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Production of Biodiesel from Jojoba Oil with Calcium Glyceroxide as Catalyst

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Preface

This thesis is a result of the study of calcium glyceroxide as a catalyst in the production of biodiesel from Jojoba oil and ethanol, under a variety of parameters. The study was conducted at the Norwegian University of Life Sciences, under the Faculty of Science and Technology.

Signature:

Ås, June 2nd, 2017

Martin Liplass Schei

Acknowledgement

My advisor professor Dr. Jorge Mario Marchetti´s help was necessary to complete this thesis. His knowledge and experience with the materials and equipment used in this study was incredibly helpful whenever some obstacle occurred.

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Finally, I would like to thank my family, friends and girlfriend for always supporting me.

Abstract

Mankind must limit its use of fossil fuels to much less than what is used today, because the supply does not replenish itself at a rate close to what we demand. Biodiesel is an energy source that could cover some of this demand. Traditionally edible oils have been used to produce biodiesel, but such oils should be used for food according to Haines and Van Gerpen (Haines & Van Gerpen 2014). Jojoba oil is not a such edible oil, thus it's more suitable for biodiesel production. The catalyst is also important when it comes to biodiesel production. This study investigated biodiesel production from Jojoba oil, ethanol and calcium glyseroxide as a catalyst. Calcinated egg shells were used to produce the catalyst. A higher proportion catalyst gave more biodiesel faster, the same applies to a higher reaction temperature.

Sammendrag

Menneskeheten må slutte med å bruke fossile energikilder i så stor grad som i dag fordi de fossile kildene ikke fornyes raskt nok til å dekke dagens forbruk. Biodiesel er en energikilde som kan dekke en del av denne etterspørselen. Tradisjonelt sett har matoljer vært brukt til å lage biodiesel, men disse burde brukes til mat ifølge Haines og Van Gerpen (Haines & Van Gerpen 2014). Jojoba olje er ikke en slik matolje, og er derfor bedre egnet til biodieselproduksjon. Katalysatoren er også viktig når det kommer til biodieselproduksjon. Denne studien tok for seg biodieselproduksjon fra Jojoba olje og etanol med kalsiumglyseroksid som katalysator. Kalsinert eggeskall ble brukt til å fremstille katalysatoren. Høyere andel katalysator gav mer biodiesel fortere, det samme gjorde høyere temperatur.

Nomenclature

Alc: Alcohol

B100: 100% pure biodiesel.

B2: Biodiesel and fossil diesel in a ratio 2% biodiesel and 98% fossil diesel.

B20: Biodiesel and fossil diesel in a ratio 20% biodiesel and 80% fossil diesel.

Cat: Catalyst.

Conversion: Moles EE/ (moles Oil +moles of EE).

EE: Ethyl ester.

FAEE: Fatty acid ethyl ester/s.

FAME: Fatty acid methyl ester/s.

G: Gram.

GC: Gas Chromatograph

NOK: Norwegian kroner.

H: Hour.

L: Liter.

Lbs: British pound ≈ 454 g.

NMBU: Norwegian university of life science.

RPM: Rotations per minute.

T: Temperature.

Tc: Calcination temperature.

Tr: Reaction temperature.

USD: American dollar.

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1 Introduction

The demand for sustainable fuels such as bioethanol, biogas and biodiesel to replace some, or all fossil fuel consumption, is rising. World energy consumption going to transport is mostly consisting of fossil diesel and gasoline, emitting fossil CO_2 when burned. World oil consumption was around 35 billion barrels a year, in 2015. This equates to more than 5 trillion L a year, and the consumption in rising (*Oil* 2017). This is a challenge if we are to stay within the two-degree goal of the intergovernmental panel on climate change, IPCC (Kørner 2012). The two-degree goal states that we should try to limit the temperature rise in the lower atmosphere (ground based measurements) to less than two degrees centigrade compared to preindustrial temperatures. This is to minimize the chances that the climate causes harm to ecosystems and mankind.

The utilization of biodiesel (B100) instead of fossil diesel doesn't force much, if any alteration to a normal diesel combustion engine, but the fuel tubes, gaskets and other nonmetallic parts can be corroded and needs to be of certain materials (*Materials compatibility*). Biodiesel can also be blended in small (0-20%) amounts together with the fossil fuel to make diesel powered vehicles use less fossil fuel. This calls for even less alterations of the vehicle as the corroding effect of B100 is greatly reduced at low, and neglectable at very low blends such as B20 and B2 respectably (Biodiesel Handling and Use Guide 2009; *Materials compatibility*). Thus, to use biodiesel as fuel in vehicles can reduce the consumption of fossil fuel by at least 10% compared to using 100% fossil fuel. Just by adding it to conventional fuel and without much change in infrastructure or vehicle design.

Biodiesels energy content is not much different from that of fossil diesel and gasoline. Both the gravimetric and volumetric energy densities are within a few percent of each other, with biodiesel being lower gravimetrically than the fossil equivalents at around 38 MJ/Kg and 35 MJ/L (LTD). Gasoline however have almost the same volumetric energy content as B100 (*Alternative Fuels Data Center – Fuel Properties Comparison* 2014), this is of course dependent on type of gasoline and type of biodiesel, temperature and other parameters that can alter the densities of the fluids. The energy density of B100 is a great advantage compared to fuel cell systems and batteries that have energy densities around one order of magnitude less than that of biodiesel, (*Overview of lithium ion batteries* 2017) (*High density fuel cell systems* 2010) when the storage and fuel cell also is considered. In heavier vehicles that require a lot of

energy, this is a particularly important point since the fuel storage system could compose a large amount of the available cargo space and/or capacity. When considering the vehicles capability of transporting goods, biodiesel seems a better choice than other renewables in the form of batteries or fuel cells as they are in 2017.

The fuel vs. food debate (Haines & Van Gerpen 2014) could challenge the sustainability of the fuel and limit the political willingness to implement biofuels. The debate highlights the fact that by using land to produce feedstock for fuel production, less land will be available for food production. This in terms causes less food to be produced, and the food price to increase, possibly causing more hunger. To address the fuel vs. food issue, biodiesel could be made utilizing other fatty acid sources than those normally used as food. Such sources could be waste oil, cellulose, algae or non-edible oils such as Jojoba oil or Jatropha oil. Instead of the more traditional corn, palm oil, sunflower, soy, sugar cane, rapeseed and more (*Biodiesel Fuel Feedstocks* 2017).

Jojoba oil is produced from the Jojoba seed of the Jojoba shrub. The shrub is native to the desserts of north America and can be cultivated on arid land (Wisniak 1987) (Undersander et al. 1990). Jojoba is cultivated mostly in the United States, but also in Israel, South Africa and Mexico, on land not suitable for much else (Sánchez et al. 2016a; Wisniak 1994). This diminishes the pressure on agricultural land to produce fuel. Jojoba oil is not an oil made of triglycerides like most other fats and oils, but instead it's an ester of long-chained alcohols and one fatty acid. The long-chained alcohols in the Jojoba oil, with carbon chain lengths varying mostly between 20, 22 and 24 (Wisniak 1987) are rare and expensive, so to separate them from the biodiesel can be economically beneficial (Sánchez et al. 2016a).

To make biodiesel from Jojoba, or any other oil, one must also have an alcohol and a catalyst or special reactor capable of preforming a reaction at high temperature and or pressure. Jojoba oil is already an ester, but the cold properties are not adequate to meet the biodiesel standards such as EN 14214 (*EN14214 Specification*). So, to improve the cold properties, the alcohols in Jojoba oil can be change with a lighter alcohol, normally methanol or ethanol, to make fatty acid methyl/ethyl esters FAME/FAEE.

There are roughly three possibilities when it comes to catalyst, those are: alkali, acid and enzymatic catalysts. The most popular ones are the alkali catalysts: potassium hydroxide and sodium hydroxide, mostly because they are cheap and readily available. KOH and NaOH have some disadvantages to them when it comes to soap formation and waste (Syakirah Talha & Sulaiman 2016). An interesting alternative is CaO derived from $CaCO_3$ found in chicken egg shell or other bone, shell or limestone. Chicken egg shells are a waste from bakeries, restaurant, chicken production and several other sources, this makes it cheap. In total, there are about 150 000 000 Kg of chicken egg shell waste generated each year in the US (Hecht 1999).

2 Literature review

Jojoba oil is expensive at around 3800 NOK/L or 450 USD/L (*Valutakurs for Amerikanske dollar (USD)* 2017) in February 2017 (*Jojoba oil from Simmondsia chinensis* 2017) for the analytic grade oil, and 12,27 USD/Lbs. or 23,5 USD/L for bulk order (*Golden Jojoba Oil* 2017). The price makes it uneconomical to just produce biodiesel and nothing more since the biodiesel would then cost much more to produce than the market value of around 0,85 USD/L in October 2016 (*Fuel prices* 2016). During biodiesel production from Jojoba oil, valuable long-chained alcohols, mostly of lengths 20, 22 and 24 carbon atoms, but also shorter alcohols are produced (Sánchez et al. 2015) (Wisniak 1987). These alcohols would be the most valuable product, and the market value of some of those could reach 55 USD/g if they are pure (Sánchez et al. 2016a).

Since Jojoba oil is too valuable for biodiesel production as only product, the work on such or similar production is scarce. NMBU have a research group that have conducted multiple experiments based on Jojoba oil (Avhad et al. 2016; Sánchez et al. 2015; Sánchez et al. 2016a; Sánchez et al. 2016b). Their work was again based on earlier work done by Canoira et al. (Canoira et al. 2006), Bouaid et al. (Bouaid et al. 2007) witch both did methanolysis of Jojoba oil. Marcos Sánchez and Mercedes Martínez, which were contributing to NMBUs recent work, was also contributing to a paper by El-Boulifi et al., investigating biorefinery concepts of fatty acid alkyl esters from Jojoba oil (El-Boulifi et al. 2015). El-Boulifi et al. made biodiesel of combining Jojoba oil and four alcohols: ethanol, methanol, 1-butanol and 1-propanol. Some work was also done by M.Y.E. Selim at el. (Selim et al. 2003) and M.S. Radwan at el. (Radwan et al. 1997) around the turn of the century. They investigated the fuels effect on a motor, not focusing on the production of the FAME itself.

Since most of the earlier work on biodiesel production from Jojoba oil was on FAME it was decided to do a closer study on FAEE. Ethanol is to a larger extent than methanol made sustainable and from renewable sources, and both will reach the same equilibrium conversion (Verma et al. 2016), thus ethanol was a better choice for us.

To produce a cheap catalyst for biodiesel production we had to investigate what others had done before us. Work on Jojoba oil and CaO from mussel shells had been done by Avhad

and Marchetti (Avhad et al. 2016; Sánchez et al. 2016a). Kesić et al. did a comprehensive review paper on calcium oxide based catalyst for biodiesel production (Kesić et al. 2016). The review paper included data from at least 49 other papers that exclusively used methanol as alcohol for the biodiesel production, and none used Jojoba oil. With CaO as a catalyst it was registered final conversion of above 98% in some cases, and with calcium glyceroxide the yield was above 90%. This was almost the same as Sánchez at el. achieved with CaO from mussel shells and Jojoba oil (Sánchez et al. 2015).

3 Theory

3.1 Jojoba oil

Jojoba oil is not like most oils. It's not a triglyceride consisting of a glycerol molecule and three fatty acids. Jojoba oil is an ester consisting of a fatty acid and an alcohol bond together by an ester bond. The properties of Jojoba oil, does not make it suitable to be used directly as a fuel although it could be used under certain circumstances since burning it releases energy like any other liquid hydrocarbon based fuel. However, it's wasteful to burn the Jojoba oil as it is since the alcohol part of the oil can be very valuable if extracted and purified (Sánchez et al. 2016a). It's economically beneficial to extract the valuable alcohols and simultaneously improve the cold properties, by replacing them by a light, cheap alcohol like ethanol or methanol. What the Jojoba oil molecule could look like can be seen in Figure 1.

$$H_3C\text{-}[CH_2]_m\text{-}COO\text{-}[CH_2]_n\text{-}CH_3$$
$$m=18,20 \text{ or } 22$$
$$n=17,19 \text{ or } 21$$

Figure 1: Example of simplified Jojoba oil molecule.

In Figure 1, m and n have the values in about 95% of all Jojoba oil molecules. (m) represents the alcohol part of the molecule and n represents the fatty acid part of the molecule. The fatty acid and alcohol part of the Jojoba oil also contain one or more double bonds in about 95% of the molecules. The double bond occurs somewhere within the $[CH_2]_x$ parts of the molecule, often with 9 carbon atoms in the alkyl group on the side of the molecule that's not closest to the ester bond (Wisniak 1987).

3.2 Alcohol

The choice of alcohol was ethanol due to its renewability and production from renewable sources, we use bioethanol if possible. Methanol is more used in biodiesel production than ethanol, because of its lower cost, but the yield in terms of biodiesel is the same (Verma et al. 2016). Methanol is mostly produced from fossil sources and is not renewable like ethanol shown in Figure 2.

$$H_3C\text{-}CH_2OH$$

Figure 2: The structure of an ethanol molecule.

3.2 Catalyst

To break the ester bond in Jojoba oil, the activation energy needs to be overcome. The activation energy is energy the reactants (molecule, or molecules) needs to transform into the products. In our case the ethanol and Jojoba oil needs energy to transform into Jojobyl alcohols and EEs. Some of this energy is only needed temporarily and is released as heat when the products are formed. The rest of the energy goes into chemical energy in the products since the reaction is endothermic. The reactants achieve the activation energy as a result of the probability distribution of heat in the reactor. Some of the molecules in the reactor will at any given time have a greater speed than others and this speed is a measure of heat. The more heat the reactor contains, the higher is the average speed of the molecules in the reactor and the higher is the likelihood that one of the molecules achieves the activation energy.

By adding a catalyst, the activation energy is lowered. The likelihood that one of the molecules in the reactor achieves the activation energy is increased without the need for the same amount of heat that would have been needed if there were no catalyst present.

