			
Jatropha [2]		15.6	6.5	43.5	34.4					



**Figure 2:** Oleic acid as an FFA.

Biodiesel can be produced in a reaction which is known as transesterification. In this reaction which is shown in Figure 3, glycerides and alcohols are turned into FFAE and glycerol.



**Figure 3:** Transesterification reaction in the presence of a catalyst.

The glycerides are converted stepwise, first into DGs, MGs and then finally into glycerol yielding one FAAE in every step. This is an equilibrium reaction which is usually done in the presence of a catalyst in order to increase the reaction rate. As it is an equilibrium reaction it can be directed by controlling the concentration of the reactants and the operating conditions. These principles are called Le Chatelier's principles or alternatively, the equilibrium law. The most common methods used to shift the reaction towards the product are i) to increase molar ratio, ii) increase temperature and/or pressure and iii) remove products [5, pp. 31-85]. Molar ratio is the amount of alcohol to oil and by increasing alcohol quantity the reaction shifts to the right. The same is achieved by removing the product biodiesel and glycerol while the process is ongoing or stepwise. In the case of transesterification, increased temperature will also shift the reaction to the right. The alcohol used can vary, but due to the fact that heavier alcohols are generally more costly, the most common one employed is methanol. Ethanol is also used where its availability and price can compete with methanol [5, p. 31]. The alcohol used will change the name of the FAAE by substituting the alkyl with the name of the alcohol. Ethanol based biodiesel is known as FAEE while methanol based ones are known as FAME.

## 2.2 Properties of diesel fuels

Before going into the reasons and benefits of making and using biodiesel, an explanation of the function and key parameters of diesel fuels in general is required. Diesel fuels are used in compression combustion engines and the fuel has several characteristics which are important to how well the engine will perform when the fuel is used. The diesel engine works by injecting a mixture of fuel and air into a combustion chamber where it is compressed until the fuel mixture



ignites. Cetane number, volatility, viscosity, pour point, cloud point and heating value are among the more important properties of diesel fuels.

*Cetane number* is a measure of ignition delay. Cetane is a colorless, liquid hydrocarbon that ignites easily under compression, It has therefore been given a base rating of 100, and is used as a standard measure of the performance of compression ignition fuels. A higher cetane number means a shorter ignition delay time which gives a more complete combustion of the fuel. Cetane number requirements depend on engine design and size, load variations and starting and atmosphere conditions. There are no benefits of using fuels with a higher cetane number than the recommended specification for a specific engine, but using a fuel with a lower cetane number than this can lead to rough operation, lower power output, more deposits and greater wear [5, p. 138].

*Volatility* is a measure of how easy the fuel releases vapors. High volatility fuels can be dangerous as there will be an air fuel mix above it which can ignite. How volatile a fuel is indicated by its *flash point*, which is the lowest temperature where the fuel can form an ignitable mix.

*Viscosity* is a measure of the resistance of a fluid to flow. This is caused by friction between the molecules of the fluid. High viscosities can cause problems to injector nozzles by forming deposits and also leading to incomplete combustion due to poor mixing of fuel with air.

*Pour and cloud point* are characteristics connected to cold condition operation. Cloud point is the temperature where wax crystals will start to form and the pour point is the temperature at which the fuel can no longer flow. The lower these values are the better, and they can be improved with additives.

*Lubricity* is the ability of the fuel to function as a lubricant. Diesel engines are designed to be lubricated by the fuel itself and low lubricity will cause the engine to wear out faster.

The *heating value* is the amount of energy that is released when the fuel is burned and determines the maximum power that the engine can put out. There are two different values for



this, lower and higher heating value. The lower heating value is found by subtracting the heat of vaporization of the water vapor from the higher heating value. This is not done with higher heating value as the water is assumed to be in liquid phase after combustion.

## 2.3 Properties of Biodiesel

Vegetable oils can be used directly in diesel engines, but doing so without modifying the engine can cause increased engine wear from corrosion and deposit formation as well as operating difficulties. The main reason for this is the higher viscosity of the oils which lies above  $30 \text{ mm}^2/\text{s}$  [5, p. 463]. The high viscosity of the oils comes from the branched structure of the TGs which causes the molecules to have higher resistance to flow. A comparison of the properties of fossil diesel no. 2, a common diesel, and biodiesel are shown in Table 2.

**Table 2:** Properties of No. 2 Diesel and biodiesel fuels [7, p. 11].

Fuel property	Diesel No.2	Biodiesel
Higher Heating Value (MJ/L)	38.36	35.40
Lower Heating Value (MJ/L)	35,96	32.93
Viscosity at 40 C ( $\text{mm}^2/\text{s}$ )	1.3–4.1	4.0–6.0
Specific Gravity at 15.5 C (kg/l)	0.85	0.88
Density at 15.5 C (lb/gal)	7.1	7.3
Carbon (wt. %)	87	77
Hydrogen, (wt. %)	13	12
Oxygen (wt. %)	0	11
Sulfur (wt. %)	max 0.0015	0.0-0.0024
Boiling Point (C)	180–340	315–350
Flash Point (C)	60–80	100–170
Cloud Point (C)	-35 to 5	-3 to 15
Pour Point (C)	-35 to -15	-5 to 10
Cetane Number	40–55	48–65

Biodiesel doesn't have the same branched structure as the molecules of vegetable oils and therefore have lower viscosities which are closer to that of petrol diesel. Other qualities, most notably heating value and cetane number, highlighted in red in Table 2, are also similar which



means that biodiesel can therefore be used as a direct replacement for fossil diesel. As biodiesel is not completely identical to fossil diesel there are some differences which gives rise to the following advantages and disadvantages.

### ***2.3.1.1 Advantages of biodiesel***

- Emissions from the use of biodiesel contain less carbon monoxide, less particulate matter and fewer unburned hydrocarbons than fossil diesel [5, pp. 253-273], [8, pp. 2-11].
- It is biodegradable, with 98 % of biodiesel from rape seed oil degrading biologically in three weeks [9].
- It is less toxic than fossil diesel [5, pp. 231-246] with biodiesel from rapeseed oil having an LD<sub>50</sub> of one tenth of that of table salt [9].
- It is safer to transport, to handle and store than fossil diesel due to its reduced volatility and lower toxicity.
- It has better lubricative abilities than fossil diesel [5, pp. 219-226].

### ***2.3.1.2 Disadvantages of biodiesel***

- Biodiesel has higher viscosity than fossil diesel. This is exacerbated at lower temperatures and can cause running and start problems in cold climates. This is usually solved by additives that reduce the freezing point or by blending [5, pp. 147-190].
- Care must be taken when storing biodiesel due to its biodegradability and its ability to absorb larger amounts of water than fossil diesel [10]. Having water in the fuel will reduce engine life due to corrosion and will reduce the fuels shelf life due to microbial growth and increased oxidation [11]. High water content will also reduce the higher heating value of the fuel. Fossil diesel can hold 50 ppm of water while biodiesel can absorb up to 1500 ppm [5, p. 27], [12] .
- NO<sub>x</sub> emissions of engines which run on biodiesel are increased by up to 10 % [5, p. 256], [8, p. 11].
- Biodiesel has around 12.5 % Lower energy content per weight and 8 % lower energy content per volume than fossil diesel [5, p. 24].





### **2.3.1.3 Blends**

Biodiesel is miscible with fossil diesel and can therefore be blended. The blends are named by the fraction of biodiesel they have mixed in. The nomenclature is B[X] where X is the percent of biodiesel mixed in and they range from B0 to B100. Blending gives several benefits by combining the qualities of both fossil diesel and biodiesel to get a fuel with desirable qualities. Fossil diesel subjected to sulfur decreasing processes often loses some of their lubricity. Blending even with as low as 1 % of biodiesel gives adequate lubricity [13]. Emissions from blends with biodiesel will all be reduced with the exception of NO<sub>x</sub> which can see a slight increase [5, pp. 253-267], [8, p. 11]. The blend will also have a higher cetane number than pure fossil diesel and they are less volatile and therefore safer to handle and transport.

### **2.3.1.4 Renewability**

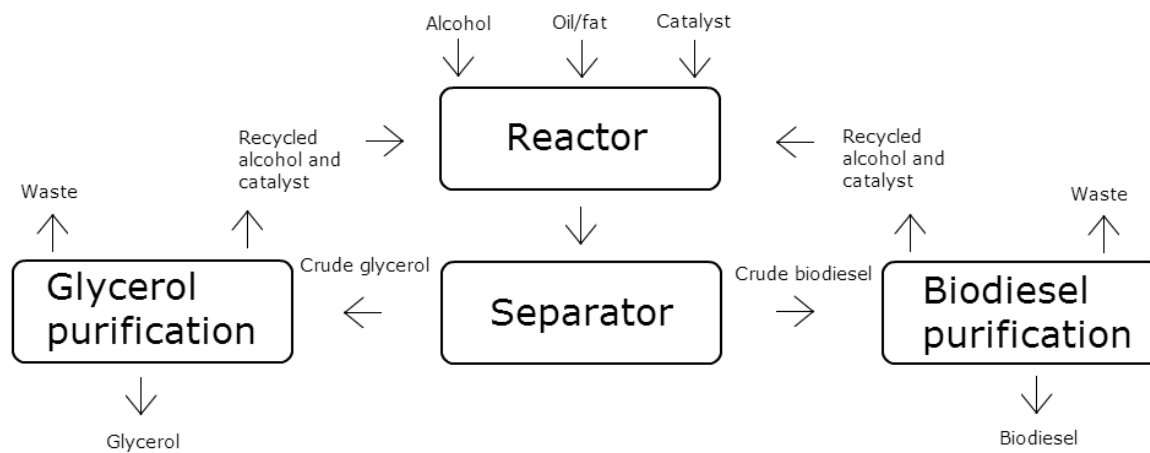
As mentioned in the introduction, biodiesel is potentially renewable. Its renewability will depend on the raw materials used and how these materials are produced. Methanol is mostly produced from syngas reaction [14] and the source of this gas comes from natural gas which is not renewable. Ethanol however is produced mainly by fermentation of sugar from sugar cane and corn, which are renewable. But even ethanol and vegetable oils can have some element of non-renewable sources involved in their production. In farming fossil fuels are being used to run equipment and for transportation [8, pp. 14-16]. If the alcohol comes from renewable sources, and if fossil fuels are phased out in vegetable oil production, biodiesel could be completely renewable.