We choose CaO stabilized in glycerol to form calcium glyceroxide as our heterogenous catalyst. A heterogenous catalyst is easier to extract and reuse than a homogeneous catalyst. The calcium glyceroxide catalyst could be made by calcinating calcium carbonate, making CaO. We got our calcium oxide from egg shells collected at a local bakery and a restaurant. To calcinate the egg shells the temperature needs to be raised to at least 700 ^{o}C for a period of 2 h (Wei & Xu 2009). The calcium carbonate releases carbon dioxide to form calcium oxide when heated sufficiently. The calcium oxide then needs to avoid contact with the air if possible, since contact with the air that contains carbon dioxide and water vapor deactivates the catalyst. The carbon dioxide and calcium oxide forms calcium carbonate if the calcium oxide is left in the ambient air (Sánchez et al. 2015). Calcium oxide and water forms $Ca(OH)_2$ and this is not a good catalyst for the intended reaction to produce biodiesel. The calcium glyceroxide catalyst was put in the reactor with the Jojoba oil. The oil keeps the catalyst and air apart and the catalyst should be stable in the oil for many weeks, ready to initiate the reaction whenever the alcohol is added to the mix.

3.3 Esters

Both Jojoba oil and biodiesel are esters. Commercial biodiesel is often FAME or FAEE, but could also be other, heavier esters, made from heavier alcohols. However, the esters must conform to the biodiesel standards to be sold as biodiesel. An ester bond is shown in Figure 3.

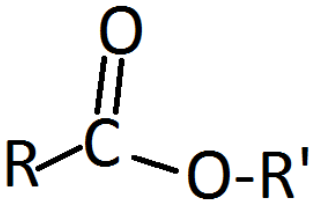

Figure 3: An ester, where R is a hydrogen atom, alkyl or aryl group. R' is an alkyl or aryl group. In the case of FAEE, R is CH_3.

4 Materials and equipment

4.1 Materials

Egg shells collected from “Jo Anitas” and “Vitenparken”.

Glycerol from Sigma Aldrich.

Waste fish oil from Akva Ren company from Tromsø, Norway.

Oleic acid from Sigma Aldrich.

Jojoba oil from Simmondsia chinensis in analytic specification of DAC produced by Sigma Aldrich.

Ethanol without fat and water produced by Kemetyl Norge AS.

Tetradecane from Sigma Aldrich.

Pyridine from Sigma Aldrich.

All chemical reagents were used as purchased with no further purification.

4.2 Equipment

Two mortars, one ceramic to examine egg shells, and one to calcinate and pulverize egg shells.

Calcination furnace (Narbetherm P300, Germany).
Ceramic crucibles, to calcinate egg shell. Purchased from VWR.

Scales, accuracy $1/10^{th}$ of a g and $1/1000^{th}$ of a g, dependent on demand. (A&D Instruments LTD.EK-2000i and GR-202-EC respectively. India).

Blender, 800 w max setting and 5 different power modes. Only the lowest used. (Braun 4186, Czech Republic).

Syringes to transfer the materials to and from jars and vials.

Magnet, plastic coated magnetic stirrer to mix the reactor content.

Sample jar, lidded 5 mL glass sample jars.

Vials, 1,5 mL.

4.2.1 Reactor

Magnetic field generator, VWR advanced VMS-C10, to rotate the magnetic stirrer.

Base of reactor, 500 mL Quark.

Three necked reactor top, 500 mL Quark.

Rubber tubes to circulate the water.

Water heater and circulation pump, VWR International, Article number: 462-0212, Serial number: 1A12C1005, USA.

Cooling column, Pyrex Quickfit CX5/23/CS 24/29.

Cold water supply.

Plug to minimize evaporation.

Syringe with needle.

Thermometer.

4.2.2 GC

Description of the system and procedure.

The GC used is a Bruker Sion 356 with FID detector. The Injector temperature is at 320 ^{o}C and the detector is at 350 ^{o}C. The carrier flow is 1 mL/minute of Hydrogen which is also use for the detector flame in combinations with pure air filter by the zero air equipment. The oven temperature profile starts at 80 ^{o}C and then increases at a rate of 10 ^{o}C/minute until it reaches 260 ^{o}C and stays there for 15 minutes before cooling down.

The sample is injected in a split/splitless injection type for 1 minutes with a split ratio of 10:1. The sample injected is 1 µL of solution.

The detection is done via a PC software from the same Company as the GC, and the integration is done manually within the software.

The column used is an Agilent Technologies J&W Scientific that is 15 m long, 0,32 mm of diameter and 0,1 µm of fil, thickness.

The system is calibrated using the internal standard method with a response factor. Any sample preparation is done by taking 0,0050 g of sample and 0,0050 g of Tetradecane (internal standard) and add 1 ml of pyridine to the solution.

As mentioned, the system use a response factor, and this is a value that needs to be obtained for each component based on pure chemicals. The way to obtained is by using the following formula

$$f_{r_j} = \frac{m_{is}}{m_j}\frac{A_j}{A_{is}} \quad (1)$$

Where:

m_j = mass or concentration of the standard component.

m_{is} = mass or concentration of the internal standard component.

A_j = area of the standard component.

A_{is} = area of the internal standard component.

Based on those pre-obtained values is that the % of each component can be obtained using the following formula.

$$\mathrm{Pr}_x = \frac{m_{is}}{m}\frac{A_x}{A_{is}}\frac{1}{f_{r_x}} * 100 \quad (2)$$

Where.

Pr_x = weight percentage of the component X presented in the unknown sample.

m = mass or concentration of the unknown sample.

m_{is} = mass or concentration of the internal standard.

A_x = registered area of component X in the sample.

A_{is} = registered area of internal standard component.

f_{r_x} = response factor for component X.

The response factors used in this work can be seen with their standard deviation in the following table.

Table 1: The response factors and their standard deviation.

Component	Response Factor	Standard deviation
Jojobyl alcohols	0,9138	0,00817
Ethyl Esters	0,823	0,00826
Jojoba Oil	0,6313	0,00665

5 Methods

5.1 Treatment of egg shells

To do all the reactions planed we had to collect a substantial amount of egg shells. A local restaurant/bakery collected most of the egg shells needed and kept the eggs in an open plastic bucket the week prior to us coming to pick it up.

The first load of egg shells was collected and put in a plastic box with about 1 L of cold tap water. The shells soaked in water for some minutes while hand stirring. Then the egg shells were crushed by hand to pieces smaller than 5 mm diameter. The water was poured out of the box and the box got refilled with tap water about 5 times, this caused much of the solidified egg white and yolk to be washed out. About half of the protein membrane also got separated and washed out at this stage.

When the pieces of egg shell got to be smaller than about 5 mm in diameter they got put in a blender. In total about 150 g of egg shell and 1 L of cold tap water was put in the blender at once. The blender was turned on in 10 seconds intervals and the water was changed to new tap water between each run. This blender procedure was repeated about 10 times until the water was containing little membrane and other impurities as shown in Figure 4.

Figure 4: The blender used for cleaning the egg shells.

The size of the pieces was now down to less than 3mm in diameter. Then some of the blended egg shells got crushed further in a mortar to see if it was possible to remove more of the membrane this way, but this was not very successful. The process with the mortar caused the egg shells to become a fine powder. Lots of the powder was so fine that it followed the water when we did the previous process of adding water and pouring off the top water. This caused us to lose a considerable amount of egg shells. The crushing by mortar also took a lot of time, around 1 minute/g.

The eggs that had the rounds in the blender in Figure 4, was then boiled in tap water to see if more of the protein membrane would come off, but this did not help in a significant way. The shells were then put in a frying pan to dry at around 200 ^{o}C. The blender was tried again for 20 seconds and this caused some of the membrane to come loose, this could just be from blending, and the heat treatment might not help at all. The egg shells were then put back in the frying pan and heated to such high temperature that it got brown. The temperature probably reached 300 ^{o}C, and the brown color was probably due to some oil/fat spilled on the eggs in the restaurant or from the frying pan itself. This made the first batch of egg shell, herby denoted as batch 1.

To study the possibilities of further cleaning, membrane removing and increasing surface area some g of batch 1 was put in a porcelain mortar and crushed to a fine powder. The crushing by mortar takes a lot of time, around 1 minute/g to form a nice powder that did not seem to become much finer upon further crushing. One can of course use whatever time required to form some other wanted powder size, but to the naked eye 1 minute/g seemed sufficient. The egg shell with the final mortar crushing, herby denoted as batch 1A was poured into a small lidded plastic box.

Some more of batch 1 was put in the mortar with some tap water to see if this aided the crushing, but this made little to no difference. The water got filled with fine powdered egg shell quite fast and made it hard to impossible to see what one were crushing. After crushing it for 3-4 minutes the water with crushed egg shell from batch 1, herby denoted as batch 1B was put in a transparent jar to study the behavior of the fine powder. The treatment batch 1B had been given was not helping protein membrane removal. It was impossible by eye to see if the fine powder was calcium carbonate, protein membrane or a mixture of both either stuck together or by themselves. Doing the same procedure as before with adding water and shaking or stirring and pouring the top water off would cause a lot of the egg shell to be lost. It’s also unlikely that the remaining egg shell would contain a much higher calcium carbonate to membrane ratio.

The next batch of egg was much larger at close to 3 Kg. With the knowledge from the tests on batch 1, 1A and 1B it was decided to only perform the blender procedure. The egg shells were collected over the course of one week. After the gathering, they were put in the same plastic bath as batch 1 with some cold tap water and lightly hand crushed to better fit the blender. Then the egg shells were put in the blender at about 200 g portions and one L of cold tap water and blended at a low power setting for 1 minute. The blended egg shells were put back in the now cleaned plastic bath and was stirred together with water and the top water was poured off about 10-15 times. When the water no longer had much protein membrane in it the crushed egg shells were put in a large dark plastic jar shown in Figure 5.

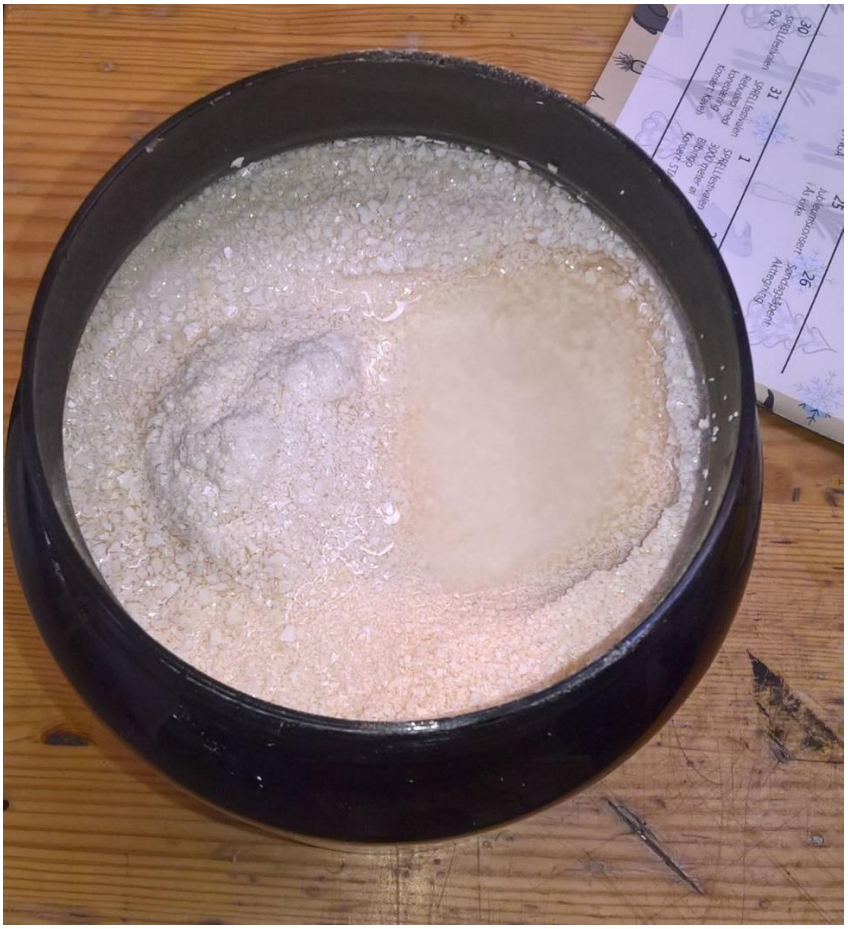

Figure 5: Batch 2 in the black plastic jar.

This batch was called batch 2 and were kept in the jar without being dried first, so the egg shell particles were always covered in water.

The final batch, batch 3 was given the exact same treatment as batch 2 but in addition it was dried in the oven at 140 ºC for 95 minutes to remove moisture. Then it was stored in an air tight plastic container shown in Figure 6.

Figure 6: The large yellow container contains batch 3 and the smaller container on the right contains batch 1.

Batch 3 was weighed at 4 stages, untreated, lightly crushed and wet, crushed in blender and wet and after drying in the oven. The weights and weight loss are represented in Table 1.

Table 2: The weight of batch 3 at different stages of preparation, and the total weight loss in percent due to the treatment.

Weight untreated egg shells.	740 g
Weight of wet egg shells lightly crushed by hand.	1038 g
Weight of wet egg shells crushed in blender for one minute.	855 g
Weight of egg shells after drying in oven at 140 ºC for 95 minutes.	650 g
Weight loss in % from untreated to dried.	12,2

The material washed away in the blender was mostly protein membrane from the inside of the shells, egg white and possibly some flour or similar bakery products. Table 2 shows approximately 1/8 of the collected egg shells by weight seems to be possible unwanted light

substances that can be washed away. And about 1/4 of the crushed wet shells are water. Some additional Kg of egg shells (Batch 4 pictured in Figure 7) were collected, stored in a plastic bag and given no further treatment until use.

Figure 7: Egg shells as collected from the restaurant kept in a plastic bag and used as batch 4 and 5, rinsed lightly in tap water, and done nothing but lightly crush to fit mortar and crucibles, respectively.

To see if crushing made a difference to the waters ability to sticking to the surface of the egg shell, some of batch 4 were lightly rinsed in tap water and put in a drying locker at 50 ^{o}C for more than 50 h. The data are represented in Table 3.

Table 3: The data from rinsing egg shells from batch 4.

Weight of rinsed wet egg shells	28,26g
Weight of rinsed dried egg shells	23,61g
Weight loss in % during drying	16,5

As can be seen in Table 3, the water content of wet rinsed egg shells seems to be about 1/6 of the total weight, this is a lot less than the 1/4 weight loss in the egg shells that had been given a minute in the blender (batch 3) as can be seen in Table 2. The larger water content of crushed egg shells is probably caused by the much larger surface area in the crushed shells, that water can stick to.

5.1.1 Calcination

To be able to use egg shells containing $CaCO_3$ as a successful catalyst for biodiesel production it must be activate by calcinating the egg shells.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

Calcination of calcium carbonate were CO2 is released to form calcium oxide

The calcination occurs above 700 ^oC and needs at least 2 h to be completed (Wei & Xu 2009). However, this requires a lot of surface area, as we experienced. When we did calcination at 700 ^oC for 5 h the results were, that not all of the egg shells were calcinated and there were still some carbon left on the egg shells, as can be seen in Figure 8.

Figure 8: On the left are egg shells from batch 5 that are completely untreated in the mortar and lightly crushed in the crucibles to better fit. On the right are egg shells calcinated at 700 ^oC for 5 h. The black parts of the egg shells are believed to be carbon.

The calcinated egg shells are composed of about 98% CaO, 1% MgO and 1% other substances like Na_2O, P_2O_5, SO_3, and SrO (Buasri et al. 2013). The weight loss during the calcination process of the egg shells were measured to understand what was going on. This was done to estimate how much egg shells were needed to get the required amount of catalyst for the reactions. The data are represented in Table 4.

Table 4: The data from calcination of wet egg shells from batch 4.

Weight of rinsed wet egg shells from Batch 4	35,85g
Weight after calcination	14,63g
Weight loss in % during calcination	59,2

As can be seen from Table 4 the weight loss is roughly 60%. The weight loss was also investigated on batch 2 this resulted in roughly the same result. The weight went from 49,8 g to 16,9 g thus 2/3 of the mass was lost. This was a little bit more than from batch 4 and can be traced back to the higher water content in batch 2, presented in Table 3 and Table 4. This means it should be at least 3 times the weight of calcinated egg shells needed worth of wet egg shells for calcination to be certain of enough catalyst. The results of calcination at 800 ^{o}C for 5 h in one mortar, and final crushing can be seen in Figure 9. The need for that much more egg shells than catalyst caused a problem since we, at first, only had one ceramic mortar to calcinate the egg shells in, depicted in Figure 10. The egg shells in the bottom of the mortar was not calcinating properly even after 5 h at 800 ^{o}C, and we had to get more crucibles to calcinate more egg shell at the same time.

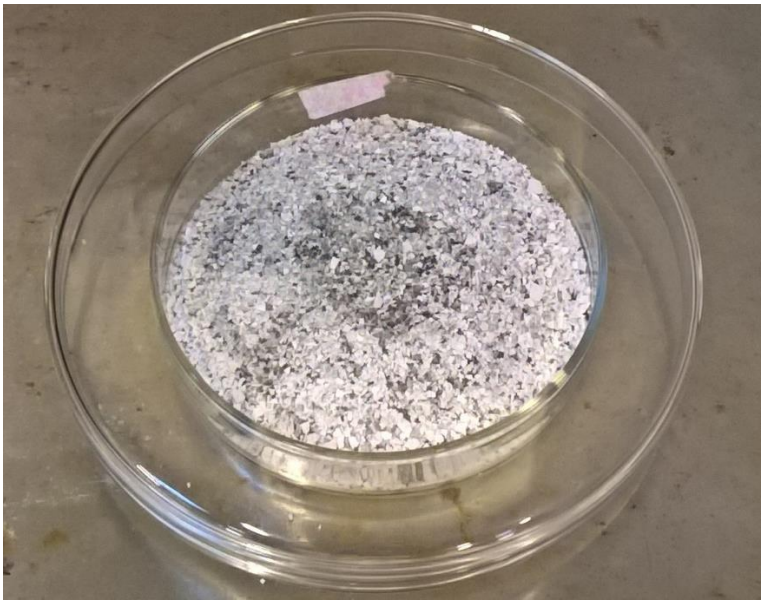

Figure 9: Egg shells from a batch of about 60 g calcinated at 800 ^{o}C for 5 h in one mortar. After calcination, the egg shells were crushed and transferred to a petri dish for transport to the reactor.

When we got the extra surface area that the additional crucibles offered the problem was solved and we could calcinate more than 100 g at once at 800 ^{o}C and 5 h, pictured in Figure 10.

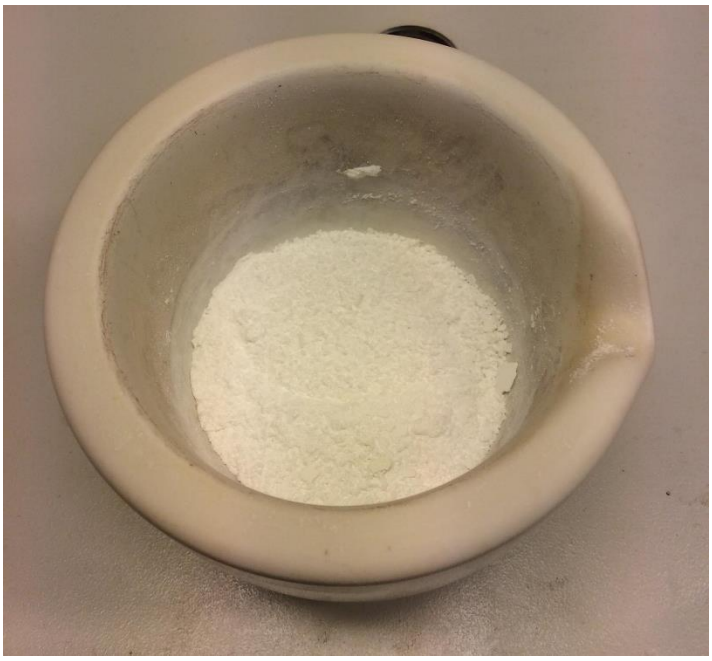

Figure 10: Egg shells calcinated at 800 ^{o}C for 5 h and then crushed in the mortar depicted.

In the middle of our experiments we got complaints on the smell coming from the calcinating egg shells. The leftover proteins and other organic substances emitted bad smell when heated to about 300 ^{o}C and above. The solution was to do calcination during night when no one was around. This in terms gave the oven less time to cool down before usage of the catalyst. The temperature was as high as 270 ^{o}C when it was time for catalyst preparation before reaction 8 and 9. On reaction 8 there was no noticeable difference between the catalyst prepared and earlier catalyst preparation. However, during preparation of catalyst for reaction 9 the increased catalyst amount and resulting increased heat content made some of the glycerol evaporate during transport from the calcination oven to the reactor. This was noticed as condensed glycerol on the lid of the petri dish that contained the catalyst. The glycerol also went easier down into the calcinated egg shells, within a few seconds because of the lower viscosity due to the much hotter calcinated egg shells than earlier. This was a challenge on all the reactions since the glycerol percolated trough the calcinated egg shells and stuck to the petri dish together with some calcinated egg shells if left for more than a few minutes, as pictured in Figure 11.

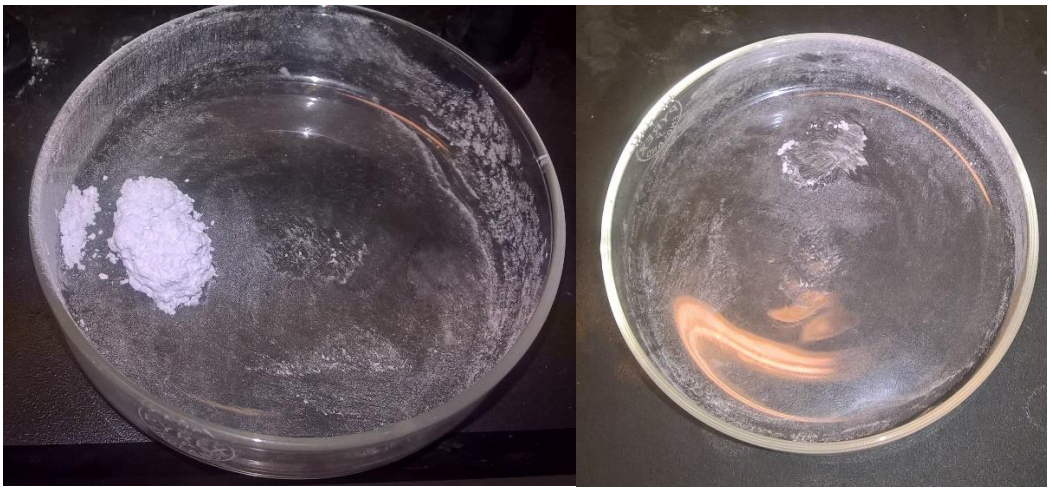

Figure 11: The petri dish used to transport the catalyst, and some catalyst stuck to the bottom caused by glycerol. The petri dish after most of the stuck catalyst was removed and put in the reactor on the right.

The stuck catalyst did not go into the reactor and did not participate in the reaction. The amount of stuck catalyst was calculated by weighting the petri dish after emptying the content into the reactor, and after cleaning the petri disc. The result was that 0,13 g, 0,06 g and 0,22 g of catalyst got stuck to the petri dish during reaction 10, 11 and 12 respectively. Reaction 12 had the second most catalyst stuck, reaction 5 had about 1/3-1/2 a g stuck witch was the most, and reaction 11 was a typical amount at less than 0,1 g. It was expected that proportionally more of the glycerol than of the calcinated egg shells got stuck since the glycerol was the main cause.

A small amount of calcinated egg shells were set aside to see if anything happened to it in contact with the air. The results can be seen in Figure 12.

Figure 12: The calcinated egg shells just after calcination on the top left, after one week on the top right, after two weeks on the bottom left and after 3 weeks in the bottom right. The calcinated egg shells were kept in a locker in low room temperature at around 17 ºC.

The calcinated egg shells expanded, probably because of water vapor or carbon dioxide in the air. This would likely have caused the calcinated egg shells to form calcium carbonate or calcium hydroxide. There might not be much calcium oxide left, and the calcinated egg shells stored for several weeks as in Figure 12, will probably not be a good catalyst to make biodiesel.

5.1.2 Preparation of catalyst

After calcination of the egg shells, the calcinated egg shells were all put in the mortar first used for calcination. After they were put in the mortar, they got crushed for a few seconds to make it into a finer powder with increased surface area as shown in Figure 10. The required amount of it was weighted and transferred to a petri dish, then 10% by weight of the calcinated egg shells worth of glycerol was also added to the petri dish, and another larger petri dish was used as a lid to minimize the likelihood for contamination. The catalyst was then transported from the room with the oven, depicted in Figure 13 to the reaction lab, in the petri dish shown in Figure 11.

Figure 13: The oven used to calcinate the egg shells and the mortar and crucibles to contain the egg shells during calcination.

Meanwhile the oil was warming up in a beaker with temperate water to liquefy it from its semi solid state. The oil was then transferred to the reactor to be heated by the circulation pump with hot water. The aim was 65 ^{o}C before the calcinated egg shells and glycerol was added, but to save some time we sometimes added the CaO and glycerol at a marginally lower temperature. The temperature of the circulating water and reactor was monitored with 10 minute intervals and adjusted if it was unsatisfying, meaning that temperatures were kept within a few tenths of a degree when close to temperature equilibrium. This was the case for all the time using the water heater with the exceptions mentioned when they apply. The oil only took about 20 minutes to reach 60 ^{o}C from refrigerator temperature (0-4 ^{o}C), so the effect on the catalyst of adding the oil before 65 ^{o}C was reached should be minimal. Then the petri dish was emptied into the reactor where the oil and magnetic stirrer already were present and rotating at 200 rpm. The stirrer kept mixing and preparing the catalyst in the oil and for 1 h, then the reaction was started by adding ethanol and adjusting the water heater temperature if needed.

5.2 Reaction/method

5.2.1 The first reaction

The calcination of egg shells was first performed on some of the egg shells from batch 4. The egg shells were rinsed in tap water, put in a mortar and lightly crushed to make a greater surface area. The shells were then put in the oven and the oven set at a heating rate of 5 ^{o}C/minute until it reached 800 ^{o}C. Then it stayed at 800 ^{o}C for 5 h and used another 10 h to reach close to 200 ^{o}C. The calcinated egg shells were taken from the oven and weighted in a petri dish. Then 10 % by weight of glycerol was added to the calcinated egg shells, and the mixture was mixed with some waste fish oil in the reactor at 200 rpm and 65 ^{o}C. Some stirring issues was occurring at 20 minutes into the catalyst preparation and they got worse as time went by. The magnetic stirrer would not spin properly and the issue was suspected to be caused by soap formation in the reactor. To test this hypothesis some more of the calcinated egg shells were mixed with glycerol and put in a separate reactor with some oleic acid to see if this formed soap. The results were a lot of soap formation, so a solution had to be found to this problem. The solution became to replace the waste fish oil with Jojoba oil.

5.2.2 The second reaction

The second reaction (reaction 1 with Jojoba oil) was performed with 84,3 g of Jojoba oil, 54,0 g of ethanol, and 1,70 g of glycerol and 16,88 g of calcinated eggshell from batch 4 to form the catalyst. The calcination took place at 800 ^{o}C for 5 h and took about 10 more h to cool down to approximately 200 ^{o}C. After the calcination was done, the calcinated eggshells and glycerol was mixed in the Jojoba oil at 200 rpm for one h and 65 ^{o}C in the reactor. Since it was decided to do the reaction for a full 12 h it had to be done on two consecutive days. 12 h was chosen based of the data from earlier reactions done by Avhad (Avhad et al. 2016). The other parameters were chosen based on work done by Sánchez (Sánchez et al. 2015; Sánchez et al. 2016a; Sánchez et al. 2016b). The parameters used for all the experiments, except the one with waste salmon oil and oleic acid, are listed in Table 5 underneath.

Table 5: The different parameters chosen for all experiments.