## **2.4 Production**

### **2.4.1 Industrial production**

The production of biodiesel generally follows the flow chart shown in Figure 4. Alcohol, oil/fat and catalyst are added to a reactor while being stirred for a certain amount of time depending on the operating conditions and catalyst used. The product is then separated into crude glycerol and crude biodiesel. These are then purified to yield the end products. The separation and purification methods used will depend on the catalyst employed. This reaction can also be

done in a two steps where around 80% of the alcohol and the catalyst are added to one reactor. The products from this reactor after a certain amount of time will have its glycerol removed and then lead to a second reactor with the addition of the remainder of the alcohol and catalyst [5, p. 37]. The benefits of a two stage process are less alcohol consumption and a more complete reaction due to removal of glycerol which shifts the reaction to the right.



**Figure 4:** Process flow scheme for biodiesel production.

## 2.4.2 Reactor types

### 2.4.2.1 Batch reactor

Batch reactors are one of the simpler reactor types. It consists of a reactor vessel with a stirrer. The reactants are added to the reactor and left there until the reaction reaches completion. Batch reactors are best suited for low volume operation as they need to be shut down between each batch. As they have to be refilled, their products can be more variable than that of continuous reactors. Operating conditions like temperature and pressure are easy to maintain due to the simplicity of the reactor design [15].

### 2.4.2.2 Semi-batch

The semi-batch is similar to the batch reactor, but here reactants can be added as the reaction is taking place. This allows for greater control of equilibrium reactions and other



reactions where a reactant can limit reaction rates. Otherwise this reactor type has the same benefits and disadvantages as the batch reactor.

#### **2.4.2.3 Plug flow reactor (PFR)**

In a PFR the reactants and catalyst is lead through a tube and allowed to react. This type of reactor is best suited for high volume production due to low labor costs [15]. This type of reactor has poor temperature control. A catalytic reactor or a packed bed reactor is a variant of a PFR where the catalyst is fixed in the reactor tube as the reactants pass by.

#### **2.4.2.4 Continuous stirred tank reactor (CSTR)**

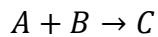
This type of reactor functions like a PFR, having an in and outflow. The difference is that the reactor is well stirred and therefore is assumed to have a uniform composition throughout the reactor. It offers good temperature control and low operating costs. It does; however, have the lowest conversion per reactor volume [15].

The most commonly used reactor types in industrial scale biodiesel production are continuous flow reactors, either CSTRs or plug flow reactors [5, p. 37]. This is due to the large volumes that need to be produced in order for the plant to be economically viable as well as a requirement of uniform products. Some smaller plants and research institutions use Batch reactors due to ease of operation and low volumes.

### **2.4.3 Reaction rate**

A key factor of whether a reaction is viable is the speed it completes under. A measurement of this is the reaction rate  $r$ , which is how fast reactants are being consumed to form another substance. An example of a simple reaction rate is shown in equation 1 for the reaction shown in Figure 5, where two substances A and B react to form C. This reaction rate is dependent on the concentrations of the reactants  $C_A$  and  $C_B$  as well as the reaction rate constant  $k$ . As the reaction continues the concentrations of A and B declines and thereby reduce the reaction rate.

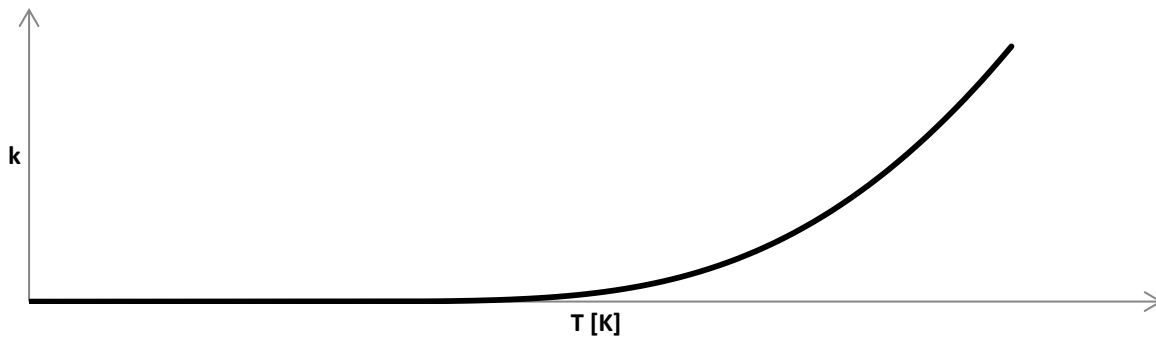
$$r = kC_A C_B \quad (1)$$



**Figure 5:** A simple example reaction.

$k$  is specific for each reaction and is almost always strongly dependent on the temperature, but independent on the concentrations of the reactants. The temperature dependence of  $k$  is given by the Arrhenius equation shown in 2 where  $A$  is a preexponential factor,  $E$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the temperature in Kelvin. In biodiesel production the reaction constant  $k$  will take the form shown in Figure 6 meaning increased temperature will yield higher reaction rates. Transesterification is endothermic and requires a certain amount of energy to initiate the reaction. This is due to the activation energy which can be seen as a barrier that the molecules will have to overcome in order to be able to react.

$$k(T) = Ae^{-E/RT} \quad (2)$$



**Figure 6:** Values of  $k$  for biodiesel.

The reaction shown in Figure 5 is irreversible, but if the reaction was reversible like the transesterification reaction in Figure 3 there would be two reaction rates. One for each direction, and when both of these reaction rates are equal the reaction is said to be in equilibrium. As mentioned earlier, the manipulations of the concentrations and operating conditions can be used to control this equilibrium. As the reaction mechanism of biodiesel production involves several



reaction steps and multiple reactants, the combined reaction rates can form a complicated expression, especially when there are catalysts involved.

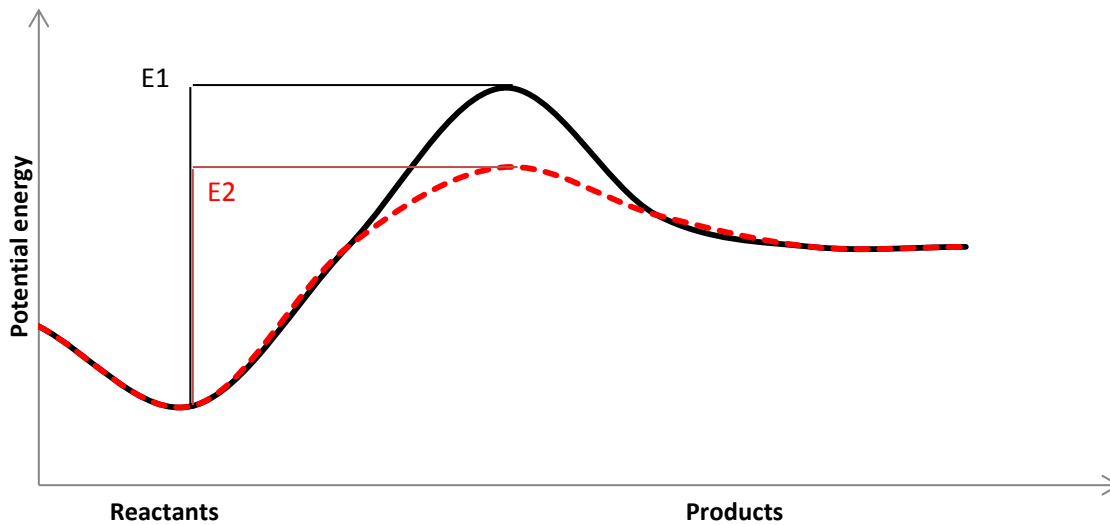
#### 2.4.4 Conversion

Conversion is a measurement how much of the reactants that has been formed into the desired product and is shown in equation 3.

$$X_a = \frac{\text{Mole of FFA reacted}}{\text{Moles of FFA fed}} \quad (3)$$

#### Reaction mechanisms

Esterification can take place under room temperature conditions, but it is slow and the conversion would be low [5, p. 35]. Higher temperatures, pressures and molar ratios increase the reaction rate and final conversion, but come at the cost of increased energy use and therefore reduced efficiency which can make the process uneconomical. A way to increase the reaction rates without the use of high energy input and high molar ratio is with the use of catalysts. The purpose of a catalyst is to reduce the activation energy of the reaction so that it can take place at a lower temperature. Figure 7 visualizes the effect of a catalyst on the activation energy where it reduces the activation energy from E1 to E2.

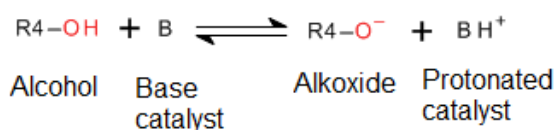


**Figure 7:** Catalysts effect on activation energy showing catalyst in red and without catalyst in black.

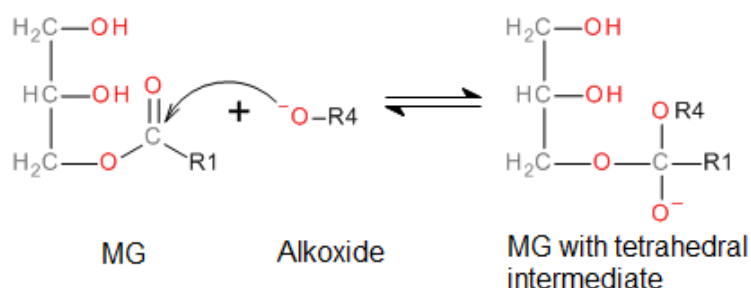
There are mainly two types of catalysts used in biodiesel production, acid and base and both have their distinct mechanisms. The base and acid transesterification mechanisms has been reviewed by Schuchardt et al. [16], while the esterification mechanic has been reviewed by Clark [17].