Reaction temperature	55 ^{o}C, 65 ^{o}C, 75 ^{o}C
Calcination temperature	700 ^{o}C, 800 ^{o}C, 900 ^{o}C
Calcinated egg shell amount	16,87 g ± 1/3 by weight
Alcohol to oil molar ratio	6:1, 9:1, 12:1

It was also decided that 100 mL=86,2 g of Jojoba oil would be sufficient, and that for the first reaction with Jojoba oil the parameters in the middle of the range in Table 5 would be chosen. The parameters chosen gives a reaction temperature of 65 ^{o}C, calcination temperature of 800 ^{o}C, 12% catalyst of combined oil and alcohol weight (16,87 g) and a molar ratio of 9:1 of alcohol to oil.

The first day 6 h of reaction took place. The alcohol was added at room temperature so the temperature in the reactor dropped when it was added, but not for long. Within 5-10 minutes the temperature was back at the preset temperature. The clock was started at the same time the alcohol was added. This time is denoted as t=0 meaning 0 minutes have passed since the alcohol was added and the reaction started. Samples were taken at t=0, just before adding alcohol and just after, and then every 5 minutes until t=20.

5.2.3 Sample taking

The procedure of taking a sample was performed as follows: the magnetic stirrer was turned off and the sample was extracted using the syringe. As soon as the syringe had close to half a mL of sample in it, the magnetic stirrer was turned back on, the syringe was disconnected from the needle and the content of the syringe transferred to a labeled 5 mL glass sample jar, as shown in Figure 14.

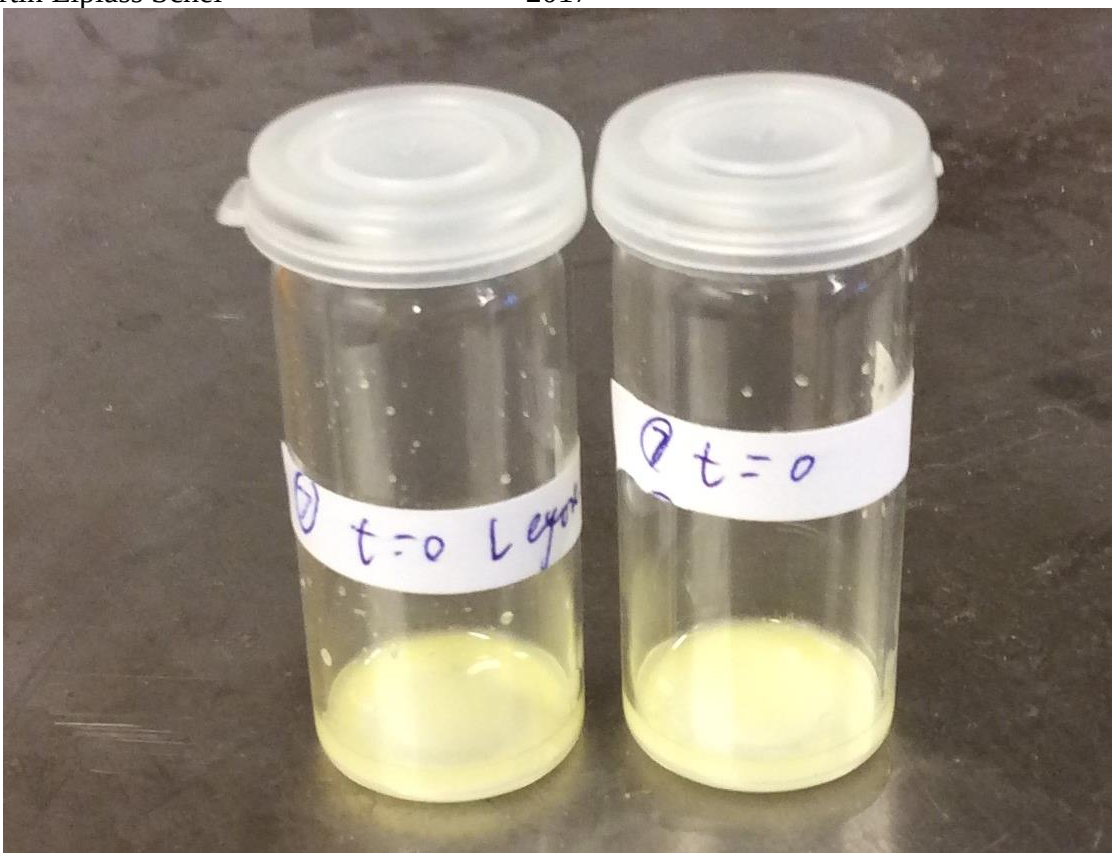

Figure 14: Two labeled sample jars from reaction 7 with lids and content from the reactor taken just before and just after the alcohol was added to the reactor.

The syringe was then filled with air and connected to the needle. Then we pressed some of the air through the needle. The 5 mL jar with the sample was lidded and set aside, as pictured in Figure 14. When the next sample was taken the rest of the air in the syringe was pressed through the needle to remove any potential plug or material that had not been in the reactor since the last sample was taken. This was to ensure a sample as representative as possible of the content of the reactor at the time of sample taking. Because the first samples were taken at short intervals the samples were not put in the refrigerator immediately after extraction, but at about 1 h intervals the samples were put in the refrigerator to stop the reaction and store them for later analysis. The samples cooled down to room temperature within only few minutes because of their small size, so the reaction should not have continued for many minutes after a sample was taken.

After the first 20 minutes of the reaction samples were taken every 10 minutes until 1 h had passed (t=60). From t=60 to t=180 samples were taken every 0,5 h and after 3 h (t=180) samples were taken every h. The last sample of day 1 was at t=360, and denoted as t=360 day 1 of the cut off time. The water circulation pump shown in Figure 15, that heated the reactor to

65 ^{o}C and the magnetic stirrer was turned off, but the water to the cooling column was kept running another h. The cooling water was kept running to avoid the alcohol or other reactor content to escape the reactor shown in Figure 15. The reaction could have continued even after the circulation pump with hot water was turned off. A fresh sample was therefore taken before the water heater and circulation pump was turned back on again the next day (day 2).

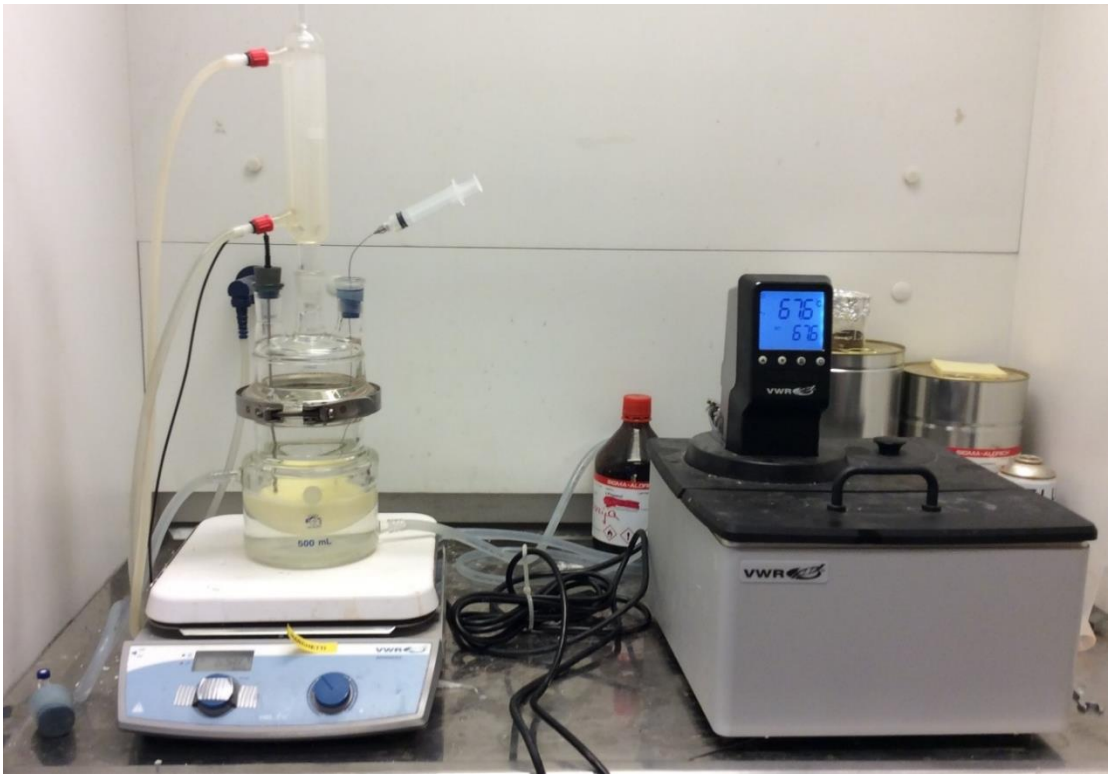

Figure 15: The reactor with cooling column, syringe, magnetic stirrer to the left and the circulation pump and heater to the right.

The temperature in the room was 20 ^{o}C, the same as in the reactor, when the heater and circulation pump were started the second day. The first sample taken the second day was denoted t=360 day 2, and it would tell us if indeed the reaction continued after we turned the stirrer and circulation pump off. It was also expected that the reaction would be slow the first time of day 2 because the reactor was not at 65 ^{o}C until about 30±10 minutes had gone of day 2 (380<t<400). The possible continued reaction after the heater was turned on day 1 would probably to some extent be balanced by the expected slow start on day 2, so in total. When t=720 the result should not be much different from what would have been if the reaction was carried out in one day. New samples were then taken every h of day 2 until the total of 12 h

had passed and t=720. Then the reactor was cleaned with paper towels and ethanol to remove what was left in it, and it was ready to do a new reaction the next day.

5.2.4 Later reactions

The later reactions were carried out in the same manner as reaction two, with the exceptions that the cut of time of the reactions and some of the reaction parameters listed in Table 5 was changed. When the set catalyst preparation temperature was different from the set reaction temperature, the water heater was adjusted in advance of the adding of alcohol. When reaction temperature was 55 ^{o}C the water heater was turned down about 10 minutes before adding the alcohol because of the high heat capacity of water it took some time to cool down. Adding the alcohol lowered the temperature more than enough but the hot water reheated the reactor and content to just above 60 ^{o}C again even though 1 L of cold water was added to the water tank just before adding the alcohol. The temperature was to high (above the intended 55 ^{o}C) the first 25 minutes of reaction 12. When reaction temperature was set at 75 ^{o}C, the start of the reaction was at a too low temperature, since catalyst preparation was at 65 ^{o}C. However, the reactor reached the required temperature faster since heat could be added to the circulating water at a higher rate than the water could emit heat to the environment at reaction temperatures of 75 ^{o}C and 55 ^{o}C respectively. In the high Tr reaction, the temperature got within one degree of 75 ^{o}C within 10 minutes after adding the alcohol.

Because we did 12 h reactions the cut off time was also varying, but samples were taken before the reactor was turned on again the second day. Since the temperature difference between the surroundings and the required temperature in the reactor was varying with some of the experiments. The time to reach the preset reactor temperature on day 2 was varying, but by less than 10 minutes from that of reaction 2.

5.3 Sample storage

The samples were stored in a refrigerator shown in Figure 16 at 0-4 ^{o}C until analysis to minimize reaction taking place between the time of sample taking and the time of analysis. However, some reaction has taken place.

Figure 16: The samples stored in cardboard boxes in the refrigerator.

When we analyzed the samples being in the refrigerator the longest they showed little consistency and the conversion was occasionally higher in a sample taken earlier than one taken later in the reaction. This was the case with samples from reaction 1,3 and 4, that was prepared to investigate pretreatment of the catalyst. All the samples with very high final conversion in the 80-90% range, had been in the fridge for almost 3 months, as the GC was out of order. The conversion was also much higher than the expected in general. It was decided to do an additional reaction with the same content and in the same manner as one of the earlier reactions that had suspicious results.

The results were not consistent with previous data, and thus implied that, in fact there was some reaction taking place between the earlier samples were taken and the GC analysis were conducted. To be certain that the results from the additional reaction were correct we ran yet another reaction with the same parameters as the second run, and the two latest reactions both gave consistent results. Since some further reaction was expected when the last reaction was prepared it was decided to make some additional samples, shown in Figure 17. These samples were stored for some time in different environments to see the effect on the samples.

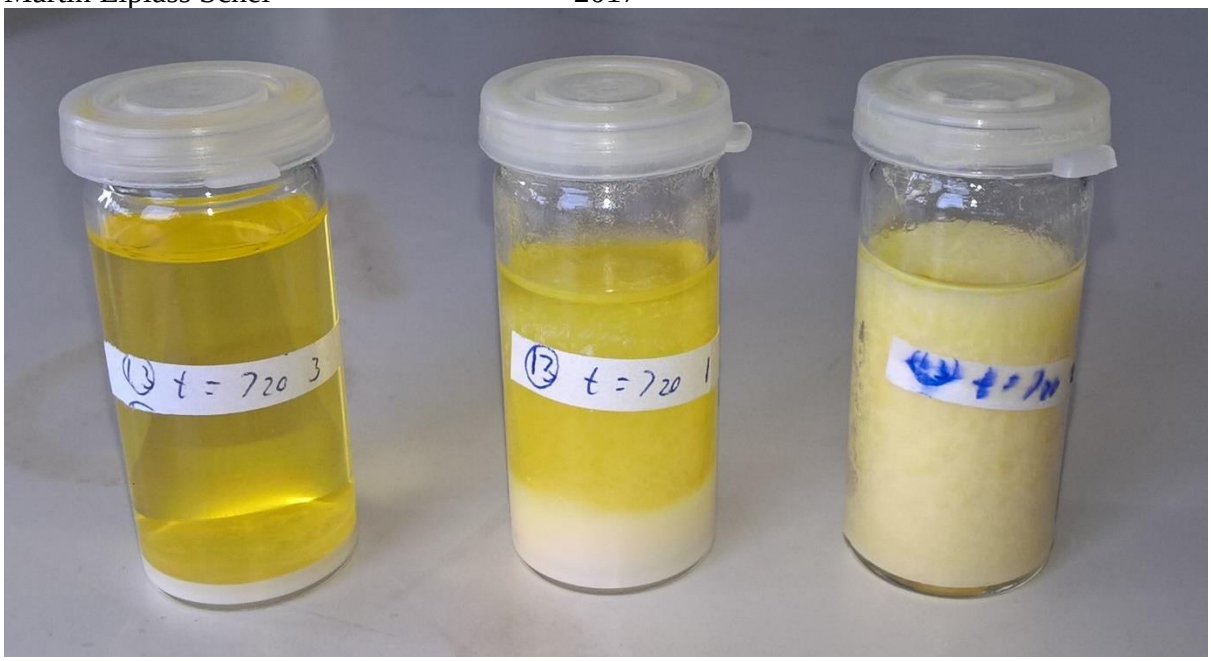

Figure 17: Three of the large samples taken from reaction 13 at t=720 minutes to investigate the effects storage had to the samples. From left to right, the samples are: Stored in the fume hood at room temperature, stored in the fridge at 4 ^{o}C and partially solidified and furthest to the right the sample from the freezer, completely solidified.

The additional samples were extra-large, and taken at t=720 minutes, not to disrupt the reaction or remove too much material from the reactor during reaction. The size was bigger to ensure there was enough sample to prepare many samples for the GC at different times. The additional samples were stored in a fume hood at room temperature (18-25 ^{o}C), the refrigerator that stored all the other samples at 0-4 ^{o}C and a freezer set to about -20 ^{o}C. By analyzing those samples with a week intervals and comparing to each other, the rate at which the reaction continued would be clear to us. The sample stored in the fume hood stayed completely liquid whilst the other two solidified. The samples in the refrigerator only partially solidified. The sample in the freezer was completely solidified as far as the eye could see. To analyze the samples, they were removed from their storage place, and placed in room temperature. The sample from the fridge needed some time to warm up, just like the Jojoba oil when every reaction was started. The sample stored in the freezer needed about 20 minutes to liquefy completely so that the analyzed sample would be representative for the average content of the stored sample.

The extra-large size of the additional samples might make an impact on the reaction rate, by making the possible phase boundaries divided by volume smaller in the extra-large

samples than in the normal ones. To see if this was the case we also analyzed the normal sized sample from this reaction after 2 weeks in the fridge, and the results were very similar to that of the extra-large sample that had been stored in the same manner, only deviating by less than 2% points.

5.4 Reaction content

The content put into the reactor is listed in Table 6, but the content that at any given time participated in the reaction is different.

Table 6: The measured weights of the different components, the molar ratio of alcohol/oil and percentage of glycerol to calcinated egg shells, by weight, and calcinated egg shells to oil by weight. The notes are indicating what was the aim for the reaction, and 2nd indicates that the reaction is the second with those parameters. More information on what the parameters were can be found in Table 5.

Reaction number	Oil (g)	Alcohol (g)	Calcinated egg shells (g)	Molar ratio alc:oil	Glycerol (g)	Glycerol to calcinated egg shell (%)	Calcinated egg shell to oil (%)	Note
1	84,3	54,0	16,88	8,97	1,70	10,07	20,02	Batch 4
3	87,2	54,8	16,83	8,80	1,70	10,10	19,30	Batch 2
4	85,5	55,4	16,90	9,07	1,71	10,12	19,77	Mid range
5	86,4	55,1	16,86	8,93	1,68	9,96	19,51	High Tc
6	53,5	35,0	10,46	9,16	1,07	10,23	19,55	Low Tc
7	86,7	73,8	16,86	11,92	1,68	9,96	19,45	High alcohol
8	87,7	37,3	16,89	5,96	1,70	10,07	19,26	Low alcohol
9	86,3	55,9	22,47	9,07	2,21	9,84	26,04	High catalyst
10	86,7	55,5	11,27	8,96	1,10	9,76	13,00	Low catalyst
11	85,8	55,4	16,90	9,04	1,71	10,12	19,70	High Tr
12	86,4	56,1	16,89	9,09	1,71	10,12	19,55	Low Tr
13	86,7	55,3	16,87	8,93	1,67	9,90	19,46	Mid range 2nd
14	84,3	54,9	16,81	9,12	1,69	10,05	19,94	Mid range 3rd
15	85,2	54,7	16,89	8,99	1,73	10,24	19,82	Low Tr 2nd
16	86,5	55,5	11,10	8,98	1,07	9,64	12,83	Low Cat 2nd
17	82,4	69,8	16,79	11,86	1,70	10,13	20,38	High Alc 2nd
18	84,8	37,8	16,37	6,24	1,62	9,90	19,30	Low Alc 2nd
19	88,8	57,2	22,48	9,02	2,25	10,01	25,32	High Cat 2nd

The volume of oil was reduced in reaction 5, because the catalyst was black like in Figure 8, and we did not want to use an unnecessarily large amount of much oil. Since the calcinated egg shells were black we expected it to not have been fully activated in the furnace.

During catalyst preparation, some of the oil and catalyst could get flung up onto the walls of the reactor as shown in Figure 18.

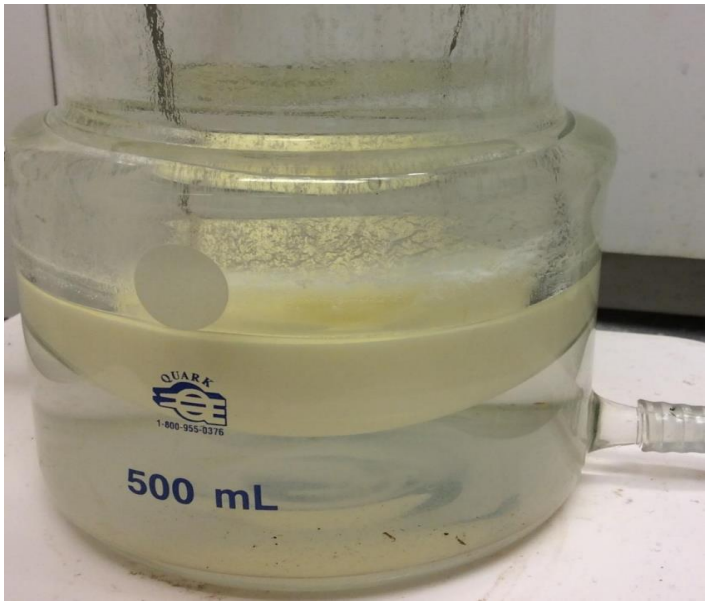

Figure 18: The reactor with content on day 2 of a reaction. The material on the walls on the inside of the reactor is mostly catalyst.

When the samples were taken, the sample could be of different content than the average reactor content since there would not be perfect mixing. The different densities of the content also contributed to it separating when the mixing was stopped. The catalyst sunk to the bottom and was not present in the samples in such a large degree as in the reactor. The alcohol tended to evaporate, so that the gaseous phase of the reactor content was consisting of a high percentage of ethanol vapor. It could have been a few g of ethanol vapor in the total of the close to 3 L volume gaseous phase of the reactor. The alcohol condensed in the condensing column and on the walls of the reactor, and then it poured down into the bottom of the reactor again. This caused the oil and biodiesel that had been flung onto the walls to be washed away easier than the catalyst. So, with time the amount of catalyst not in solution increased to possibly multiple g, as can be seen in Figure 18. In total about 23 samples, like the ones in Figure 14 and 16, were taken during every single reaction. The average size of each sample was about

0,45 g or 0,5 mL (calculated from 3 samples from reaction 10) so that the combined sample size from one reaction could exceed 10 g or 10 mL. Of the total reactor content volume of about 170 mL this is not very much, but it could have made a small difference to the results.

5.5 Gas chromatography

Gas chromatographic analysis of the samples was performed to see what was produced and consumed in the reactions and in what quantities. After the samples were taken from the reactor, the samples from reaction 1-4 were stored in a refrigerator at 0-4 ^{o}C for about 10 weeks. The samples from reaction 5-12, were stored for a week or so, and the rest of the samples were analyzed right away.

5.5.1 Preparation

The procedure of preparing the samples for analysis in the GC were performed as follows. First the samples were removed from the refrigerator and sorted by the reaction they were taken from. Then 1,5 mL vials, depicted in Figure 19 and 20, to run in the GC were labeled according to what the content were going to be.

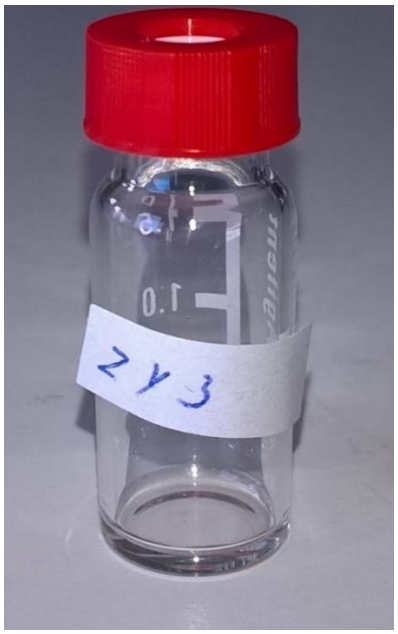

Figure 19: One of the labeled 1,5 mL vials with lid, used to analyze the samples on the GC.

Figure 20: The scale and vial, used to weight the amount of tetradecane and sample that were later analyzed by the GC.

The GC vials were put on a scale reading 0,1 mg at 1 mg accuracy, as shown in Figure 20. One droplet of sample material was transferred using a drop counter, the aim was 0,005 g, but one droplet weighted 0,008-0,011 g most of the time. Then a similar amount of tetradecane was transferred to the same vial, and the weight of both the sample and tetradecane was written in a table. In some of the 10 mL sample jars that had been used to take samples from the reactions there were two phases in the solution. The two phases were more of a norm in the first 0-2 h of reaction. In the later samples, there were much more of a homogeneousness to the sample content. The sample jars with more than one phase visible were shaken to try to mix the content before some of the content was transferred to the vials. In some cases, we made multiple vials from one sample jar containing more than one phase. The aim was to see if there were any difference between the samples phases and what the difference might be. Analysis revealed that the top phase was consisting of mostly ethanol added to the reactor and the bottom phase was mostly the Jojoba oil and catalyst.

When the vials had the tetradecane and sample in them they were set aside with a lid. A total of 20 or so vials were prepared in the same manner from reaction 1-12, and only a few vials at the time from reaction 13 and later, since they were analyzed right away. After preparation, the vials were transferred to a fume hood and 1 mL of pyridine was added to each vial. The vials were then moved to the GC, shown in Figure 21, given a shake to mix the content of each vial, and put in the GC together with the data required to distinguish the vials later. It was decided to name the samples so that the last sample of one day, for instance the t=360 day1 sample would be named just 360. The first sample of day two would then be named 362 and plotted at t=362. This to make them appear at slightly different places in the plots and to quickly be able to distinguish them.

Figure 21: The GC used to analyze the samples.

The first vials, made to test if the GC was operating like we wanted to, were prepared and tested two months in advance of the others. This was also done to see if indeed we had made FAEE in our experiments. Due to some misunderstandings, the first of the vials analyzed after the two months had passed, was performed with 0,05 g instead of 0,005 g as the targeted amount of tetradecane and sample. This caused greater spikes in the graphic results shown in Figure 22, but it wasn't harder to distinguish what was signal from sample and what was unwanted noise.

5.5.2 Running the Gas chromatograph

To analyze samples from reaction 1-12, the GC was set to run with samples being prepared at the same time. The GC analysis method was an AOCS Low Flow Method, using 43 minutes to analyze each sample, so there was plenty of time to make new samples before the GC was done analyzing what it already had in queue. When there were some results ready, the graphics of a late sample (t>400) was compared to an early sample (t=0) and the difference was investigated. This in addition to earlier work done on analysis of FAME from Jojoba, made it clear what was the spikes from the different components. The software of the computer linked

to the GC did the integration of the area of the spikes, shown in Figure 22 and selected by us and we put that results into an excel sheet to calculate the conversion from Jojoba oil to FAEE.

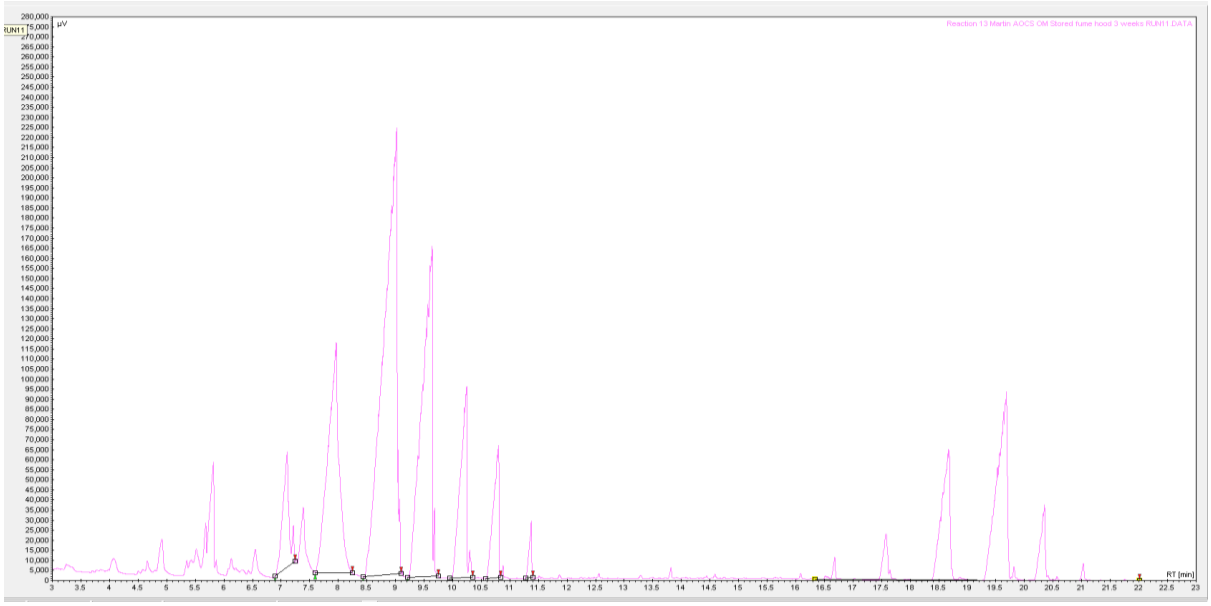

Figure 22: The data output from the GC analysis. Time in minutes is on the x-axis and voltage of the signal in microvolts is on the y-axis. The spikes to the right, at around 20 minutes are a result of the different esters in the oil. The spikes to the left, at 6,7-11,5 minutes, are EE, Jojobyl alcohols and some impurities.