#### **2.4.4.1 Base transesterification mechanism**

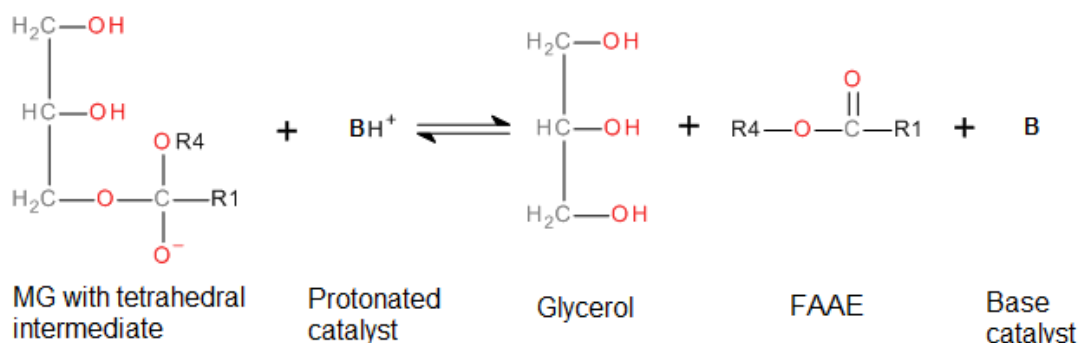
The mechanism of base-catalyzed transesterification of DG is shown in Figure 8, Figure 9 and Figure 10. The mechanism is the same for DGs and MGs. First Alcohol reacts with the base catalyst to produce an alkoxide and protonated catalyst shown in Figure 8. The alkoxide initiates a nucleophilic attack at the carbonyl group of the MG which generates a tetrahedral intermediate which is shown in Figure 9. The tetrahedral intermediate causes the FA to split from the glycerol while the glycerol gets protonated by the protonated catalyst, regenerating the base catalyst so that it can be used again, all which is shown in Figure 10.



**Figure 8:** Base transesterification mechanics 1. A base catalyst takes a proton from an alcohol to generate an alkoxide and a protonated catalyst.



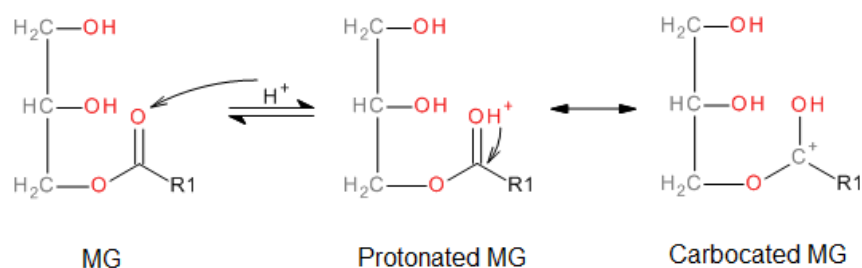
**Figure 9:** Base transesterification mechanics 2. The alkoxide initiates a nucleophilic attack on the carbonyl group of the MG which generates a tetrahedral intermediate.



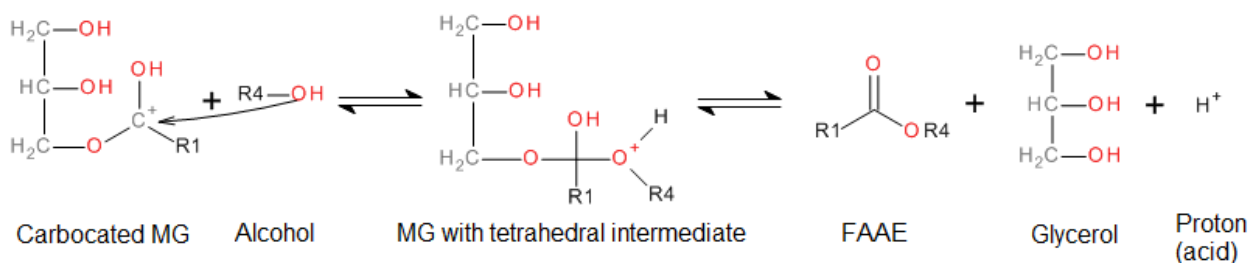
**Figure 10:** Base transesterification mechanics 3. FAAE splits from glycerol while the protonated catalyst donates a proton to the glycerol.

#### 2.4.4.2 Acid transesterification mechanism

The mechanism of the acid-catalyzed transesterification of a MG is shown in Figure 11 and Figure 12. Again this process is shown for MG, but will be the same for DGs and MGs. The carbonyl group of the ester is protonated by the acid environment. This leads to the carbocation of the carbonyl group. A nucleophilic attack of alcohol produces a tetrahedral intermediate, which causes the FA to split off from the glycerol and regenerate the catalyst  $H^+$ .



**Figure 11:** Acid transesterification mechanic 1. MG gets protonated and then undergoes carbocation.

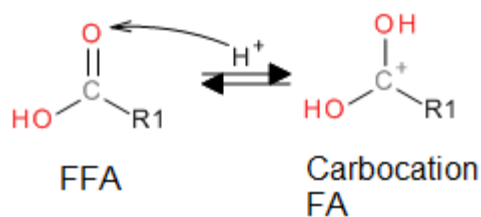


**Figure 12:** Acid transesterification mechanic 2. The carbocated MG reacts with alcohol to form a MG with a tetrahedral intermediate. This then splits up into FFAE, glycerol and a proton.

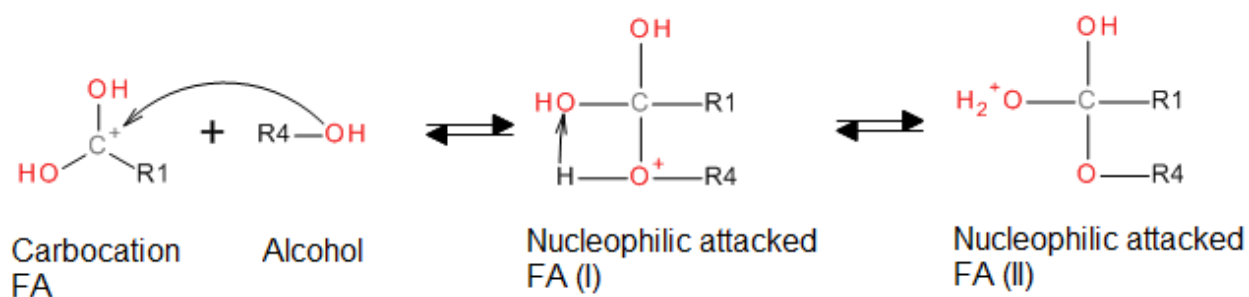
#### 2.4.4.3 Esterification mechanism

Acid catalysts can also esterify FFA. This happens like shown in Figure 13, Figure 14, Figure 15 and Figure 16. FFA first gets a proton from the acid catalyst. The protonated FA then reacts with and alcohol to yield a nucleophilic attacked FA (I). After this a proton is transferred within the molecule to one of the other hydroxyl groups which give a nucleophilic attacked FA (II). From this molecule water splits off, and then finally the remaining molecule loses a proton, thus regenerating the catalyst and yielding a FFAE.

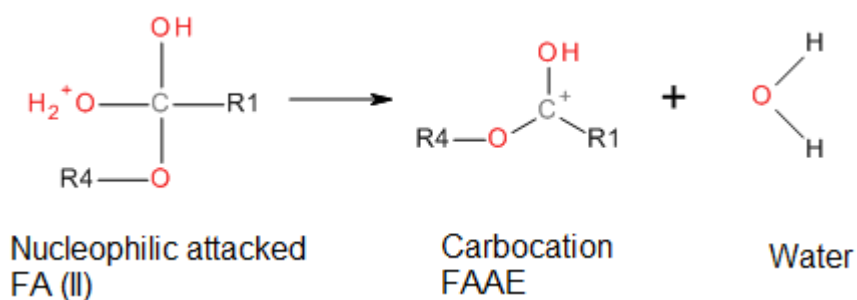




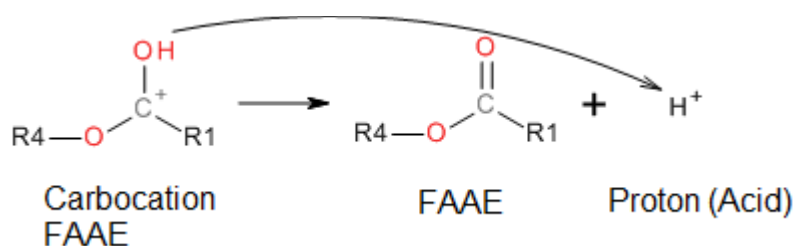
**Figure 13:** FFA gets a proton from an acid yielding a carbocation FA.



**Figure 14:** An alcohol initiates a nucleophilic attack on the FA. A proton then gets transferred to one of the hydroxyl groups.



**Figure 15:** A water molecule splits of the nucleophilic attacked FA.



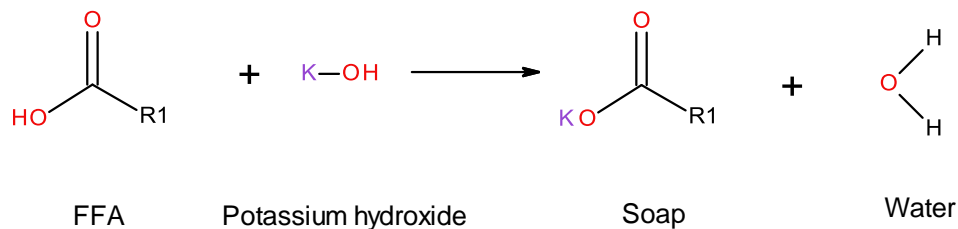
**Figure 16:** A proton splits of the carbocation FAAE yielding an FAAE and a proton.

## 2.5 Catalysts

The catalysts come in two forms, homogeneous and heterogeneous. A homogeneous catalyst is in the same phase as the reactants, and in the case of biodiesel, this means the liquid phase. Heterogeneous catalyst is in a different phase than the reactants which means that the catalyst is solid.

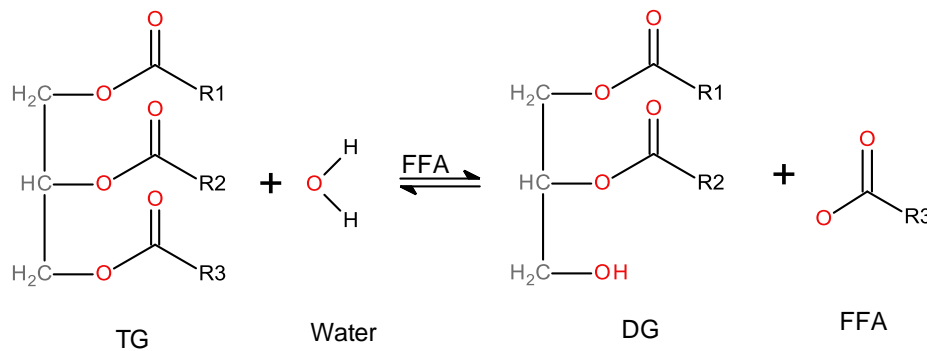
### 2.5.1 Homogeneous base catalyst

Homogeneous base catalysts are the fastest and most efficient of the catalysts in use today and as a result they are also the most used catalyst [5, p. 71]. The two most used of these homogeneous base catalysts are potassium hydroxide and sodium hydroxide [18]. They do, however, have one major drawback and that is that in the presence of FFAs there is saponification (formation of soap) which is shown in Figure 17.



**Figure 17:** Saponification in the presence of free fatty acid and a homogeneous base catalyst (KOH).

This reaction is undesirable and there are several reasons why. Firstly the reaction is irreversible and FFA and catalyst will be consumed which means lower overall yield due to consumed reactant. There is also the need to add excess catalyst to achieve the desired final conversion at an acceptable time. The water produced can function as a catalyst inhibitor and in addition in the presence of FFA it can hydrolyze FFAE and glycerides into FFA [19] through the reaction that is shown in Figure 18.



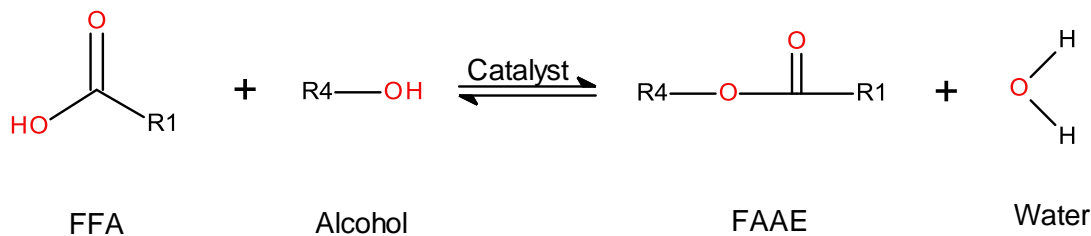
**Figure 18:** Hydrolyzation of TG in the presence of water and FFA. The process is the same for DGs and MGs.

The saponification and hydrolysis reactions represent a positive feedback loop where more and more soap is produced at the detriment of catalyst, reactants and product. Soap in large enough concentrations acts as an emulsifier making glycerol miscible with the product. This causes issues in the separation and purification steps needed to get the final product. In oils and fats with low fraction of FFA the effect of the saponification reaction does not have a significant impact on overall conversion to biodiesel, but if the oil contains more than 5 % FFA the effects can make the entire process uneconomical [5, p. 68], [8]. The typical reaction times with homogenous base catalyst lie between 1-2 hours at reaction temperatures of around 60-70 C [18].

### 2.5.2 Homogenous acid catalyst

High quality Raw materials with low amount of FFA are refined oils and are costly [18]. These are often also edible and the production of biodiesel from these sources competes with food production and leads to a price increase in food. The biodiesel from these feedstocks are considered to be first generation biofuels. Feedstock price from first generation feedstocks has up to a 90 % [5, p. 68] share of the total cost of the product biodiesel. This has led to a search for second generation raw materials and methods to convert these alternative feedstocks to biodiesel. The feedstocks that are being evaluated are waste oils from food industries, wood, algae and non-edible oils from plants that in their growth do not compete with food production [5], [18]. A downside of these feedstocks is that they have a higher content of FFA as well as other impurities which makes the use of homogenous base catalyst unfeasible. For these high FFA oils there are

currently two methods used to convert them to biodiesel. One alternative method revolves around physically removing the FFA before utilizing a homogenous base catalyst. This is not an ideal approach as you are losing part of the feedstock by removing it. Another method tries to convert the FFA into biodiesel through the esterification reaction which is shown simplified in Figure 19. The most used homogeneous catalyst employed for this purpose is sulfuric acid due to its low cost [5, p. 56].



**Figure 19:** Esterification reaction.

Homogenous acids are; however, up to a thousand times slower than homogenous bases for the transesterification [5] with reaction times varying from 4 hours to 3 days [18]. Homogeneous acids is therefore used as a pretreatment step in a two-step process where the FFA is first esterified with an acid catalyst, and once the FFA level is low enough is transesterified in a second reactor with an homogenous base catalyst. One of the downsides of acid catalysis is that acids are highly corrosive and the equipment which can withstand them can be expensive.

### 2.5.3 Heterogeneous catalysts

For both homogenous catalysts the end products needs to be washed and neutralized before they can be used, which produces large amounts of waste water [18]. These purification steps can be simplified by employing heterogeneous catalysts. They are made from materials with active sites that act basic or acidic, or by affixing acidic and basic materials to solid substances and structures. The supports materials that are used in heterogeneous catalysts include structures made of silica, metals and polymers.

Important characteristics of heterogeneous catalysts are their surface area, number of active sites, active site strength, porosity and stability. It is desirable to have a catalyst with a large



number of active sites that are strong as well as a high surface area which all leads to better reaction rates [20]. A catalyst with a high porosity will have increased surface area, but if the pores are too small the large glycerides and heavy alcohols will have problems reaching the active sites. Some support materials can act hydrophilic which can hinder diffusion of the reactants. A good stability of the catalyst means it is resistant to high temperatures, chemicals, physical shock and that it also prevents leaching of the active materials. One of the selling points of heterogeneous catalysts is their ability to easily be reused, but even they can lose their activity level, becoming deactivated after use. This can be due to substances blocking the active sites or leaching of the active material. In such cases it is desirable that the catalyst can be easily regenerated to regain its catalytic activity. A drawback with heterogeneous catalysts is that they are slower than their homogeneous counterparts due to diffusion limitations [20].

#### **2.5.4 Heterogeneous base catalysts**

The active sites of heterogeneous base catalysts can be based on alkali earth oxides like CaO and MgO, transition metal oxides like MnO and TiO, basic zeolites and hydrotalcites [6]. It is important that these active materials don't leach as it will lead to saponification in the presence of FFA. Reactions with these catalysts typically reach completion after 2-5 hours [6].

#### **2.5.5 Heterogeneous acid catalysts**

Acid catalysts can contain sulfonic acid groups or  $\text{SO}_4/\text{ZrO}_2$  surface coatings. They can also be made from a wide range of inorganic and polymeric acids. The major advantage of heterogeneous catalyst is no saponification and simultaneous esterification and transesterification. They are also not corrosive, unless they leach. Park. et. al [21] reported over 95 % conversion of FFA with two commercial acid polymer resins, Amberlyst 15 and Amberlyst BD20 with oleic acid and methanol after 6 hours. They are; however, as their homogeneous counterparts slower than bases at transesterification and also have a tendency to get deactivated by water [6].



## 2.6 Effect of Alcohol carbon chain length

As mentioned earlier, the price is a major consideration in the choice of alcohol for the esterification and transesterification reactions, but it is not the only one. Generally, the longer the carbon chain length the longer the reaction times [5, pp. 54-55], [22]. This is due to a lower solubility that a longer chain alcohol has in basic catalysts, steric effects and polarity. The choice of alcohol can also affect the purification steps. Ethanol for example is an azeotrope with water which makes the removal of water in the purification and separation steps of a reactor more difficult.

## 2.7 Other reaction rate improvement methods

One of the reaction rate limitations is that alcohol, TGs and catalyst needs to come in contact. By adding cosolvents, which increases miscibility of the reactants, this limitation can be reduced. Some of the cosolvents that can be used are tetrahydrofuran and methyl tert-butyl ether [5].

Alternative agitation through microwave and ultrasonic irradiation has shown increase in reaction rates exceeding what would be achieved by thermal heating with the same energy input [5, p. 57].

### 2.7.1 Supercritical process

By increasing temperature and pressure to a point where the alcohol is brought to a supercritical state the mass transfer rate, and thereby the reaction rate, are increased dramatically. No catalyst is needed and typical reaction completion times are around a few minutes [18]. This method allows almost any raw material to be used and yields pure products, but it does; however, require a large amount of energy input to get to the super critical state and a high molar ratio which makes the process costly. It is possible to add a cosolvent or an inert gas like CO<sub>2</sub> which is easier to bring to a supercritical state to reduce energy use.



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## 3 Materials and methods

### 3.1 Materials

Oleic acid diethyl ether, methanol, phenolphthalein and melamine were supplied by Sigma-Aldrich. Ethanol 96%, anhydrous ethanol were supplied by a local supplier. Amberlyst 15 wet ion exchange and Amberlyst bd20 wet ion exchange was supplied by Dow chemical company.

### 3.2 Equipment

For the reactions a 500 ml glass batch reactor from Quark Glass with a magnetic stirrer from VWR was used. Accessories to the glass reactor includes a syringe with a long needle, a condenser and a temperature measurement instrument that connected to the magnetic stirrer all which is shown in Picture 1. The condenser had a plug loosely attached to top to prevent alcohol from escaping. The glass reactor was heated by circulating warm water supplied by a VWR warm water bath shown in Picture 2.



**Picture 1:** Glass reactor with accompanying accessories.



**Picture 2:** Warm water heater with circulatory pump.

### 3.3 Methods

#### 3.3.1 Catalyst pretreatment

100g of catalyst was placed in a sieve funnel covered with a filter paper as shown in Picture 3. 150 ml of 50 % ethanol/water, 70 % ethanol/water 96% ethanol, anhydrous ethanol and acetone was run 5 times each through the sieve with the catalyst. This process is shown in Picture 4. The catalyst was then left to dry at 70 C in an oven for 72 hours and stored in a closed container. Picture 5 shows the different rinsing liquids before being used.