5.5.3 Error in GC

To estimate the total error, we set up a blind test were one of us prepared about 10 samples, and two of us analyzed the samples to see what the difference might be. It turned out to be only a few percent on each spike in the graphics, shown in Figure 22, and thus even less on the final conversion. There was also done multiple analyses on the same sample prepared for the GC. One sample from reaction 12 at t=420 minutes was prepared about 7 different times and then analyzed, this would give us an estimate on the error made by the GC and what was the correct placement of the peak in the graphics in Figure 22. It would also include the error made by weighting the sample and taking sample from the sample jar and transferring it to the vials used for analysis. Because the samples were not perfectly mixed when taking the sample from the sample jar, the content transferred to the vials might differ slightly.

Because we discovered that there was in fact some reaction going on in the fridge, we decided that we had to redo the reactions, and the samples from reaction 13 to 19 were analyzed as fast as possible after the samples were taken.

6 Results

6.1 First results

The first samples analyzed by the GC was samples from reactions that had taken place around one week in advance of the analysis. At first the results looked quite nice, but there was unexpectedly much fluctuation in the conversion in samples from one specific reaction. As can be seen in Figure 23, there was some of the results that clearly did not fit in with what is to be expected. The expected being that the conversion increases with time at a somewhat steady rate.

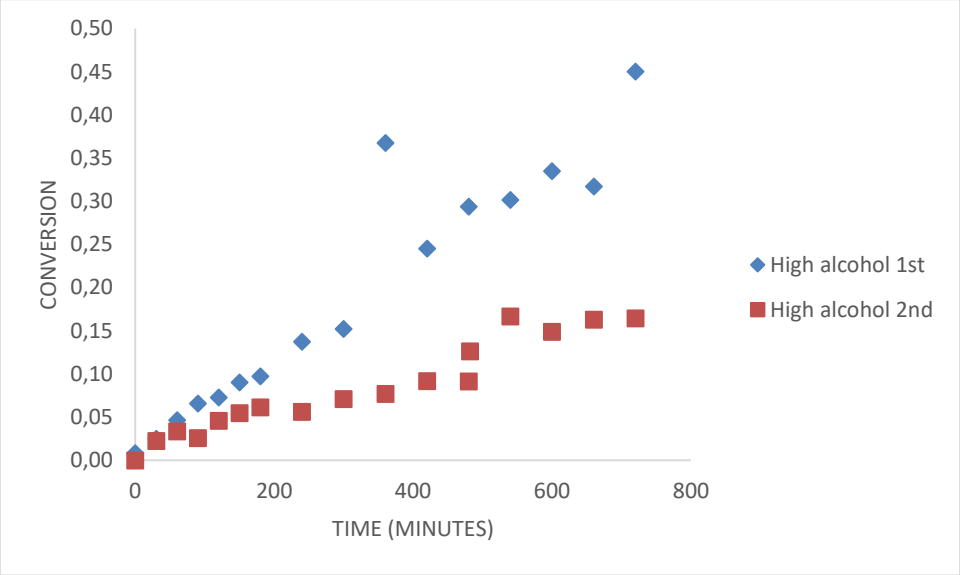

Figure 23: The results from the two reactions with high alcohol amount. Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken minutes on the x-axis. High alcohol 1st (reaction 7) had been stored in the fridge for about one week upon analysis. High alcohol 2nd (reaction 17) were analyzed right away.

The results from the samples t=480 and 482 in High alcohol 2nd, are a bit apart in conversion, implying that some reaction took place during the night. The sample at t=540 from the same reaction is also higher than what would give the better linear fit, but that might just be some error at some point from reaction to plot.

6.2 Effects of pretreatment

Reaction 1,3 and 4 was done about 2-3 months in advance of their respective analyses. This caused the results from those reactions to be fluctuating a lot more than what was already happening in the results that had been in the fridge about one week. The inconsistency of the results from reaction 1,3 and 4 can be seen in Figure 24.

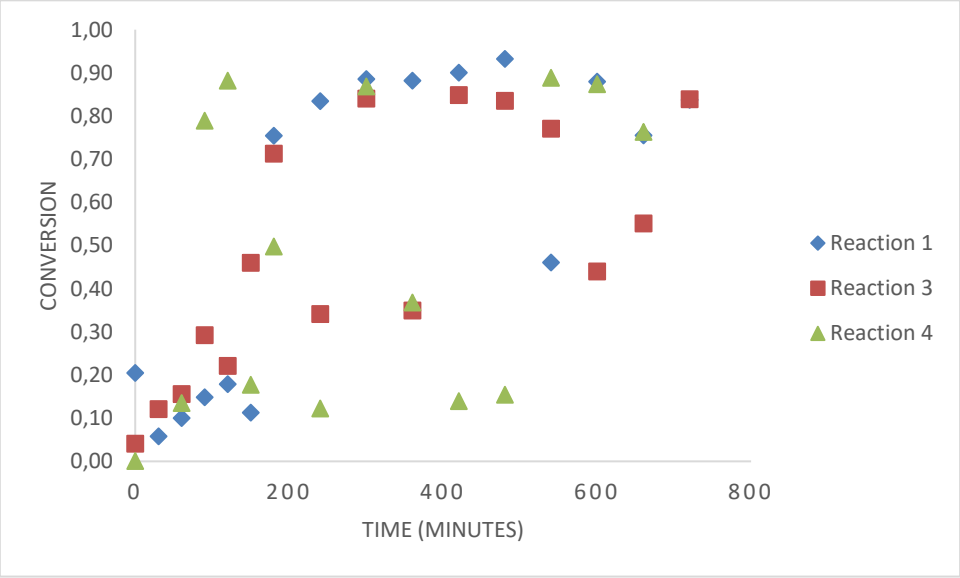

Figure 24: The results from reactions 1,3 and 4, were pretreatment was investigated. On the x-axis, there's time minutes from reaction was started to the sample was taken, and on the y-axis, conversion. All the samples have been in the fridge for about 10 weeks.

Conversion in reaction 4 seem to go from 13% at t=60, up to 88% at t=120, and back down again to 12% at t=240. This is not what we expected, and can't be explained easily by anything other than that the reaction continued in the fridge. The only results that can be drawn from those reactions seems to be that equilibrium conversion seems to be higher than 85%. All the other results are from samples that got analyzed just after the reactions took place, unless other is stated in the captions underneath the figures.

6.3 Repetitiveness of the GC results

To be certain that the new results from the samples that had not been stored was correct we ran the mid range parameter reaction 3 times in the GC and the result are displayed in Figure 25.

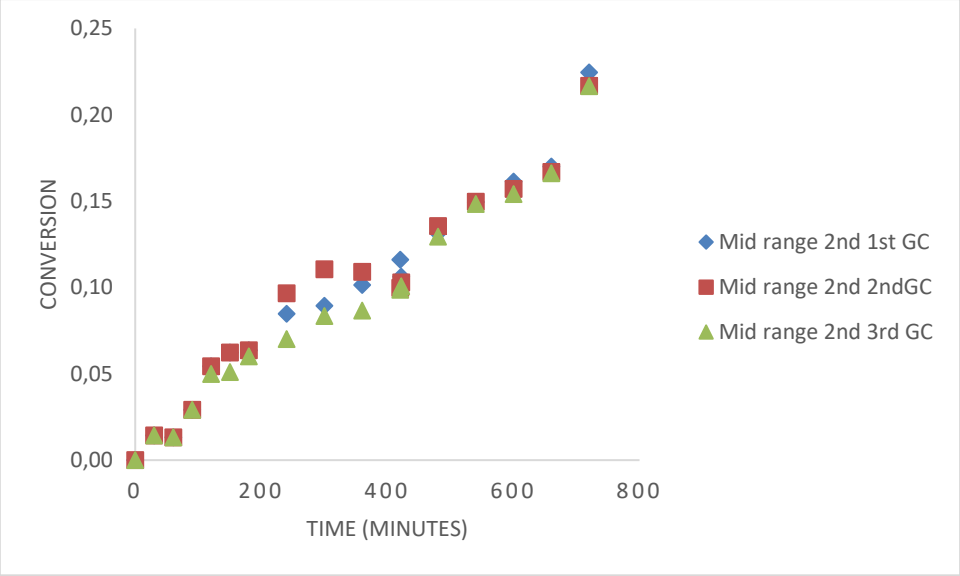

Figure 25: The results from three different analysis of the same samples, in the same vials in the GC. The samples are from reaction 13. Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken minutes on the x-axis.

6.4 Rerun of the mid range reaction

Since the GC was not the issue causing the much lower conversion in the samples analyzed right away, we ran two new reactions with the mid range parameters to compare. The results from those two reaction are shown in Figure 26.

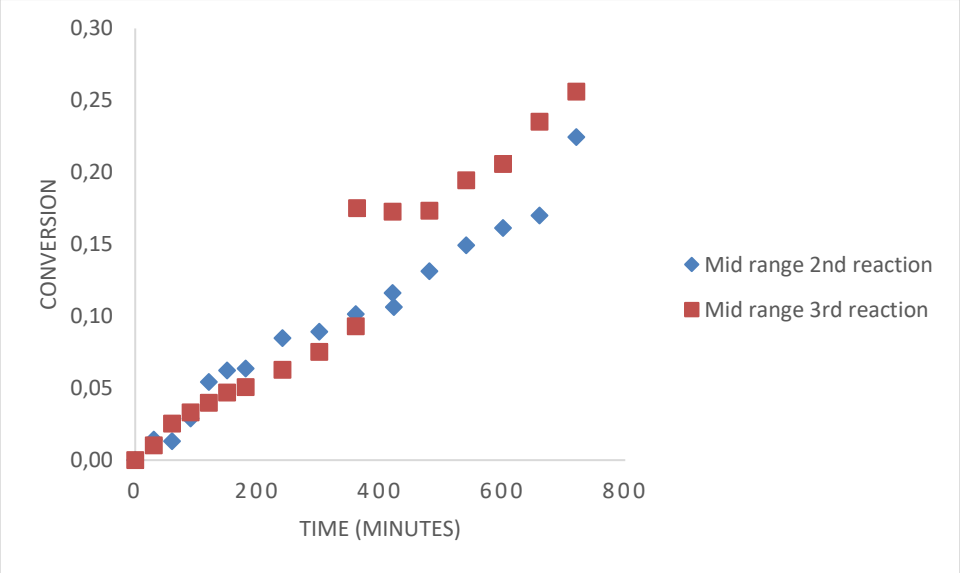

Figure 26: The results from two different reactions with the same parameters. The Mid range 2nd reaction (reaction 13) had a pause between days of only one night, approximately 15 h. The pause was at t=420. The Mid range 3rd reaction (reaction 14) had a pause between day lasting a weekend, approximately 60 h, and the pause was at t=360. Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken minutes on the x-axis.

6.5 Alcohol

The results from the three reactions done to investigate the effect of 8,12 and 16 molar ratios of alcohol to oil are displayed in Figure 27.

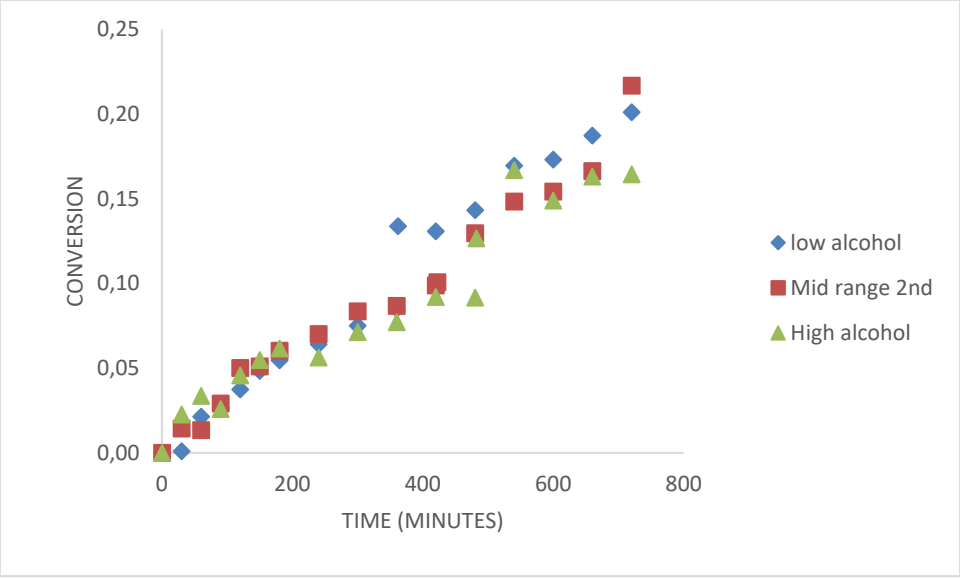

Figure 27: The three reactions with varying alcohol content (reaction 13,17 and 18). Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken minutes on the x-axis.

6.6 Catalyst

The three reactions done to investigate the effects of varying the catalyst amount are displayed in Figure 28. Conversion reaching just above 22% in the case of the high catalyst amount.