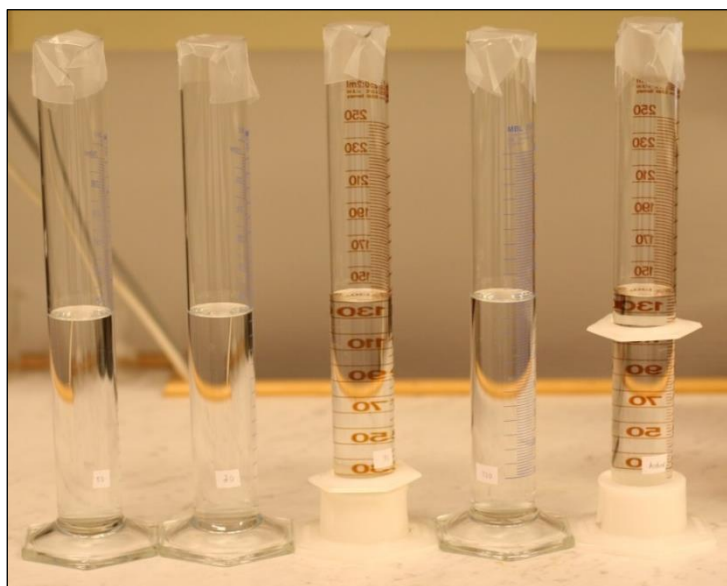




**Picture 3:** Amberlyst 15 catalyst before pretreatment in a sieve funnel covered with filter paper.



**Picture 4:** catalyst in the process of pretreatment.



**Picture 5:** Rinsing liquids, from right to left, 50 % ethanol, 70 % ethanol, 96 % ethanol, anhydrous ethanol and acetone.

### 3.3.2 Catalyst leaching tests

To test for Acid or base leaching, catalyst and ethanol was added to beakers and set to stir at room temperature at 60 C for 30 minutes. The indicator phenolphthalein was added to a sample of the ethanol in the beakers and afterwards one drop of NaOH was added. If there was no color change immediately after the addition of phenolphthalein to the sample the catalyst was determined not to leach base. If there was a color change after the addition of NaOH to the beaker the catalyst was determined to not leach acid. Phenolphthalein was also added to dry catalyst, if there was no color change the catalyst itself was determined to not leach base. Picture 6, Picture 7 and Picture 8 show the different color variations.



**Picture 6:** Sample with 50/50 ethanol diethyl ether and phenolphthalein added.



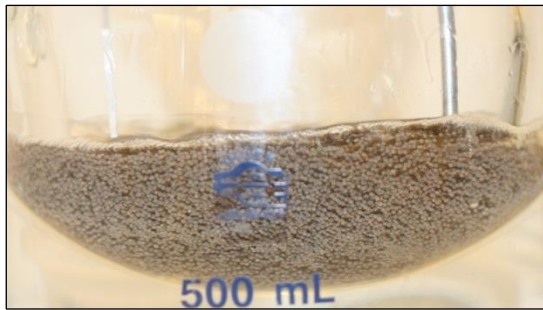
**Picture 7:** Sample after titration with color indicating neutral solution.



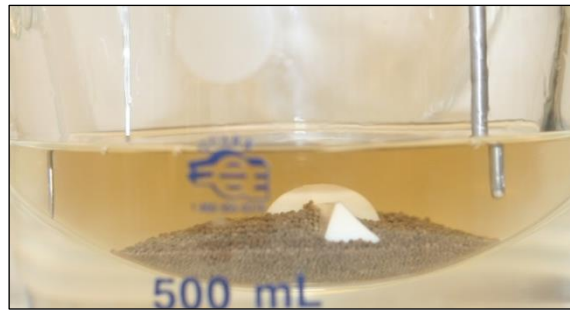
**Picture 8:** Sample after titration with color indicating basic solution.

### 3.3.3 Parameter screening experiments

The experiments were conducted in a 500 ml glass batch reactor. The oleic acid and alcohol was measured and added to the reactor and was brought up to the target temperature under stirring which was set to 200 rpm. When the reaction mixture reached the target temperature a zero sample was taken and the catalyst was added and time started. Samples of 0.5 ml were taken at 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360 minutes. In order to avoid getting catalyst in the needle sample, the stirring was stopped for 5 seconds so that the catalyst would settle. This is shown in Picture 9 and Picture 10.



**Picture 9:** Reactor under operation with reactants and catalyst.



**Picture 10:** Reactor with stirring stopped to allow the catalyst to settle so a sample could be taken.

One experiment was run for 50 hours to determine when the reaction equilibrium was reached. Each sample after it was taken was left in an ice bath for 1 minute to stop the reaction. The sample was titrated as soon as possible after it was taken.

### 3.3.4 Oleic acid self-catalysis experiment

A single experiment was run with no catalyst to test if the oleic acid can self-catalyze and if so, how it would affect the overall conversions of the other experiments. The oleic acid and ethanol was preheated to the target temperature in separate containers before being added to the glass reactor. As soon as the reactants were added a zero sample was taken and time started. The rest of the procedure during this experiment was the same as the parameter screening experiments.

### 3.3.5 Biodiesel conversion determination

The biodiesel amount in samples was determined by titration as described in the testing standard EN 14104 [23]. During the reaction FFA will be consumed and since the other reactants and the product have a negligible effect on PH there will be a drop in acidity. The ratio of FFA consumed to FAME formed is one to one and a drop in acidity will mean an increase in biodiesel yield. 20-60 mg of sample dissolved in a 10 ml 50/50 mix of 96% ethanol and diethyl ether with a few drops of the indicator phenolphthalein was added to a beaker. Phenolphthalein is colorless in acidic solutions and purple in basic solutions. KOH is added to the beaker until a color change is observed. At this point the acid in the beaker has been neutralized and with the concentration



and amount used of the KOH solution known, the original acid fraction of the sample can be calculated. The formula is shown below in equation 4.

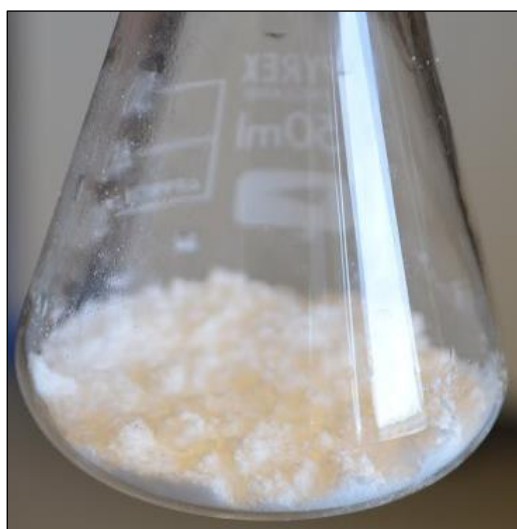
$$\text{Acid value} = \frac{\text{Volume}_{\text{KOH}}(\text{ml}) \times \text{Concentration}_{\text{KOH}}(\text{M}) \times \text{Molar weight}_{\text{KOH}}\left(\frac{\text{g}}{\text{mol}}\right)}{\text{Sample weight (g)}} \quad (4)$$

The conversion is calculated based of the zero point samples. Therefore every Zero point sample was titrated 5 times, in order to reduce the error that would propagate, shifting the entire plot up or down. The other samples were titrated 2 times each.

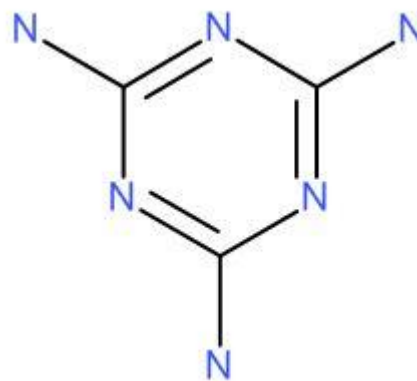
## 4 Results

### 4.1 Preliminary experiments

As heterogeneous catalysts shows promise of being able to deal with alternative feedstocks that contain high levels of FFA it was decided to do a parameter screening of such a catalyst in the presence of a FFA. Oleic acid was selected due to its abundance in several oils which is evident from Table 1. Ethanol was selected due to it being renewable and less toxic than methanol. The first work was done to find a suitable catalyst to do a parameter screening of. The catalyst had to have the following characteristics, it should work and there should be little or no other works done on the same subject by others. Three catalysts were tested before a suitable one was found. Melamine which is shown in Picture 11 is an organic base resin with the chemical structure shown in Figure 20 was tested first.



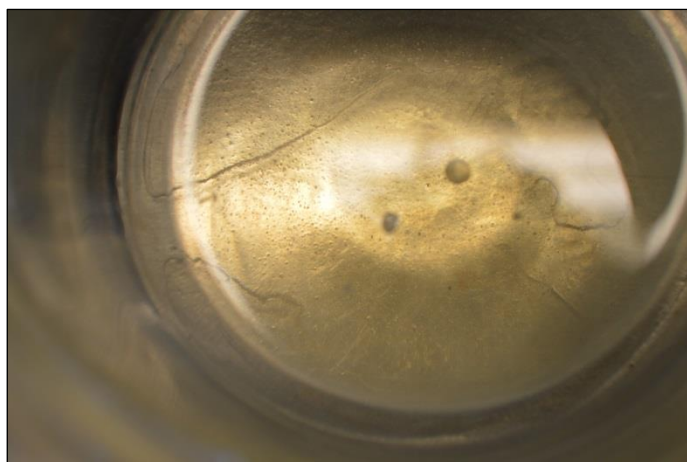
**Picture 11:** Melamine in a beaker.



**Figure 20:** Chemical structure of melamine.

Several issues were observed with melamine: firstly it gave negative conversion, which was puzzling as melamine is basic and negative conversion means a higher measured acid value. Melamine also seems to dissolve in the reaction mixture and eventually disappeared completely.

This can be seen in Picture 12 which shows the reactor after 6 hours compared to a sample taken five minutes after the reaction had started shown in Picture 13.



**Picture 12:** Reactor with oleic acid, ethanol and melamine catalyst after reaction completion of 6 hours.

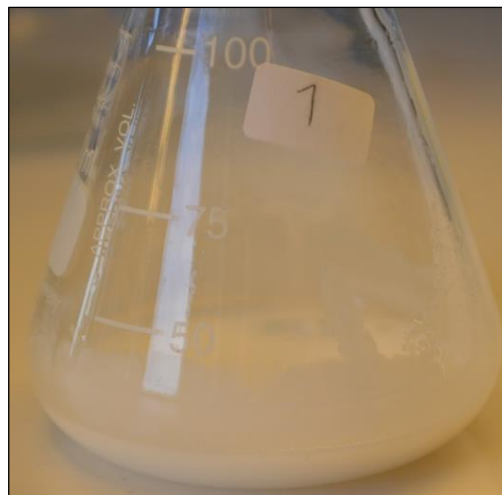


**Picture 13:** Sample of experiment with oleic acid, ethanol and melamine taken after 5 minutes of reaction time.

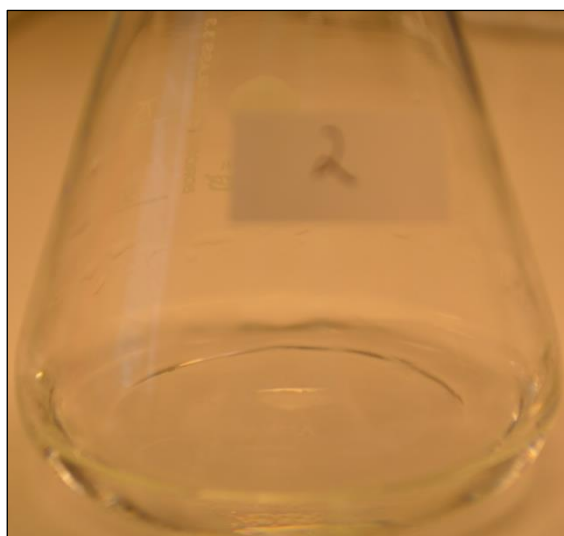
It was believed that melamine might react with oleic acid so three other FFAs were tested with it and ethanol. The acids and melamine were stirred for 2 hours and in all cases the mixture formed a white foamy and sluggish substance as can be seen in the before and after pictures of Picture 14, Picture 15, Picture 16, Picture 17, Picture 18 and Picture 19.



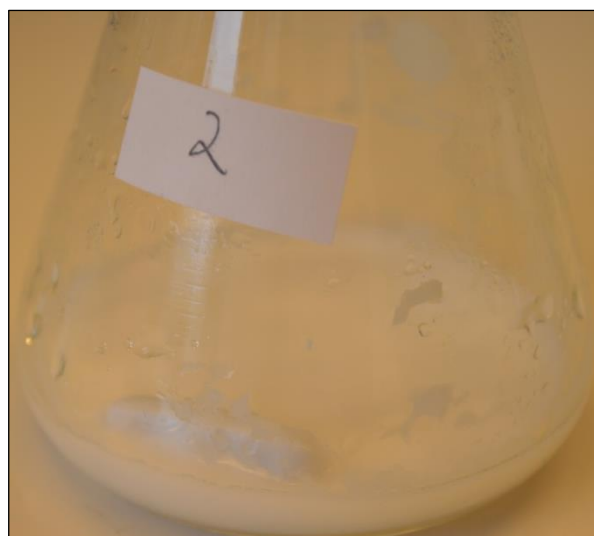
**Picture 14:** Ascetic acid and ethanol before stirring.



**Picture 15:** Ascetic acid and ethanol with melamine after 2 hours of stirring.

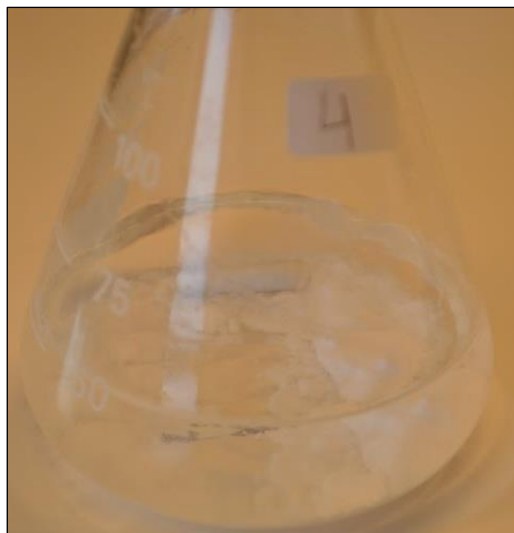


**Picture 16:** Formic acid and ethanol in a beaker before stirring.



**Picture 17:** Formic acid and ethanol with melamine after 2 hours of stirring.





**Picture 18:** Myristic acid with ethanol, diethyl ether and melamine before stirring.



**Picture 19:** Myristic acid with ethanol, diethyl ether and melamine after 2 hours of stirring.

An attempt was made to stabilize melamine through calcination at 400 C. The calcined melamine can be seen in Picture 20 and it was then crushed in a mortar as can be seen in Picture 21. This did; however, not improve the results and melamine as a catalyst for the parameter screening was not suitable.



**Picture 20:** Melamine calcined at 400 C.



**Picture 21:** Calcined melamine crushed in a mortar.



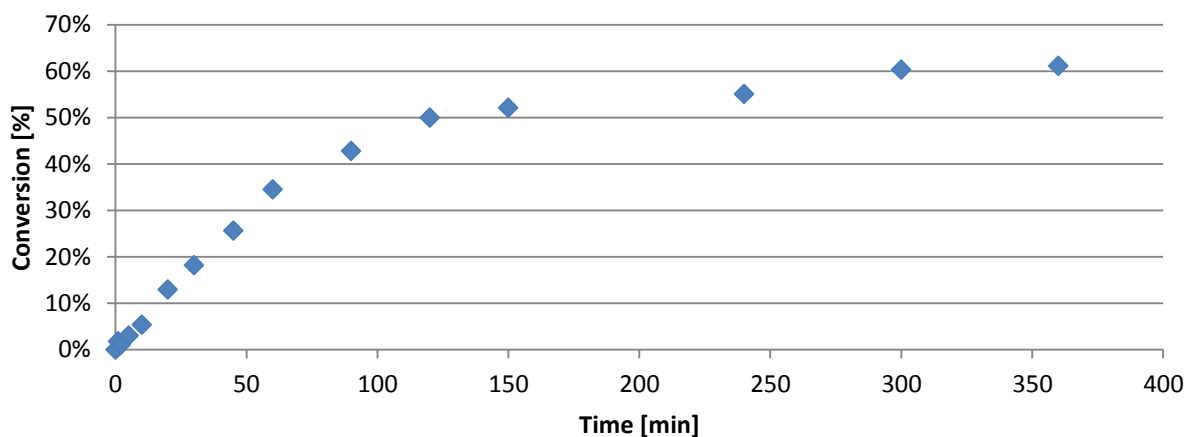
Esterification was then attempted with Amberlyst BD20 and Amberlyst 15 wet ion exchange, two commercial acid polymer resins from Dow chemical company as they had been shown to work with methanol and oleic acid [2], but initial experiments with these catalysts yielded no conversion. Even a switch of alcohol from ethanol to methanol did not improve the results. There was then an attempt to regenerate the two commercial catalysts with sulfuric acid, but when treated in this way the catalysts leached acid which was undesirable. After some research it was decided to reproduce results from the paper: “Esterification of free fatty acids using water-tolerable Amberlyst as heterogeneous catalyst” by Park. et. al. [3]. In that work Amberlyst 15 wet ion exchange and Amberlyst BD20 was used with oleic acid and methanol. The purpose of using the same catalysts, alcohol and procedures as the paper was to exclude any errors made in the previous attempts. The catalyst that was settled on was Amberlyst 15 wet ion exchange shown in Picture 22.



**Picture 22:** Amberlyst 15 wet ion exchange catalyst.

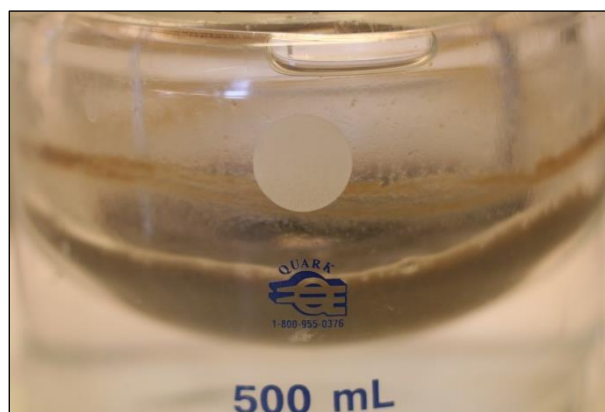
According to the data sheet of the catalyst it had to be pretreated with a water miscible solvent before being usable [1], but a specific method of doing this and which solvent to use was not mentioned, but the report by Park et al. [3] mentions a method and this was adapted as a pretreatment procedure. Using catalyst treated with this method, esterification using oleic acid

and methanol yielded results close to that of the aforementioned report and can be seen in Graph 1.



**Graph 1:** Conversion of oleic acid in the presence of methanol and Amberlyst 15 with operating conditions 60 C, 20 % catalyst amount and 9:1 molar ratio.

The catalyst did; however, fragment during reaction when methanol was used as shown in Picture 23. Picture 24 shows the catalyst recovered from this experiment. This fragmentation did not occur with the catalyst when run under the same conditions with ethanol, with the recovered catalyst from the experiments run under those conditions shown in Picture 25



**Picture 23:** Reactor running with oleic acid, methanol and Amberlyst 15 wet ion exchange. A portion of the catalyst has fragmented.

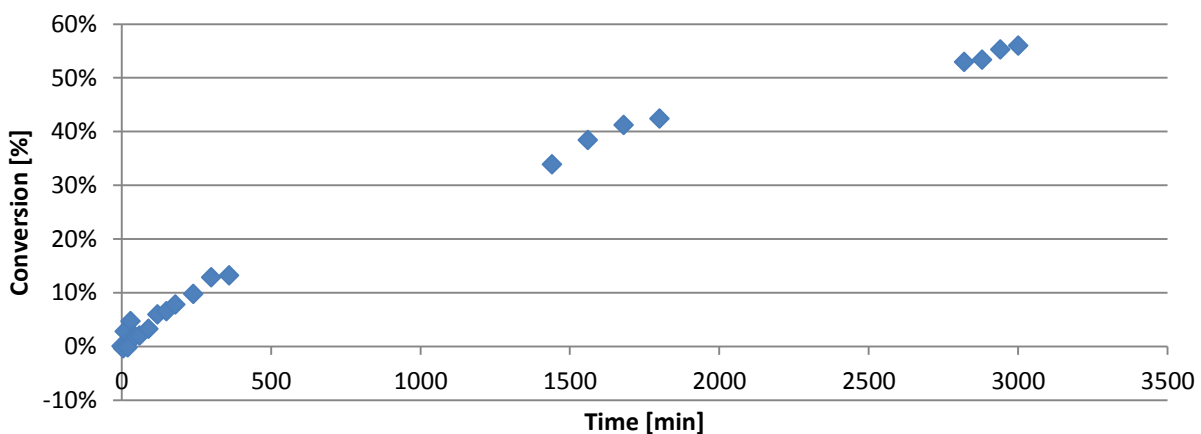


**Picture 24:** Recovered catalyst from the run with oleic acid and methanol. Some of the catalyst is fragmented.



**Picture 25:** Amberlyst 15 wet ion exchange recovered from a run with oleic acid and ethanol at 60 C, 20% catalyst amount and 6:1 molar ratio.