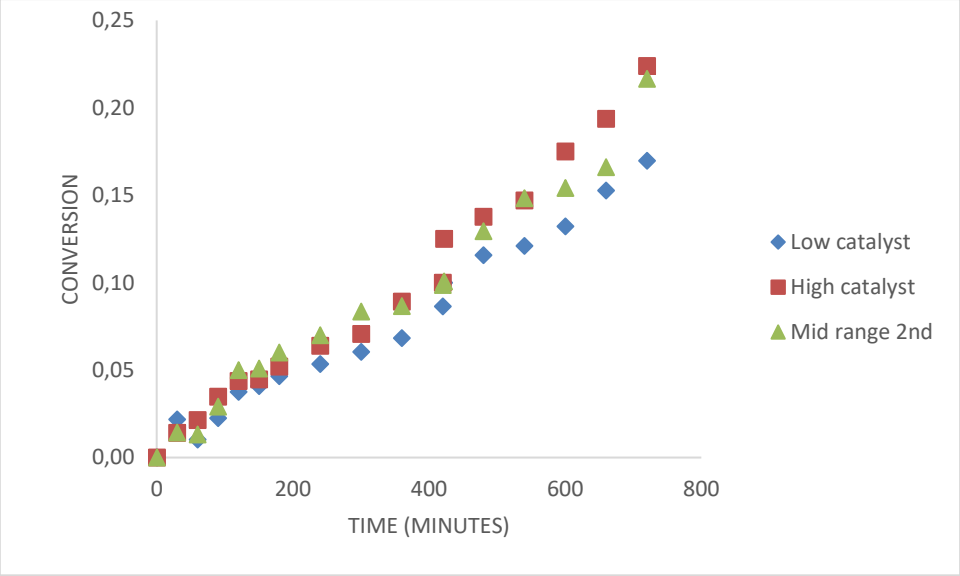

Figure 28: The three reactions with varying catalyst amount (reaction 13,16 and 19). Time in minutes from reaction was started to the sample was taken on the x-axis, and conversion on the y-axis.

6.7 Storage analysis

The samples stored in various locations gave the results shown in Figure 29.

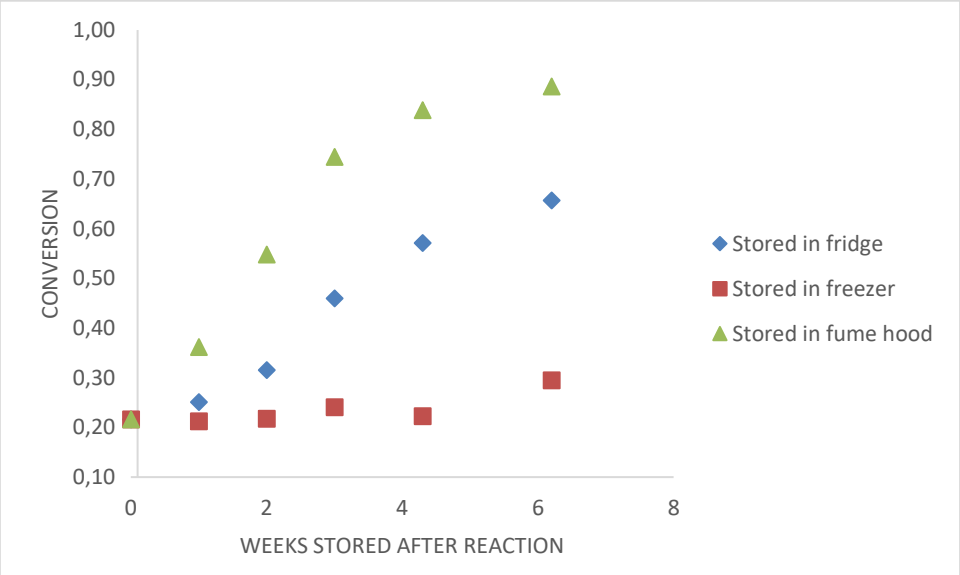

Figure 29: The results from storing the samples in the fridge, freezer and the fume hood. The samples are from reaction 13. Conversion on the y-axis, and time, in weeks stored before analysis on the x-axis.

6.8 Effect of preparing a sample

We set aside two sample jars in the fume hood. One, we analyzed every time we analyzed the other stored samples and the other only got analyzed a few times to see if mixing the sample when taking the sample caused the reaction to speed up. The results are visible in Figure 30.

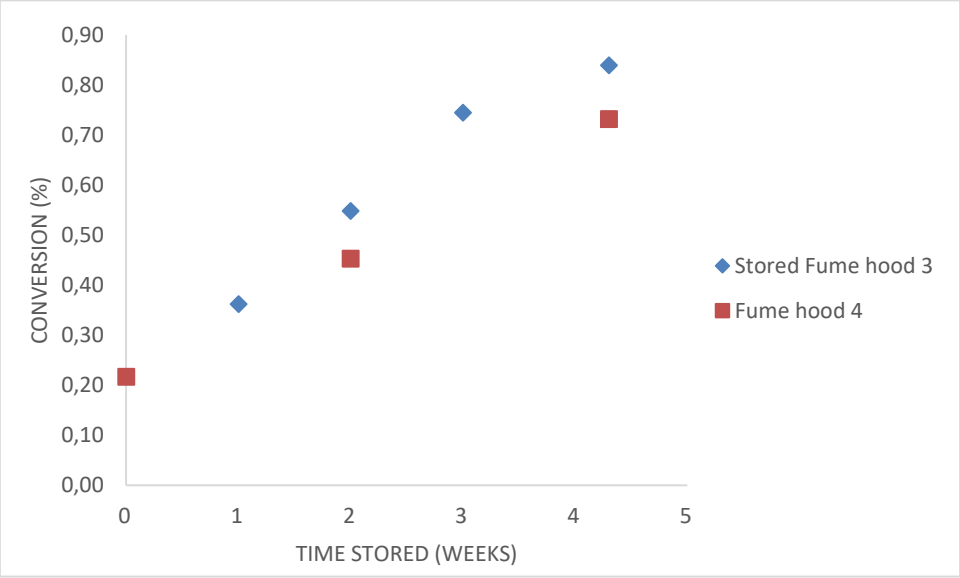

Figure 30: The difference between two large samples stored in the fume hood to see if there was any difference between analyzing the samples few and many times. Fume hood 4 only got two samples taken from it after the sample was put in the fume hood. The Fume hood 3 sample was used to make 4 vials for the GC after the sample was put in the fume hood.

6.9 Effect of temperature

The effect of changing the reaction temperature is displayed in Figure 31.

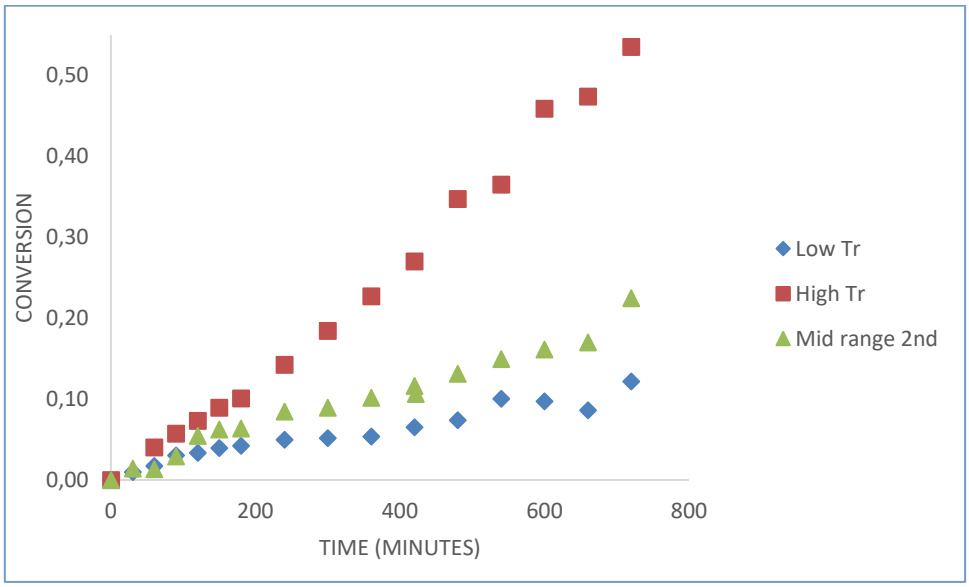

Figure 31: The three reactions with varying reaction temperature (reaction 11,13, and 15). There was only done one reaction with a reaction temperature of 75 °C (high Tr), and the samples from that reaction was stored in the fridge for 10 days. The time in minutes from reaction was started to the sample was taken are on the x-axis and conversion on the y-axis.

6.10 Adjustment of high temperature results

The results from the high Tr reaction are displayed in Figure 32, and the results from all the reactions investigating Tr are displayed in Figure 33.

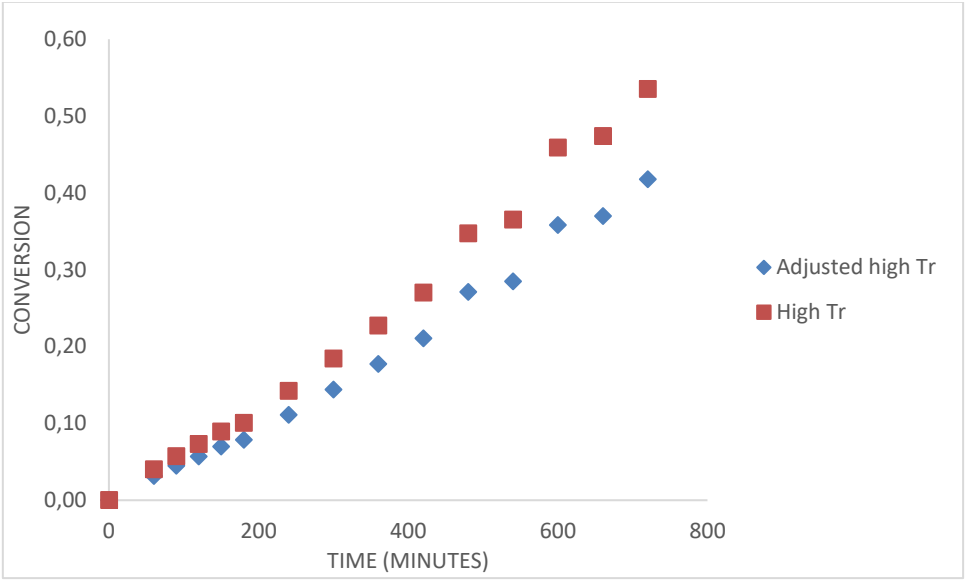

Figure 32: The reaction with high reaction (reaction 11) temperature stored in the fridge for about 10 days. The adjustment is done on basis of the results from the storage analysis. The Adjusted high Tr has been adjusted down 22% to compensate for the continued reaction in the fridge. Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken are on the x-axis.

6.11 Temperature, adjusted

Figure 33:

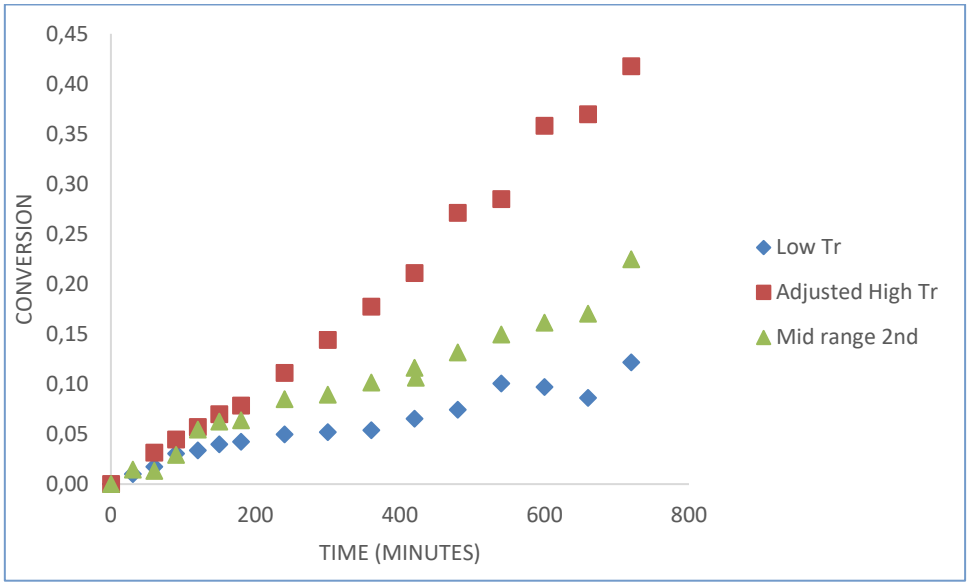

Figure 33: The three reactions with varying reaction temperature (reaction 11,13 and 15). The results from the reaction with high Tr have been adjusted down by 22% to compensate for the fact that there was about 10 days from reaction until analysis of those samples. Conversion is on the y-axis, and time in minutes from reaction was started to the sample was taken are on the x-axis.

6.12 Blind test

The results from the blind test is displayed in Table 7.

Table 7: The conversions from 11 analyses done with unique vials in the GC. The vials were prepared from the same sample. The average of all the samples and the standard deviation is listed underneath the conversion.

Conversion (%)	8,35	8,36	8,76	8,82	8,40	8,16	7,72	9,57	8,26	9,46	7,78

Average (%)	8,51
Standard deviation (%)	0,60

7 Discussion

7.1 Expectations

Within the parameters and intervals we worked in, we expected the reaction rate to be increased if the catalyst amount or the reaction temperature got increased. If alcohol amount was increased we expected final conversion to be higher, because the reaction is a two way reaction. Le Chatelier`s principle states that such a reaction gives more products if reactants are added. The system will move towards a new equilibrium. This is what we expect from adding more alcohol at the start of the reaction, more of the oil would turn into EE. However, the reactions didn't last long enough to reach equilibrium so the effect might not be visible in our results.

We would also expect that conversion increased with time, starting at 0% and ending at equilibrium conversion, if there was enough time to reach it.

7.2 Continued reaction in the fridge

The results from the first reactions (1-4) are clearly corrupted by what seems to be continued reaction in the fridge. This is also supported by the storage analysis that gives a reaction rate of approximately 5-15% points extra conversion for each additional week the samples had been stored in the fridge, at least for the interval 30-60% conversion. This was dependent upon the initial conversion or time spent in the fridge it seemed. The first week of storage, the sample increased conversion by 3% points, from 22 to 25%. The second week conversion increased further by 7% points, and the third week, conversion was up by 14% points. Furthermore, the results from reaction 5-12 was stored in the fridge for 1-2 weeks, so we decided to do those reactions once more. Extrapolating back, and getting the results that way would give us too much uncertainty to say much about the results conclusively. The only reactions we did not do twice were the reactions 1-4 that investigated pretreatment of the egg shells, and reaction 11 that was the high Tr reaction samples.