According to Park et al [21], 6 hours was the time needed for the esterification of oleic acid with methanol and Amberlyst 15 wet ion exchange to reach equilibrium. In order to find the time at which the reaction of oleic acid with ethanol and Amberlyst 15 wet ion exchange reached equilibrium one experiment was run for 50 hours. Graph 2 shows the results of this experiment and it can be observed that even after the 50 hours the equilibrium was not reached. Due to time constraints and a desire to compare results to the Park et al. [3] a reaction time of 6 hours was selected.



**Graph 2:** Oleic acid with ethanol and Amberlyst 15 wet ion exchange at 45 C, 20 % catalyst and 6:1 molar ratio.

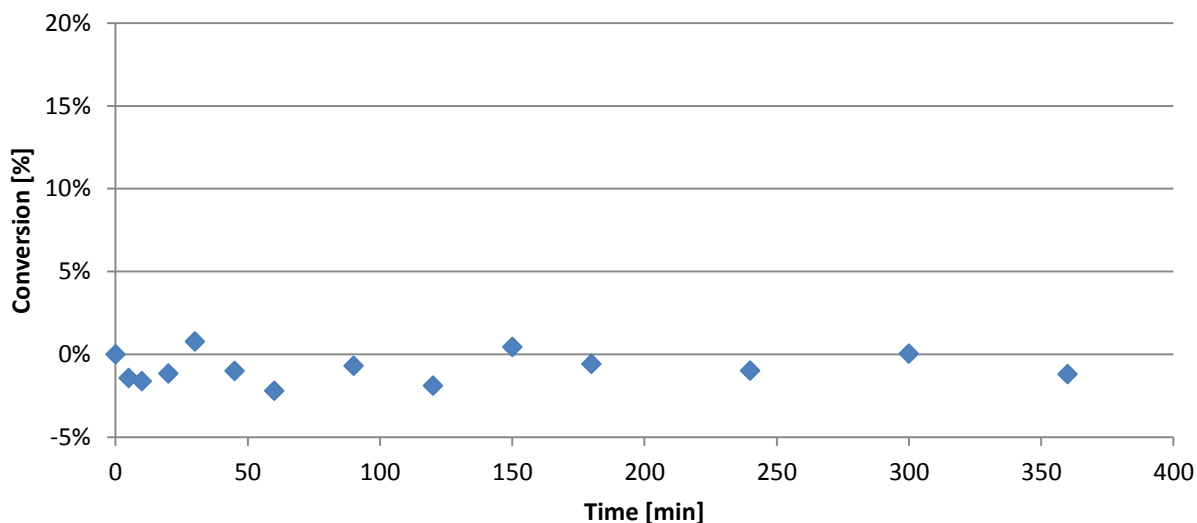


## 4.2 Catalyst leaching tests

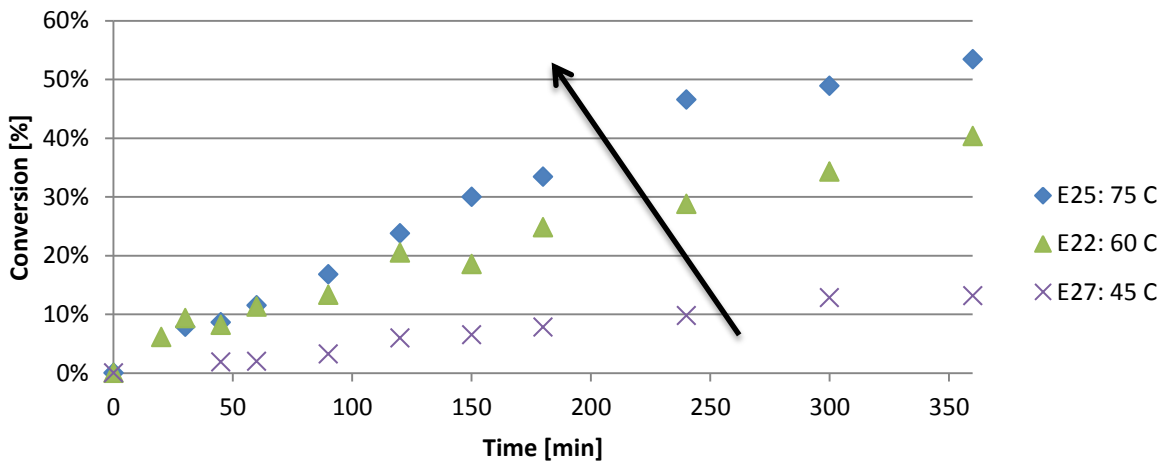
None of the catalysts tested with the exception of the catalysts that were treated with sulfuric acid leached acid or base.

## 4.3 Parameter screening

The result of the experiment without catalyst is shown in Graph 3. The data points can sometimes be negative, but this is due to measuring uncertainty and the average is around 0 % conversion. As there is no observed conversion, the self-catalytic effect of oleic acid in the presence of ethanol is assumed to be negligible.

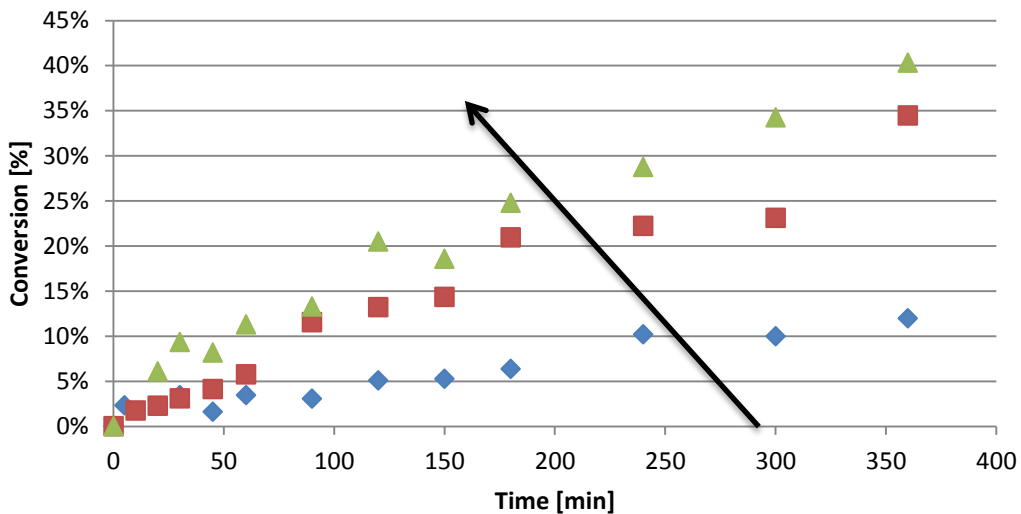


**Graph 3:** Baseline experiment with ethanol and oleic acid at 60 C, 0 % catalyst amount and 6:1 molar ratio.



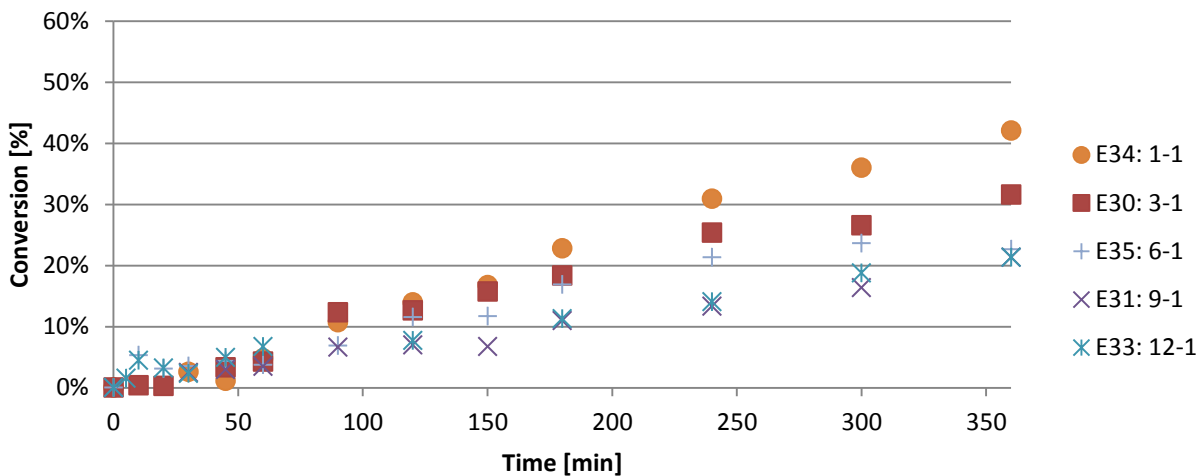
**Graph 4:** Results of experiment 25, 22 and 27 with temperature as variable. The arrow shows increasing conversion with increasing temperature.

Graph 4 shows the conversion of oleic acid to biodiesel under different temperatures. The other factors, molar ratio and catalyst amount were fixed at 6:1 and 20 % respectively. There can be seen a trend of increasing conversion with increasing temperature.