7.3 Adjustment of the high Tr results

The results from the high Tr reaction was adjusted down by 22% of the conversion at any given point. The amount that it should be adjusted by was decided based on the time the sample had been in the fridge (10 days) and the continued reaction rate in the fridge. All the samples from the high Tr reaction were adjusted as if they had been 10 days in the fridge. In fact the earlier samples had been there for up to one day longer since they were taken about 30

h before the last samples from the same reaction. The storage analysis in Figure 29 in Results had a continued reaction of 3,4% points the first week in the fridge, and the second week it reached another 6,5% points conversion. By taking the 3,4% points and adding 3/7 of the extra conversion from the second week in the fridge, we end up with 3,4% + 2,8% points. A total of 6,2% points. This meant that in the 10 days the samples from reaction 11 was stored the conversion was expected to have risen by 28,6%. The sample stored in the fridge had an estimated jump in conversion from a conversion of 21,7% to a conversion of 27,9% after the 10 days in the fridge. Thus, the adjustment should be to subtract 22% of the conversion at any given point in reaction 11.

7.4 Effects of alcohol concentration

The effect of varying the initial alcohol content between 6:1 and 12:1 molar ratios of alcohol to oil did not seem to give much different results as can be seen in Figure 27. From t=0 until t=360 the results are well within the margin of error. In this timespan, the difference between the three reaction conditions are less than 2% points. The reaction with low alcohol content seem to jump from about 8 to about 13% conversion during the night. While the reaction with the medium alcohol content does not increase conversion much during the night between the two days reaction was conducted. The conversion in the last sample from day one and the first sample from day two are equal, but the second sample the second day has an increase in conversion of about 3% points from the two samples before. An explanation could be that the conversion increased during the night, but that the first sample the second day did show too low conversion. Nevertheless, the jump in conversion between days are smaller than that of the low alcohol reaction.

The reaction with the high alcohol content also had an increased conversion during the night between reaction days. The conversion increased by about 3-4% points. This is a little bit less than the 5% points of the low alcohol reaction, and a bit more than the medium alcohol content reaction. If we just look at Figure 27, it seems that the highest conversion is achieved by the low alcohol content followed by the medium one, but the results are too close to call, considering the possible errors throughout the reaction and analysis.

If we consider the increased conversion between days, and compensate for that, the results are even closer together. The medium alcohol reaction might then be the one with the highest conversion in the later stages of the reaction (after t=360 minutes), but the results are

all too close together to tell witch one's giving the fastest reaction rate and the highest conversion after about 10 h of reaction.

The fact that increased alcohol content in the range tested does not affect the conversion could be a result of mass transfer limitations.

7.5 Effects of catalyst amount

Increased catalyst amount should give a higher reaction rate and thus a higher conversion at any given time until the reactions reach their final conversion. The final conversion would not be affected by the catalyst amount, but we do not reach final conversion in our experiments with the possible exceptions of some of the samples stored for some months. The jump in conversion between days are of a similar amount on all the three reactions, as can be seen in Figure 28. From t=0 until t=300 minutes the medium catalyst amount and the high are equal, and the reaction with low catalyst amount are the lowest in conversion. The reaction with low catalyst amount stays the lowest in conversion throughout the entire reaction. From t=300 minutes and out the high catalyst reaction yields the highest conversion and ends up 1% point above the medium catalyst, and 5% points above the low catalyst reaction. It's much less noise and a much more similar jump in conversion between days in the results from these three reactions than in the results from the reactions investigating alcohol content. This makes us a lot more confident in these results than in the results from the three reactions investigating alcohol content.

7.6 Effects of reaction temperature

The increased reaction temperature should, just like the increased catalyst amount, cause a faster reaction and thus a higher conversion at any given point in time. The jump in conversion between days are similar in all the reactions with varying reaction temperature. The samples from the reaction with the low reaction temperature are the lowest in conversion from t=120 minutes and until the end of the 12 h the reactions took place. In the first 2 h of the reactions it's impossible to distinguish the results from each other because the conversion is too low, and the errors are too large in comparison. The results from the high temperature reaction had to be adjusted because the time from the samples were taken until GC analysis was conducted was 10 days. The adjustment factor was discussed and we ended up with adjusting the results down by 22% of the conversion at any given point. The high temperature reaction gave the highest conversion throughout the entire reaction even though it's hard to be

certain of the results during the first 2 h of the reactions. The reaction conducted at 65 ^{o}C (mid range) had a conversion between the conversion of the high and low Tr.

7.7 Error estimation

We did multiple things to try to best estimate the errors that would occur throughout the reactions and analysis. Some of the possible errors related to reaction is mentioned in section 5, Methods. Those errors include: inaccurate scales, not perfect mixing in the reactor, materials not participating in reaction (mostly catalyst and ethanol), and volume varying from reaction to reaction since initial volume could be a bit different. The volume of the reactor content would also decrease because of the sample taking. The mixing not being perfect, and time varying a bit from stirring was turned off until we managed to take the sample could also mean that the reactor content separated into the two phases, ethanol on top and oil on the bottom. This could explain the fluctuating results in reaction 1-4 that had time to reach close to equilibrium conversion. If one of the samples were containing mostly oil the equilibrium conversion in that particular sample could be very low indeed, it might be just 10-30% like the results we see in Figure 24. That kind of an error would also be amplified as time goes by in the fridge, since the conversion in a sample containing mostly oil would not increase much in conversion as time went by. The samples that contained the same content as the reactor would, on the other hand continue to increase its conversion until it reached somewhere close to 90%. This could explain the point t=360 minutes in Figure 23 1st reaction since all the peaks are much lower than in the other samples from that reaction, but that error might also just be a statistical error. This kind of error would not make a great impact on the results if the samples were analyzed right away. Because the EE and oil would stay in the same phase and thus be in the same vial for GC analysis. We then try to estimate the relationship between the oil and EE based on the GC data, and that relationship would be the same if the sample is high in ethanol or low.

7.7.1 GC error

The results in Figure 25, where we did three different tests on the same vials in the GC, proves that the results are reproducible. The highest errors are in samples from t=240-420 minutes. The errors are below 1% point in all other samples, and largest error is about 3% points at t=240 and 300 minutes. Those errors occur because of errors in the GC, as well as

errors made analyzing the results the GC produces by choosing slightly wrong peaks in the plots like the ones in Figure 22. The errors on the GC is related to the needle extracting sample from the vial. The sample extracted might be contaminated if the needle was not properly cleaned between samples were taken.

7.7.2 Total error

Figure 26 displays two reactions with the same parameters. The results from those two reactions are not the same. The errors in those two reactions are related to the errors on the GC and the errors during the reaction itself. The most obvious difference is that the "mid range 3rd reaction" have a much more significant jump in conversion in between reaction days. Much of the reason to this is that the pause was during a whole weekend in the "mid range 3rd reaction", but only one night in the "mid range 2nd reaction". Furthermore, there might be differences in the reaction temperature, barometric pressure, radiation and so forth. The reactor was cleaned between each of the reactions, and there might be small traces of content from the previous reaction in the reactor when the next reaction was to take place.

7.7.3 Analysis error

We did multiple analyses of the same sample with the results displayed in Table 7. The results from this table shows the error made by the GC and us when we made the sample for the GC. The standard deviation in the 11 samples were 0,60% points conversion. This is around 7% of the conversion in the samples analyzed. The error represented in this table does not include the error made before the sample was prepared for analysis in the vials depicted in Figure 19. The additional error made during reaction and sample taking are thought to only add a few tenths of a percental point to the standard deviation in Table 7. Making the total error somewhere around 10% of conversion at any given point.

7.8 Effect of pause

The pauses between days were conducted because the reactions took a total of 12 h + 1 h catalyst preparation and the time needed to melt the oil, prepare the reactor and clean it afterwards. The pauses were conducted between t=360 minutes and t=480 minutes in all the reactions, and were normally only one night, or about 14 h. We took samples before and after the pauses, to see if the conversion increased during the night. We expected the conversion to increase slightly during the night and the reaction rate to be slow the first part of day 2 because

we started the clock the moment we turned the water heater and circulation pump on. In total, we expected the increased conversion to be balanced out by the slow reaction in the first h of day 2. This does not seem to be the case. In most of the reactions it seems the increased conversion during the night was more than what was lacking from the slow reaction of day 2. In Figure 26 the results from a pause lasting a whole weekend in reaction 14, a second rerun of the mid range parameters, can be seen. This made the jump in conversion between days a bit bigger at 9% points and not compensated by the slow reaction the second day. Since the pause was approximately the same length in all the reactions, (except reaction 14) approximately the same error would occur in all the samples. The room temperature varied by a few degrees from day to day, so this would make little to no impact on the jump in conversion. The reactions investigating reaction temperature could also make an impact on the jump in conversion. The reaction at Tr=75 ^{o}C would have used a longer time to cool down to the ambient air temperature, so that the reaction rate was higher in the start of the pause between days than it would have been in the Tr=65 ^{o}C and Tr=55 ^{o}C reactions. However, this effect is not visible in Figure 31 displaying the results from those reactions.

Alcohol content in the reactor might also effect the reaction rate during the pauses. It seems that the reaction containing the least amount of alcohol had the higher jump in conversion compared to the reactions with higher alcohol content. This might not be a real effect since the noise in the results from the reactions investigating alcohol content are large compare to the jump in conversion during the pauses.

7.9 Effect of storage

The samples from reaction 1-12 were stored in the fridge and some reaction in addition to the one in the reactor happened in the there. The storage analysis would give us an answer as to how fast this reaction in the fridge was. From Figure 29 it's clear that the higher the temperature the samples were stored at, the higher the reaction rate were going to be.

7.9.1 Freezer storage

The sample stored in the freezer had no significant reaction going on. The sample had to be kept in room temperature for more than 30 minutes to be completely liquefied and have time to make the sample for GC analysis. This 0,5 h for every analysis might be the biggest contributor to the conversion increase as of storage, if any such increase occurred. The sample stored in the freezer was completely solidified, by the subzero temperatures, as far the eye

could see. Mass transfer would have been very limited in the sample in the freezer when the sample was not at room temperature to make a sample for the GC. This will probably limit the reaction as well as the low temperature. There seems to be less than one percental point additional conversion for every sample taken and week spent in the freezer.

7.9.2 Fridge storage

The sample stored in the fridge had significant reaction going on during its storage. Any result from a sample of similar sort stored in such a manner for more than a few days, would need to be corrected because of the continued reaction. The reaction rate seems to be dependent on conversion. In Figure 29 the conversion increases at an increasing rate from the sample was first put in the fridge until conversion hits about 40-60%. This can be caused by the EE that decreases the viscosity of the solution and enables faster mass transfer within the sample from diffusion. The increased amount of EE is causing the sample to become more and more liquid in the fridge. In Figure 17 the sample stored in the fridge are mostly solid, but on the top of it there's a layer, a few millimeters thick, that is liquid. This layer increased in thickness as the conversion increased, and about half of the sample was liquid like this at the end of our storage analysis.

The reaction speeding up might also be caused by the oil and ethanol being more soluble in EE than each other. The increased EE content would then give a higher volume at which the reaction could take place. The reaction rate would then reach a maximum speed around the time everything in the sample were in the same phase. When everything in the sample is in the same phase there will become less and less oil and alcohol in the sample as time goes by. This means that the reaction rate, which likely is dependent upon the concentration of oil and alcohol, is going to decrease. The backwards reaction from EE and Jojobyl alcohols back to ethanol and Jojoba oil is likely going to increase its speed because of the increased amount of EE and Jojobyl alcohols.

7.9.3 Fume hood storage

The samples stored in the fume hood had an even higher reaction rate than the other two samples. And if samples must be stored in that manner, it can be expected that an additional 1% point conversion would occur every 10 h or so. This seems to be valid for the conversion interval from 20-80%. Beyond this the reaction rate slowed down as the equilibrium conversion was getting closer. The samples stored in the fume hood indicated that the equilibrium

conversion is at least 90% at 20-25 ^{o}C. This is in the same region as some of the samples from the first reactions, that were stored in the fridge for 10 weeks.

7.9.3.1 Effect of taking a sample from the stored sample

We put two sample jars of the same content in the fume hood and one of them were going to be analyzed only a few times to confirm the results from the other. What happened was that the reaction rate was not equal in both, as can be seen in Figure 30. The conversion was significantly lower in the sample that got the fewest samples made from it. This can be contributed to by the fact that the samples were shaken before the vials for the GC was prepared. This shaking mixed the content and aided the reaction rate. It did not take long before most of the catalyst settled at the bottom of the sample jars after they had been shaken to prepare a vial. The sample jars with catalyst at the bottom can be seen in Figure 17 in method. The catalyst did not settle to the bottom in the samples stored in the fridge and the freezer before they solidified. When the samples were shaken, the different phases, if present, was also mixed. This would result in a larger interphase between the different components in the jar. The concentration gradients in the samples would also build up as time went by. This gradient would be greatly reduced by a process like the shaking to prepare vials for the GC.

The effect of taking a sample seems to be limited to the continued reaction in the sample stored in the freezer. This continued reaction is not much, but it seems to be just about noticeable at a maximum of about 1% point. What is due to the act of mixing the sample when preparing a sample for the GC, and what is due to the continued reaction when the sample is stored in the fridge is unknown.

8 Conclusion

- ✓ Increased alcohol amount does not affect the reaction rate within the timespan and molar ratios we tested.
- ✓ Increased catalyst amount does increase the reaction rate and the final conversion is 5% points higher after 12 h of reaction in the case of high catalyst amount compared to low catalyst amount.
- ✓ Increased reaction temperature increases the reaction rate within the parameters we tested. The conversion after 12 h of reaction almost doubles for every 10 ^{o}C increase in temperature, this also holds true for the stored samples down to -20 ^{o}C.
- ✓ There is continued reaction when storing the samples. The lower the temperature a sample is stored at, the less the continued reaction will be. -20 ^{o}C is sufficient to stop the reaction. Agitating the samples will also cause some unwanted reaction.
- ✓ The error made by the GC is less than 1% point in conversion.
- ✓ The errors made during reaction causes less than 1% point error in conversion.
- ✓ The combined errors give an uncertainty in conversion at about 1% point.
- ✓ The pause between days makes little to no impact on the conversion, unless it lasts more than one night, or 15 h.

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