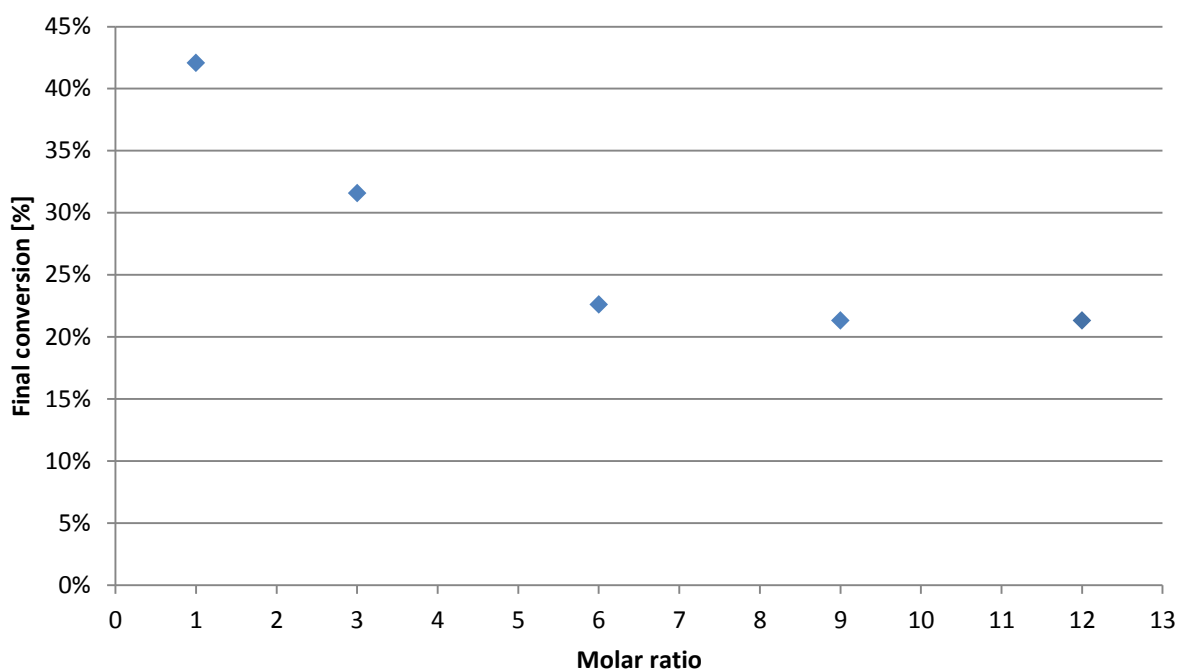
**Graph 5:** Results of experiment 28, 23 and 22 with catalyst amount as variable. The arrow shows increasing conversion with increasing catalyst amount.

Graph 5 shows the conversion of oleic acid to biodiesel with different catalyst amount. The other factors, molar ratio and temperature were fixed at 6:1 and 60 C respectively. There can be seen a trend of increasing conversion with increasing catalyst amount.



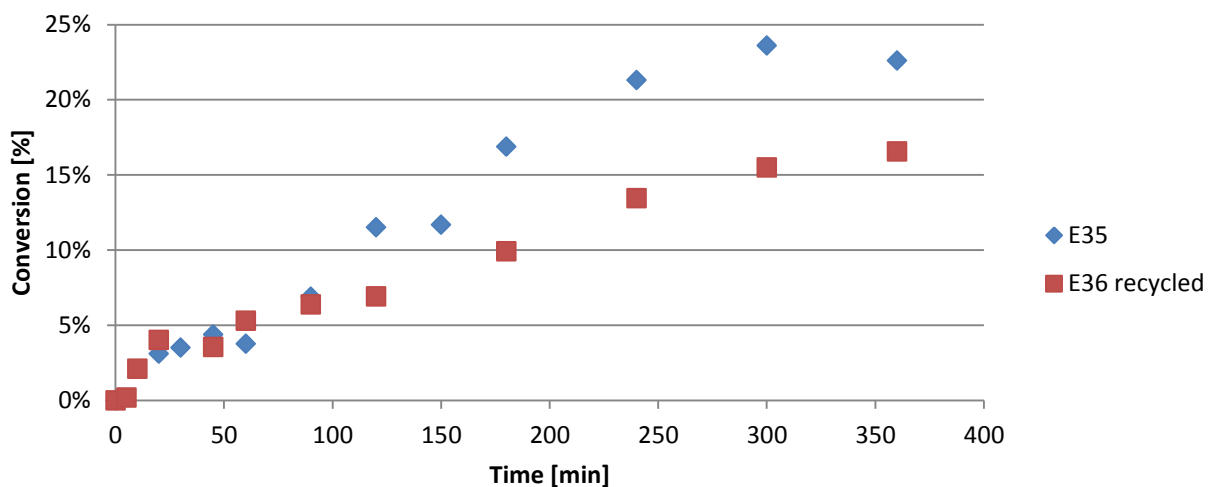
**Graph 6:** Experiments 30, 31, 33, 34 and 35 with molar ratio as variable.

Graph 6 shows the conversion of oleic acid to biodiesel with different molar ratios. The other factors, catalyst amount and temperature were fixed at 20 % and 60 C respectively. There can be seen a trend of increasing conversion with decreasing catalyst amount. This trend becomes clearer in Graph 7 which shows the final conversion of each molar ratio experiment.



**Graph 7:** Final conversion of experiments at different molar ratios with fixed catalyst amount and temperature.

As per Le Chatelier's principle, a higher molar ratio should push the reaction towards the products yielding higher conversion. The reason why the results do not reflect this may be due to the fact that the reaction hasn't reached equilibrium, and therefore the actual final conversion might be different than what is observed in the results.



**Graph 8:** Recycling at 60 C, 20 % and 6:1 molar ratio.

Graph 8 shows the conversion of oleic acid at 60 C, 20 % catalyst amount and 6:1 molar ratio at first use and second use. There can be seen a drop in conversion after a single reuse, showing that the catalyst is not suitable for further applications.





## 5 Discussion

Increasing temperatures will according to equation 2 yield higher reaction rates and more catalysts mean a higher number of active sites for the reaction to occur at. As such the increasing reaction rate with increasing temperature and catalyst amount is in line with reports [24], [25], literature [5], [18] and theory.

The interesting result is the decreasing conversion with increasing molar ratio. The explanation for this result has to do with the reaction time and equilibrium. As the equilibrium was not reached even after 50 hours, the reaction at 6 hours could be considered to be at an initial stage. Even though increasing molar ratio will per Le Chatelier drive the reaction equilibrium towards the products, the initial reaction rate is highest at a molar ratio of 1:1 [18]. As the reaction goes on the alcohol will be consumed and the reaction will reach equilibrium and the reaction rate slow down. If the experiments with the molar ratios as parameters had been allowed to continue until equilibrium the final conversions could be different in relation to each other with higher conversion from higher molar ratios.

As the reaction was not run to equilibrium not much can be said about the equilibrium and the final conversion, but the reaction is slower with ethanol than with methanol at the same operating conditions [3]. This may be due to that the ethanol molecule is larger than methanol and will cause a decrease in diffusion to the active sites of the heterogeneous catalyst.

## 6 Conclusions

Increasing temperature and catalyst amount gives increased conversion. When it comes to molar ratio there seems to be an optimum molar ratio of around 1:1, but due to the equilibrium not being reached this may not be true if the reaction is allowed to reach equilibrium. The catalyst showed limited recyclability with a drop in activity after a single reuse.





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## 7 Future work

Creating a kinetic model of the function of the catalyst and fitting it to the experimental data would provide greater insight into the workings of the catalyst.

Allowing the reaction to reach equilibrium would give a clearer picture of the reaction.

As oils are made of different FA, testing with different FAs with the catalyst will make for a more complete characterization of the catalyst.





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# Appendix

## 8.1 List of experiments

Experiment	Description
1	Test for Melamine leaching in ethanol after two hours of agitation at 20 C.
2	Test for Melamine leaching in ethanol after two hours of agitation at 60 C.
3	Test of dry melamine leaching
4	Esterification of oleic acid and ethanol with melamine at 60 C, 5 % catalyst and 6:1 molar ratio.
5	Alcohol evaporation test.
6	Melamine sedimentation timing test.
7	Melamine leaching test at 5 hours of agitation.
8	Melamine reactivity and dissolving test.
9	Esterification of oleic acid and ethanol with calcinated melamine at 60 C, 5 % catalyst amount and 6:1 molar ratio.
10	Esterification of oleic acid and ethanol with Amberlyst BD20 at 60 C, 5 % catalyst amount and 6:1 molar ratio.
11	Test for Amberlyst BD20 in ethanol after two hours of agitation at 60 C and 20C.
12	Esterification of oleic acid and ethanol with Amberlyst BD20 at 60 C, 5 % catalyst amount and 6:1 molar ratio.
13	Esterification of oleic acid and ethanol with Amberlyst BD20 at 60 C, 20 % catalyst amount and 6:1 molar ratio.
14	Amberlyst BD20 regenerated with sulfuric acid in ethanol.
15	Leaching test of Amberlyst BD20 regenerated with sulfuric acid.
16	Esterification of oleic acid and ethanol with Amberlyst BD20 at 60 C, 20 % catalyst amount and 6:1 molar ratio.
17	Leaching test of Amberlyst BD20 regenerated with sulfuric acid in ethanol at different temperatures.



- 18 Esterification of oleic acid and methanol with Amberlyst BD20 at 60 C, 20 % catalyst amount and 6:1 molar ratio.
- 19 Esterification of oleic acid and methanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 9:1 molar ratio.
- 20 Esterification of oleic acid and methanol with pretreated Amberlyst BD20 at 60 C, 10 % catalyst amount and 9:1 molar ratio.
- 21 Esterification of oleic acid and ethanol with pretreated Amberlyst BD20 at 60 C, 20 % catalyst amount and 6:1 molar ratio.
- 22 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 6:1 molar ratio.
- 23 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 15 % catalyst amount and 6:1 molar ratio.
- 24 Amberlyst BD20 Alcohol absorption test.
- 25 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 75 C, 20 % catalyst amount and 6:1 molar ratio.
- 26 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 24 C, 20 % catalyst amount and 6:1 molar ratio.
- 27 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 45 C, 20 % catalyst amount and 6:1 molar ratio.
- 28 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 10 % catalyst amount and 6:1 molar ratio.
- 29 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 9:1 molar ratio.
- 30 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 3:1 molar ratio.
- 31 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 9:1 molar ratio.
- 32 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 0 % catalyst amount and 6:1 molar ratio.



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- 33 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 12:1 molar ratio.
- 34 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 1:1 molar ratio.
- 35 Esterification of oleic acid and ethanol with pretreated Amberlyst 15 wet ion exchange at 60 C, 20 % catalyst amount and 6:1 molar ratio.
- 36 Esterification of oleic acid and ethanol with recovered pretreated Amberlyst 15 wet ion exchange from experiment 35 at 60 C, 20 % catalyst amount and 6:1 molar ratio. (reuse test)
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Norwegian University  
of Life Sciences

Postboks 5003  
NO-1432 Ås, Norway  
+47 67 23 00 00  
[www.nmbu.no](http://www.nmbu.no)